2 Science Opportunities

The proposed NSLS-II facility, a state-of-the-art medium-energy high brightness X-ray storage ring and a high brightness IR ring, will

- play a critical role in the success of DOE's Genomes-to-Life, NIH's structural genomics, and other major initiatives;
- provide a wide range of nanometer-resolution probes to meet the needs of the nation's rapidly growing nanoscience programs;
- alter dramatically the capability and variety of experimental probes of materials sciences, allowing access to new energy regimes and time-scales through inelastic and coherent scattering techniques;
- enable measurements with the high spatial, energy, and time resolution necessary to fully characterize new catalysts and to advance energy science;
- offer new insights into geophysical processes that determine the evolution of the Earth and planets;
- provide critical capabilities to study complex molecular-scale environmental processes, and to design remediation technology.

This Section outlines the outstanding scientific challenges and opportunities in the fields of Life Science, Nanoscience, Materials and Chemical Science, and Geoscience and Environmental Science and describes the impact that the superlative characteristics and combination of capabilities of NSLS-II will make in advancing research in them. The specific areas considered within each of these broad disciplines are:

- Life Science
  - Macromolecular Crystallography
  - Structure and Dynamics in Solutions and Membranes
  - Biological Imaging
- Nanoscience
- Materials and Chemical Science
  - Soft Matter and Biomaterials
  - Strongly Correlated Electron Systems
  - Magnetism
  - Growth and Processing of Advanced Materials
  - Catalysis and Energy Research
- Geoscience and Environmental Science
  - Earth and Planetary Science
  - Environmental Science

2.1 Macromolecular Crystallography

2.1.1 Overview

X-ray crystallography has transformed our understanding of biological processes. It was X-ray diffraction that provided the first clues to the structure of the DNA double helix 50 years ago, giving profound insights into how DNA is replicated. The reality that knowledge of biological structure imparts deep insights into the mechanism of action of molecules and assemblies [1,2,3,4,5], and the increasing difficulty in determining those structures as they get larger, has been one of the major driving forces in the continuing development of synchrotron radiation facilities world wide [6]. The Nobel Prizes in Chemistry awarded to Sir John Walker of the MRC in 1997 and to Professor Roderick MacKinnon of Rockefeller University in 2003 both depended on readily available synchrotron X-rays, and are proof of the crucial role synchrotron radiation facilities play in our understanding of the mechanisms of life.

The routine use of synchrotron radiation for single crystal diffraction studies has revolutionized macromolecular structural biology. With the availability of brighter X-ray sources, the size and complexity of macromolecules that can be studied has increased by an order of magnitude, or three orders of magnitude in mass (Figure 2.1.1). On the other hand, the size of the crystals that can be produced almost always decreases as the complexity of the macromolecule increases. The advancements observed for the past 15 years in the development of cloning, expression, purification, and crystallization methods have been impressive. However, crystals of the most complex structures that are suitable for diffraction are often scarce and difficult to obtain. Therefore, continuing advances in synchrotron radiation sources, detectors, and software are required to tackle the most challenging problems, which are the ones most likely to make a significant impact on our knowledge of the functioning of living systems [4].

The impact of synchrotron radiation on macromolecular crystallography must be regarded in the context of developments in molecular biology, cell biology, genomics, and bio-molecular crystallography. Crystallography is the dominant method for determining the three-dimensional atomic structure of any molecule. It is the only method for large and complex molecular structures. A current survey of the Protein Data Bank (PDB) shows that 69% of the structures deposited in 2002 were derived from synchrotron data (Figure 2.1.2). The US synchrotrons contributed over half of these, accounting for one third of all depositions. The source of this increasing role of synchrotron radiation is the large energy band width to help with phasing, the high collimation to resolve diffraction patterns from very large molecules, and the high overall intensity to make the measurements go quickly, even for small, weakly diffracting crystals. As a consequence, a larger and more diverse group of researchers are benefiting from diffraction studies at synchrotron light sources.

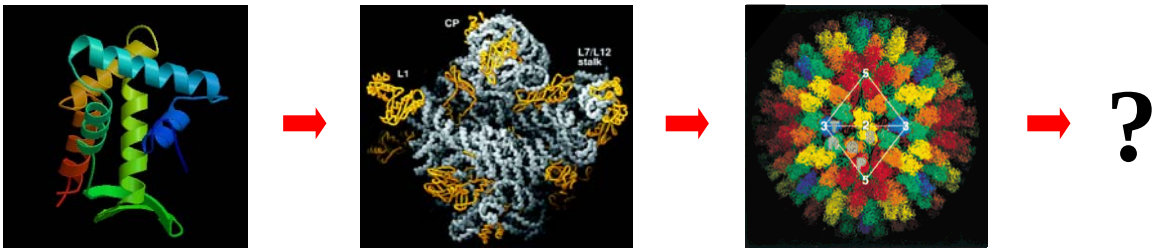

Figure 2.1.1 *Molecular complexes and assemblies are the challenge of the 21st century [5]. Conventional Conventional macromolecular crystallography has benefited from nearly every improvement in synchrotron sources. The possibilities offered by increased brightness have driven researchers to attempt increasingly difficult scientific problems, especially structures of large asymmetric molecular assemblies, which is where the cutting edge of structural biology currently lies.*

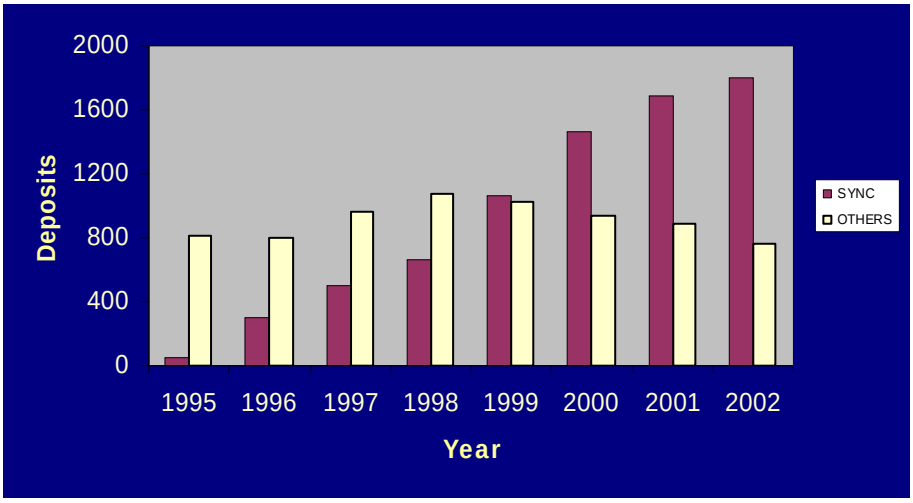

Figure 2.1.2 *Structures deposited in the Protein Data Bank originating from synchrotron radiation data and from other sources as of October 2003. Other sources include NMR and home sources. The use of synchrotron radiation has revolutionized structural biology and consequently allowed for an increased understanding of molecular functions.*

The growing use of synchrotron sources for macromolecular crystallography has increased the pressure on existing facilities to upgrade existing, or construct new, sources and beamlines. This problem is particularly acute in the Northeastern United States, where aging synchrotron sources at Brookhaven National Laboratory and Cornell University find it increasingly difficult to meet the experimental demands of a large group of crystallographers working in this region. Quoting from the 2002 BioSync report: "*Much of the growth in beam line number, quality and capability in recent years has occurred at the APS, ALS and SSRL, i.e. in the mid-west and the Bay area. While these developments are welcomed by all because of their positive impact on the nation's scientific capabilities, they pose a significant logistical problem for investigators based on the east coast, who increasingly find themselves having to travel long distances to collect data hands-on at state-of-the-art beam lines.*" This proposal to construct NSLS-II at Brookhaven National Laboratory is intended to respond to user pressure in the Northeast well into the future.

Biological and biomedical research has entered a new era, with an increasing emphasis on understanding the functional and physical connections between macromolecules. Integrative biology is a broad conceptual paradigm for discovery of how the molecular components of cells and tissues are connected in biochemical pathways, cellular responses, and functioning organs. Once the structures of these molecular components are known, deeper insights into specificity and mechanisms may be obtained similar to those achieved for individual enzymes and recognition proteins.

During the molecular biology era, structural biologists created an enduring legacy of atomic structures of many fundamental building blocks of the cell. Structural biology is now poised to make invaluable contributions to our understanding of integrated assemblies of interacting macromolecules. A taste of what is to come was unveiled recently with the structures of the ribosome and ribosomal subunits [3,4,5]; mitrochondrial F1 ATPase [1] (Figure 2.1.3); both the eukaryotic and prokaryotic cytochrome c oxidases and b/c complex [9,10,11]; the potassium channel [2,12,13]; the HIV gp120 envelope protein complex with CD4 receptor and antibody [14]; the GroEL/GroES/ADP chaperone complex [15] and the eukaryotic and bacterial RNA polymerases [16].

The first step in the understanding of these multi-protein complexes will require direct structural analysis. These complexes are very difficult to express and to purify, especially in the quantities required for crystallization experiments. The major challenges in this work will be biochemical. The challenges will be not only to handle the large size and complexity of the assemblies, but also perhaps to trap unstable short-lived complexes that exist for only a few minutes in the cell. These might include signaling

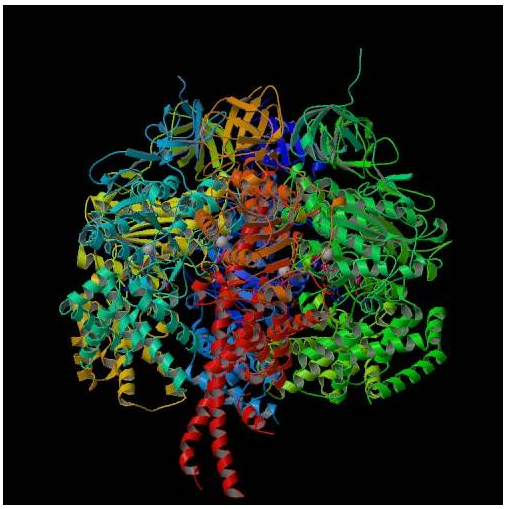

Figure 2.1.3 *The 3D molecular structure determination of F1ATPase was only possible through access to a synchrotron radiation facility [1]. Synchrotron radiation will play a crucial role in the determination of the molecular structure of complex assemblies, which is the major challenge for this century.*

complexes, where weak binary interactions contribute cooperatively to tight but often transient multi-component systems, and DNA replication, mediated by transient assemblies of polymerases, clamps*, etc.* If crystals can be obtained, they are often small and fragile, and require considerable optimization, guided by the results of diffraction experiments that can be achieved only with direct access to a bright source. Furthermore, they are difficult to stabilize for shipment, and diffraction from such crystals is generally weak, with successful data collection often requiring the intensity and fine collimation of a third-generation synchrotron source. *NSLS-II is needed to meet the needs of scientists who will accomplish this difficult work.*

2.1.2 Scientific Challenges and Opportunities

2.1.2.1 Large Molecular Assemblies

Several past successes in molecular structure determination of large complexes and assemblies are indicative of the critical role of high brilliance, high flux synchrotron sources in these studies. Early applications were the structure determination of virus particles, consisting of 180 or more proteins with a total mass of 8-9 Mdalton (including the RNA genome). These studies illustrated the difficulties in working with crystals of large complexes. Weak diffraction, close spacing of the reciprocal lattice, and radiation sensitive crystals, all conspired to make X-ray data collection possible only at synchrotron radiation sources. Recent successes with the determination of the structure of the core of much larger viruses, reovirus [17] and bluetongue virus [18], have shown the enormous potential of modern X-ray crystallography to reveal vast amounts of information. These and application of crystallography to large asymmetric complexes, the ribosome and the RNA polymerase transcription complexes being prime examples, were critically dependent on routine and frequent access to synchrotron radiation facilities.

The largest asymmetric molecular assembly whose atomic structure has been determined is the whole 70S ribosome [19] (Figure 2.1.4), consisting of nearly 100,000 atoms in 53 proteins and 3 chains of ribosomal RNA. In addition, this model also contains the three tRNA molecules bound to the A-, P-, and E-sites and a small piece of mRNA. The ribosome has two multi-protein/RNA subunits and is the site of protein synthesis. While the smaller, 30S subunit decodes messenger RNA, the large, 50S subunit catalyzes peptide bond synthesis. The model of the 70S ribosome has been constructed using the atomic

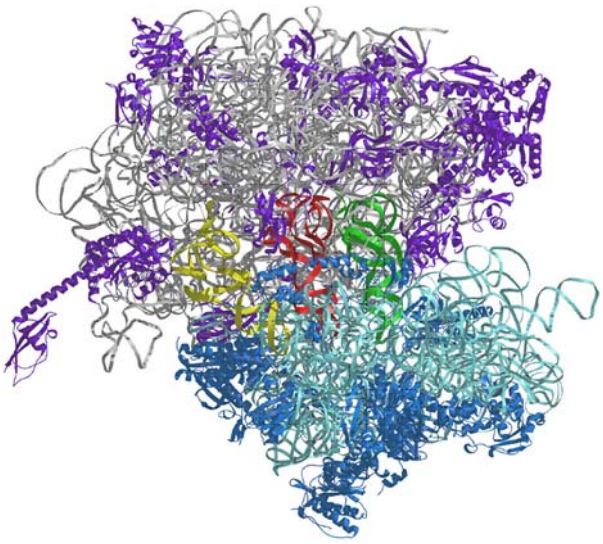

Figure 2.1.4 *View of the structure of the T. thermophilus 70S ribosome from the back of the 30S subunit; after Noller [19]. Structures like the 70S ribosome have relied both on synchrotron studies and cryo-electron microscopy results.*

coordinates of the separate higher resolution structures of the large [3] and small subunits [4, 5], solved at 2.4 and 3.1 Å resolution, respectively and a 5.5 Å resolution electron density map of the whole ribosome. This was an amazing "tour de force" that would not be possible without constant sample optimization at a bright synchrotron source.

As is characteristic of all structural studies intended to illuminate biological function, the initial structure determination of the ribosomal components is only the beginning of structural studies of many complexes with substrates and antibiotics. Future structural studies will reveal the functional states of the ribosome during protein synthesis. The approximately dozen structures of the *Haloarcula marismortui* 50S ribosomal subunit complexed with various antibiotics (Figure 2.1.5.) are having a major impact on the design of new antibiotics that target the ribosome. These account for about one half of all antibiotics used clinically, and amount to tens of billions of dollars in sales per year.

Other large assemblies comprised of proteins and nucleic acids are continuously being identified and

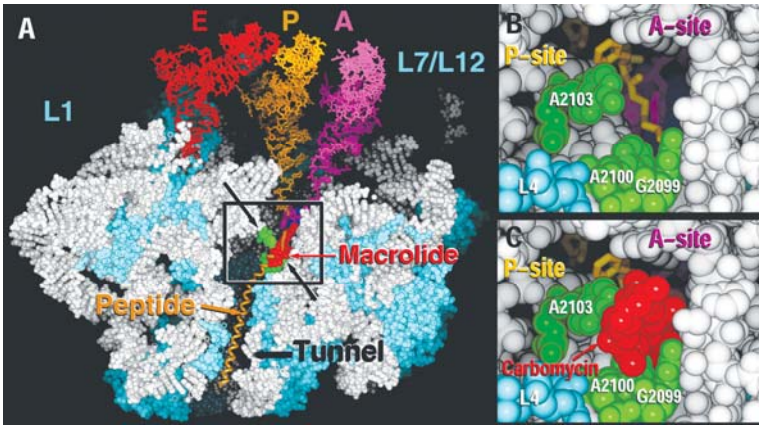

Figure 2.1.5 *The 50S ribosome: global view of the macrolide binding site for antibiotics showing how they block the peptide exit tunnel. A) The binding site for Macrolide antibiotics. B) and C) Close-up on the exit tunnel. The determination of the atomic molecular structure of large macromolecules have required years in the optimization of the crystallization process of the individual proteins and X-ray structure determination. High brightness sources can reduce significantly the time frame of such process.*

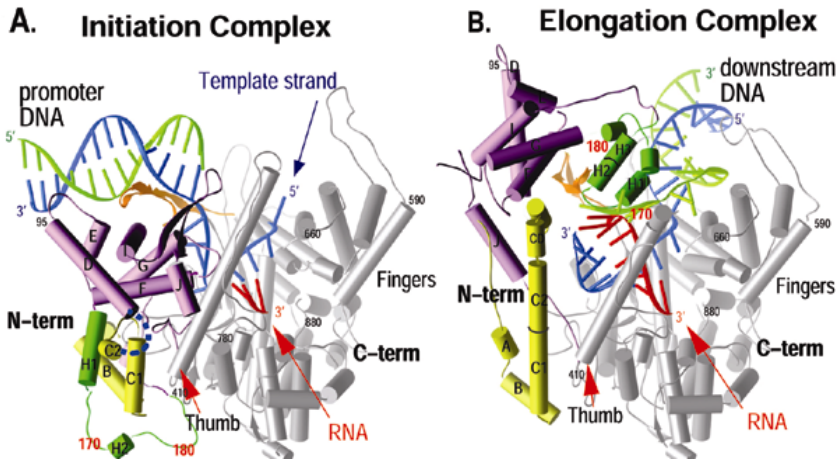

Figure 2.1.6 *Comparison of the structures of the T7 RNAP initiation and elongation complexes. The initiation complex (A) and elongation complex (B) have been orientated equivalently.*

will be the target of high resolution crystallographic studies in the future. A recent landmark where synchrotron radiation played a crucial role is the structure elucidation of eukaryotic, prokaryotic, and viral RNA polymerase complexes in various stages of transcribing DNA into RNA [16, 20, 21]. The purification, crystallization, and subsequent structure determination of RNA polymerase II from yeast, a 12 subunit, relatively unstable complex, is the prime example of the type of molecular machinery that the field is now able to tackle given regular and frequent access to high-brightness sources [20].

Many structure determinations of RNA polymerases, caught while forming RNA transcripts, are required to provide a complete structural description of transcription. The four-subunit bacterial *Thermus aquaticus* enzyme [22] and the transcribing RNA polymerase from phage T7 provide a modest sized assembly of protein, DNA, and RNA for these studies. Numerous separately determined crystal structures for both the bacterial, yeast and T7 RNAP have been captured in various states of the process [21, 23]. The T7 RNAP structures, for example, show a dramatic alteration in the structure of T7 RNAP between the initiation phase of transcription and the elongation phase (Figure 2.1.6). Significant changes are also seen in the structure during the cycle of nucleotide incorporation. The establishment of structures that include not only the polymerase but large assemblies of transcription factors that carefully regulate this important basic cellular process, particularly in eukaryotic cells, is the next frontier in structural studies of in the field of transcription.

Presently, the large macromolecular complexes to be studied by X-ray crystallography are purified from naturally occurring sources. However, many biologically important complexes are not sufficiently abundant and/or stable to be purified from a natural source, and instead they will have to be produced by co-expression of all the components in an overproducing strain or by reconstitution *in vitro* from purified components. One example of this approach is an ongoing effort to crystallize the DNA replication complexes encoded by several model replication systems, including those from bacteriophage T7 and the Herpes Simplex Virus. Many of the protein components have been crystallized individually and their structures determined (Figure 2.1.7) [24]. However, the overall arrangement of proteins within any replication complex is unknown. The physical associations of these enzymes coordinate their activities within the complex to ensure efficient replication. Current efforts are directed toward forming stable, stalled replication complexes that can be crystallized. It is very likely that crystals of the resulting complexes will be weakly diffracting and require analysis at synchrotron radiation sources. Many of the individual enzymes in the complex are highly flexible and may further degrade the quality of diffraction that can be recorded. A high brilliance X-ray source will be essential to make progress with these challenging projects.

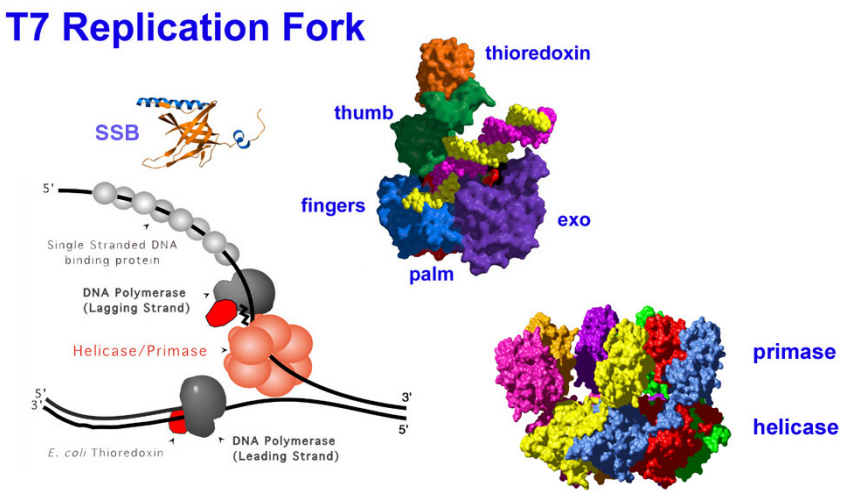

Figure 2.1.7 *DNA replication complexes: several individual protein components have been crystallized and structures determined yet the overall structure of any replication complex remains unknown. It is expected that weakly diffracting crystals from such complexes will require high brilliance synchrotron sources if any progress is to be made.*

2.1.2.2 Membrane Proteins

Membrane proteins are ubiquitous and essential to all living cells. They are found in eukaryotes and prokaryotes, as well as some viruses, and correspond to a sizable fraction of the entire genome. Membrane proteins are involved in every aspect of cellular function. Examples are the production of energy (*e.g.* the ATPase complex), the transmission of signals in nerve and muscle (*e.g.* the ion-channels), and cellular responses (*e.g.* the family of G-protein coupled receptors). Because of their ubiquity, membrane proteins are tempting targets within the pharmaceutical industry for the development of new therapeutics. Structural characterization of membrane proteins, notoriously known to be difficult to crystallize, can revolutionize our understanding of the molecular machinery of the cell.

The work on voltage-dependent K+ channel [2, 12, 13], just awarded the 2003 Nobel Prize in Chemistry, is a perfect example of the dramatic impact that structural studies of membrane proteins have in the understanding of cellular function[1]. Voltage-dependent cation channels open and allow ion conduction in response to changes in cell membrane voltage. Among other processes, these "life's transistors" control electrical activity in nerve and muscle. The voltage-dependent K^+-channels are most often found as tetramers of molecules comprising six hydrophobic helical segments S1-S6, where $(S5\text{-}S6)_4$ forms the pore and defines the ion selectivity and S1-S4 forms the voltage sensors. In the conventional model (Figure 2.1.8a) the voltage-dependent gating charges on S4 are supposed to be driven through the protein core to open the channel. The S4 helices would lie in the interior of the protein secluded from the membrane.

MacKinnon's structural work suggests a different model, that shown in Figure 2.1.8c wherein a tetramer of segments S5-S6 line the pore and S1-S4 form "voltage-sensor paddles" [2]. Obviously the disposition of these structural elements differs completely from the conventional model. The S4 with the S3 helices are found in the outer perimeter of the channel and most likely lie at the interface of the cytoplasmic side of the membrane. Functional studies of the gating mechanism reveal a movement of the voltage-sensor paddles by 20 Å across the lipid membrane (Figure 2.1.8d), and the travel of S4 would be associated to the S5-S6 segment in opening the pore.

[1] Note that the Nobel Prize in Chemistry was given also in 1988 for determination of the structure of a membrane-bound protein, and in 1997 for work that depended on another such structure.

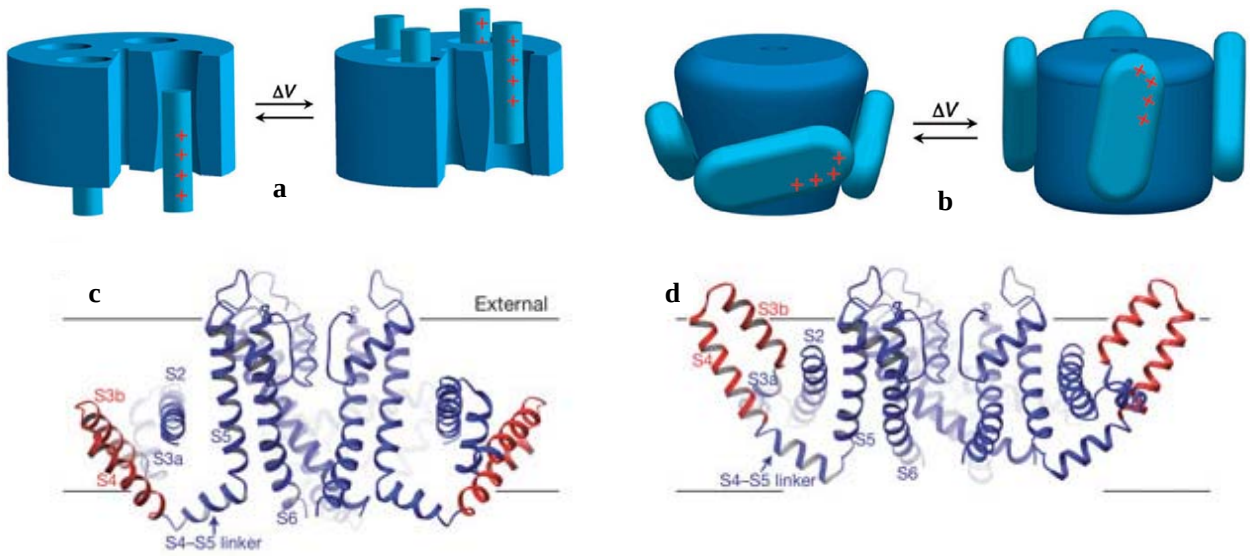

Figure 2.1.8 *Hypothesis for gating charge movements for voltage-dependent K+ channel. a) and b) The conventional and the newly proposed model for gating activation, c) and d) The structure of the channel with in red the voltage sensor paddles moving across the lipid membrane. Frequent access to synchrotron sources was essential to the insight gained to the function of the K+ channel [30].*

The successful story of the voltage-dependent K+ channel also exemplifies some of the difficulties associated with membrane-protein structure determination. MacKinnon's group often explored expression of multiple members of this family of membrane proteins to obtain sufficient quantities. In most cases the channel aggregated during concentration and never crystallized. However, they were able to express and purify the K+ channel from *Aeropyrum pernix*, an extreme thermophile that remained unaggregated in a variety of detergents. Crystals of this channel could be grown, but only in the presence of a monoclonal Fab fragment that stabilized the voltage-sensor paddles. At that point the major limitation was that the crystals were often small, and of poorer quality than "soluble" protein crystals. Local access to an extremely bright source of X-rays was critical.

Our understanding of membrane proteins is far behind that of other proteins. Only a few dozen structures of such molecules are known, a small fraction of one percent of the total. The major limitation to membrane-protein structure determination is still difficulty in production of crystals. However, some of these problems may be overcome through molecular biology; new expression systems, advances in detergent biochemistry, and new crystallization approaches such as monoclonal Fab-mediated crystallization, increase success. Nonetheless, repeated examples show us, firstly, that the rewards for structure determination of membrane-bound proteins can be great, and secondly that this work depends strongly on frequent access to a bright X-ray source to provide the constant feedback between the synchrotron and the biochemistry lab that is essential.

2.1.2.3 Structural Genomics

The availability of complete genome sequences for many organisms stimulates the imagination of all biologists. Confronted with several tens of thousands of genes, nearly all coding for cellular proteins, a structural biologist may want to crystallize them all. That is not far from the motivation behind the different approaches to this lode of protein-sequence information, each being a facet of Structural Genomics. Certainly, since proteins are central to almost all aspects of biology and disease, Structural Genomics will have an impact on the way biological problems are addressed (Figure 2.1.9). A completely different goal might be to obtain a global view of the "protein structure universe" through the identification of the total protein-folding "space" (Figure 2.1.10).

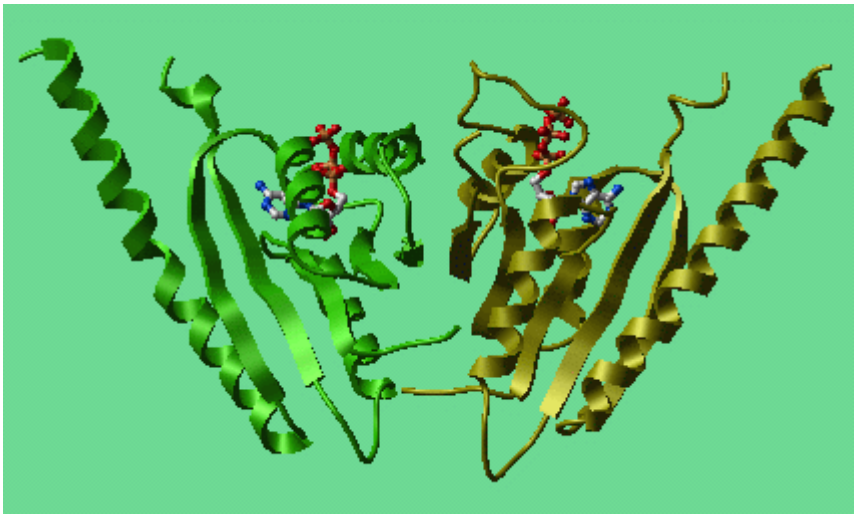

Figure 2.1.9 *The three dimensional structure of protein MJ0577 from Methanococcus jannaschii revealed bound ATP, suggesting a putative function as an ATPase or an ATP-mediated molecular switch, thus giving functional insights to all members of this family of homologous proteins [25].*

The Protein Structure Initiative (PSI), a structural genomics program funded by the National Institutes of Health - National Institute of General Medical Sciences (NIH-NIGMS), aims ultimately to provide structural information for all proteins in all naturally occurring protein sequences using a combination of experiment and comparative protein structure modeling. The goal is to carry out a pan-genomic clustering of protein sequences and determine representative structures for each sequence family. Once sufficient structures have been determined by experiment, mostly synchrotron-based crystallography, it will be possible to calculate all the rest. Currently, the NIH-NIGMS is funding nine centers to conduct a five-year pilot study to examine the feasibility of this approach. Although the first cycle of funding is nearing an end, the NIH-NIGMS Council approved, in principle, the renewal of the funding program for a second five-year term.

Different approaches to target selection are being attempted. These range from a focus on only novel protein folds, to selecting all proteins encoded by the genome of a model organism. Other target-selection strategies are biologically based, including all members of an enzymatic pathway, every protein in a macromolecular complex, interacting partners of related proteins, or gene products that are either up- and

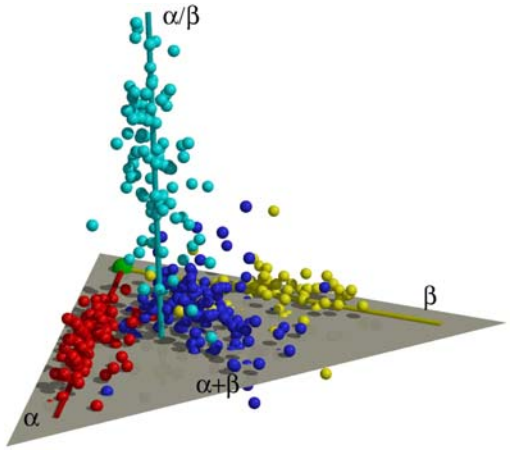

Figure 2.1.10 *A representation of the protein fold space, condensed to only three dimensions. Each sphere represents a protein fold family [26]. The determination of the atomic structure of a protein will allow to understand and to predict functions of other members of the same family.*

down-regulated during a given biological process, or proteins of unknown function and structure that are important for microbial survival.

Even with a large scale structural determination effort, the goal of the PSI is to determine sufficient structures that other closely related proteins can be modeled. The accuracy of homology models decreases sharply below 30% amino acid sequence identity. This cutoff implies that structure determination of 16,000-32,000 new proteins will allow most proteins to be modeled from 90% of all protein structure families, including membrane proteins. Once this initial set of target structures is substantially complete, structural information (experimental and computational) will be available for many proteins found in nature. Thereafter, attention will turn to structural studies of engineered proteins of industrial and pharmaceutical importance, macromolecular complexes and assemblies, and protein-ligand complexes.

NSLS-II will play a major role during and after the production phase of the NIH-NIGMS-funded Protein-Structure Initiative. Two distinct experimental activities are anticipated: crystal screening and definitive structural determination. Crystal-growing is such that approximately 20 crystals are screened *per* target protein to identify the truncated and/or mutated form, and the cryo-preservation scheme, that yields the best diffraction. Each optimally productive undulator beam line has the capacity to examine approximately 250 to 500 crystals during each 24-hour day when equipped with bar-coded, automated, cryogenic sample changing and crystal centering. NSLS-II undulator beam lines dedicated to structural biology can be used to handle this load: crystals will be screened for quality; if quality is adequate, sufficient data to solve the structure will be measured and all results recorded in an experiment-tracking database.

2.1.2.4 Drug Design

The development of new drugs in pharmaceutical companies has tended to be a rather linear process, from target identification to the selection of a drug candidate and compound optimization, with fixed criteria for passing to the next stage [27]. Although over the last twenty five years crystallographic studies have made significant contributions to the identification of a number of new ligands and inhibitors, targeting such major diseases as HIV infection (Figure 2.1.11), high blood pressure, and diabetes, X-ray crystallography has not yet realized its full potential as part of the drug-design process [28]. Mostly, current approaches to empirical screening and rational design benefit from fast high throughput methods developed for structural genomics initiatives, both for target selection and for structure determination.

Today virtually every large pharmaceutical company has a crystallography group, and many companies have one at each of their major research centers. Recognizing the need for rapid and frequent

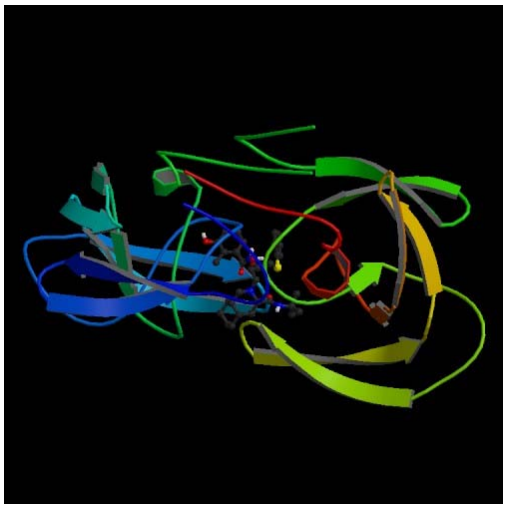

Figure 2.1.11 *The structure of the HIV-1 protease, with a model of Viracept, a potent, orally bioavailable inhibitor, in the active site. This structure was published by workers at Agouron Pharmaceuticals [31].*

access to synchrotron radiation, twelve of these companies have for years operated their own beam line at the Advanced Photon Source, and several others companies have demonstrated an interest in other beam lines worldwide.

Crystallography as performed in the pharmaceutical industry is much like the structural studies carried out in academic laboratories, with some important differences [29]. A critical challenge faced by pharmaceutical crystallographers is that the macromolecules studied are very often human proteins, since the aim is to treat human diseases. Human proteins can be very difficult to work with, and the growth of large single crystals can be daunting. Another distinct feature of pharmaceutical crystallography is the time course. Only after the first structure is determined can one begin the cyclic sequence of structures typically used to hone the chemistry of the lead compound, hoping to generate the potency, solubility, and pharmacokinetic properties required of a drug. In this phase of the program, crystallographic feedback must be rapid and accurate. Synchrotron-based crystallography helps not only with optimization of crystallization methods, but also to solve new structures easily. The synergy between the needs for automation and high throughput within both pharmaceutical research and structural genomics is clear. Each can benefit from the other's automation developments in genomics, crystal formation, and X-ray data collection. The development of convenient access to efficient synchrotron facilities is central to both efforts.

An interesting development is the emergence of a large number of start-up biotech companies that fulfill at least initially a particular niche in the drug-design process. Focused on a small, special biochemical feature these small biotechs usually have fewer resources than the large companies, and rely mainly on general-user time or on collaborations with the synchrotron facilities for their crystallographic needs. An example of such a start-up is Rib-X Pharmaceuticals, Inc. who is using the structure of the 50S ribosomal subunit for the development of new antibiotics. Especially in the case of an enterprise like Rib-X, access to a bright synchrotron is a must if for any sort of progress at all. The NSLS-II should be a magnet for small ventures like Rib-X.

2.1.3 Impact of NSLS-II

The NSLS has played a major role in the advancement of macromolecular crystallography in the US but there is a critical need to improve the capabilities of the NSLS for macromolecular crystallography. Knowing the time course of construction of high brightness macromolecular crystallography beam lines is one way to put this in perspective. Table 2.1.1 shows the commissioning dates of U.S. high brightness beam lines in chronological order; this expression of the nation's *capacity* of such beam lines might shed light on the *needs* for expansion. An original five beam lines available by 1997 was followed by thirteen more during the seven-year interval 1997-2003 (at a steady pace of about two per year). Looking ahead, eight or so beam lines now under construction (mostly at the APS, one at the NSLS, and one at the SSRL) will be commissioned during the next five years, a pace of about two beam lines per year. By 2008, about twenty-six high brightness beam lines will be in operation nationwide. Half of the nationwide brightest beam lines, of the kind that will be available at NSLS-II, will be at the APS. Just two high brightness beam lines will be in operation at the NSLS then, neither of which with exceptionally high brightness of the kind that is associated with the APS and NSLS-II undulator beam lines.

Beyond 2008, the prospect for further expansion of capacity of exceptionally high brightness beam lines is dismal. At present, just four sectors remain to be formally assigned at the APS. It seems possible, because of interest that has been expressed from other disciplines, that in the end none may be developed for macromolecular crystallography. If this is true, no further expansion of such beam lines nationwide is envisioned beyond 2008. If the need for high-brightness beam lines follows the linear slope that has been observed, these beam lines will be oversubscribed, nationwide, after this date. To make things worse, still only two moderately high brightness beam lines will be in operation at NSLS. The situation will be grim for Northeastern structural biologists. The availability of a number of beam lines at NSLS-II, perhaps in a staged expansion, would alleviate this situation, particularly for Northeast users. It goes without saying

Beamline	Device	Commissioned
CHESS A1	wiggler	before 1997
CHESS F1	wiggler	before 1997
CHESS F2	wiggler	before 1997
NSLS X25	wiggler	before 1997
SSRL 7-1	wiggler	before 1997
APS 19-ID	undulator	1997
SSRL 9-1	wiggler	1997
ALS 5.0.2	wiggler	1998
APS 17-ID	undulator	1998
APS 5-ID	undulator	1999
APS 14-ID	wiggler	1999
SSRL 9-2	wiggler	1999
ALS 5.0.1	wiggler	2000
APS 32-ID	undulator	2000
ALS 5.0.3	wiggler	2001
SSRL 11-1	wiggler	2001
APS 22-ID	undulator	2002
APS 31-ID	undulator	2003

Table 2.1.1 *Insertion device beamlines dedicated to macromolecular crystallography in operation in the US. A beamline is considered commissioned for macromolecular crystallography upon the first PDB deposition of a structure resulting from data collected at the beamline.*

that many of the experiments would benefit greatly from the fact that the brightness of NSLS-II will surpass existing NSLS beam lines by a huge factor.

The future impact of NSLS-II can be assessed in terms of the science that its user community will be able to explore. The high brightness of NSLS-II will foster research in:

- *Molecular Complexes and Machines*: crystals are small and weakly diffracting, large unit cells are not uncommon. Molecular structure determination will be possible from crystals 20 μm or smaller.
- *Structural Genomics and Proteomics*: high throughput crystal screening through improved automation will allow the assessment of crystal quality even of small crystals for molecular structure determination.
- *Drug Design:* fast screening for new drug candidates in pace with medicinal chemistry will allow the rational design of drugs to fight diseases.
- *Novel techniques:* novel applications to structure determination from 2D crystals and development of new approaches to molecular structure determination.

NSLS-II will impact the user community:

- *Increased availability*: the US capacity of high brightness beam lines will increase significantly.
- *Demand*: an increase in the number of beam lines dedicated to structural biology will allow for dedicated beam time for difficult problems such as the study of large assemblies and high through put.
- *Diversity of techniques*: macromolecular crystallography will not be the only method available at the NSLS-II to study biological interesting molecules. Other methods will allow biochemist and molecular biologist to gather information on the tertiary and quaternary molecular structures, study molecular kinetics and dynamics.

- *Location*: the geographical location will affect directly all researchers in the Northeast of the United States. These researchers in the academic, government, and pharmaceutical environments can also benefit from other facilities such as cryo-electron microscopy, nuclear magnetic resonance (NMR) and mass spectrometry, at Brookhaven and SUNY Stony Brook.

NSLS-II will become integrated to biological communities that will explore techniques and methods to advance the understanding of the mechanisms of life.

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2.2 Structure and Dynamics in Solutions and Membranes

2.2.1 Overview

Macromolecular crystallography has been enormously successful in elucidating the structure of proteins and other biomolecules. An increasingly complete collection of atomic resolution protein structures is becoming available, and a growing catalog of cellular assemblies has been identified. These data are being combined with emerging genetic and biochemical information on pathways to suggest temporal, spatial, and functional relations controlling cellular function.

However, the central question in biophysics still remains: What is the connection between structure and function of biological macromolecules such as protein, DNA, RNA, polysaccharides, and their complexes? Answering this question requires understanding the dynamics of macromolecular structures in their natural environment, where flexibility of the molecules and water, pH, and ion concentration play determinant roles. Examples include protein and nucleic acid folding and unfolding, multimeric association and disassociation, polymer collapse upon change of solvent, ligand binding and unbinding, receptor binding, force generation, electron transfer, phosphorylation events and large-scale fluctuations in macromolecules.

Studies of the structure and dynamics of molecules in solutions and membranes are an essential complement to macromolecular crystallography. Such studies are poised to provide new insights into the function, control, and dynamics of individual macromolecules and large molecular complexes. Solutions and membranes are the media where many of the most intriguing and complex biological processes take place, including molecular recognition, signal transduction, chemical sensing, transport, synthesis, degradation, replication, and defense.

Techniques such as solution scattering, spectroscopy, and footprinting provide valuable information regarding how biomolecules and molecular machines function. Time resolved X-ray studies of biomolecules in solution have evolved so that with present synchrotron sources, scattering studies at millisecond time resolution are feasible in favorable cases.

The high brightness of NSLS-II will give X-ray scattering and spectroscopy studies of biomolecules and membranes unparalleled sensitivity and time resolution, enabling more precise structure determinations and extending measurements of dynamics down to the microsecond time range.

2.2.2 Scientific Challenges and Opportunities

2.2.2.1 Protein Folding

Understanding protein folding, i.e. how a protein achieves its stable functional three-dimensional structure from a linear string of amino acids, is a key to understanding how the protein performs its biological functions. Time resolved solution scattering now allows researchers to follow the structural changes of the protein as folding proceeds.

The time scale that is characteristic of the folding process varies from picoseconds to nanoseconds, when the initial secondary structure starts to form, to milliseconds to seconds, when the folding process is completed. With the development of more accurate force fields that simulate the interactions that govern the folding process, and construction of more powerful computers (e.g. the Blue Gene project [1]), computational biologists are lengthening their calculations to the time scale of microseconds [2]. The high brightness of NSLS-II will extend the time resolution of solution-scattering measurements down to this time scale. Computations and experiments will then overlap and provide better tests of our understanding of the physics of the underlying interactions. Combined with complementary methods, especially NMR, solution scattering and computer simulation will provide a complete time course for how proteins fold.

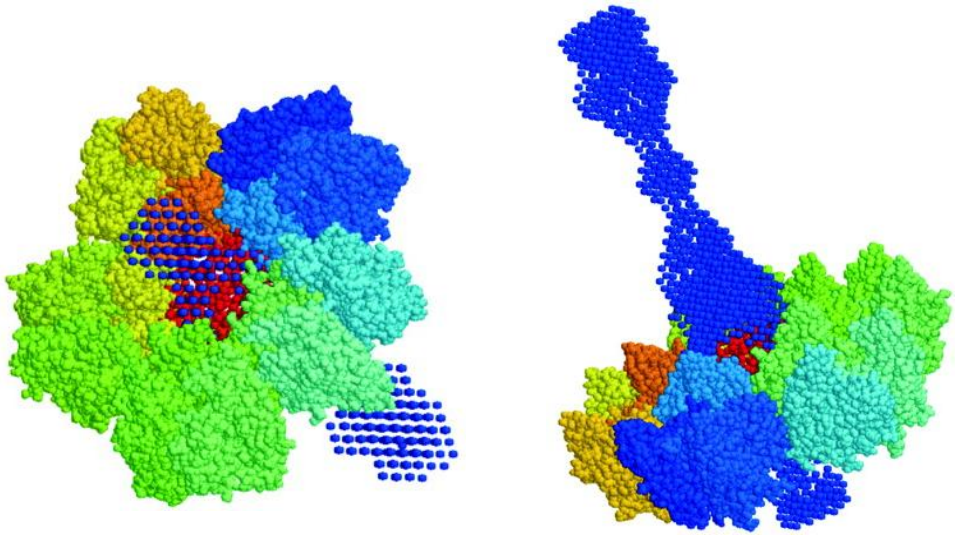

Figure 2.2.1 *Low-resolution structural model of the bacteriophage PRD1 vertex complex restored from solution scattering data [5], viewed from different angles. Both the structures of the individual components and the overall structure of the complex are obtained from analysis of solution scattering data.*

2.2.2.2 Structural Kinetics in Biological Macromolecular Complexes

High-resolution methods, both X-ray crystallography and NMR, have difficulties dealing with macromolecular complexes, where changes in shape may accompany the biological function that is under study. These structures are difficult to crystallize and are too large for NMR studies. Also, even if the complex does crystallize, the crystal structure may be misleading because shape changes are constrained.

In contrast, small angle solution scattering can provide structural information that reveals global conformation changes in biomolecules and molecular complexes in solution, and is thus complementary to protein crystallography. Traditionally used to characterize the radii of gyration and the folding states of proteins in solution, newly developed shape-reconstruction algorithms [3, 4] have transformed solution scattering into an effective technique for determining the low-resolution, basic shape of these complexes [5] (Figure 2.2.1). This approach also holds great potential for resolving the structural kinetics of macromolecular complexes using time resolved solution scattering to produce low-resolution movies of events such as the assembly and operation of molecular machines.

The idea behind these methods is that although the molecules in solution are randomly oriented, and much of the structural information is lost in the isotropic average, some information that is characteristic of the shape envelope of the biomolecules remains in the measured one-dimensional scattering curve. In many cases the subunits that make up a protein complex are rigid and their atomic structures are known. Solution scattering provides a useful tool for putting the pieces of this puzzle together to reveal the functional structure of the protein complex. Because knowing the shape of components reduces the degrees of freedom in the model, overall shape determination becomes much simpler and more reliable. This may suffice to define a low-resolution shape envelope. This low-resolution structure information is often invaluable, especially when combined with other experimental evidence. The low-resolution structures obtained also can be used to help determine phases in the analysis of crystallographic data [6].

These shape-determination algorithms operate by iterative modification and evaluation of a model against experimental data with a pre-defined penalty function. As with all optimization problems, quick convergence to an unambiguous solution depends not only on the selection of the model and the optimization algorithm, but also on the quality of the data. Data quality can be especially important for solution scattering since the scattering signal is weak in general, and varies by two to four orders of magnitude within the interesting q range.

The high brightness of NSLS-II will provide high intensity, highly collimated, and small X-ray beams for SAXS measurements, resulting in high quality data necessary for accurate shape determinations. Together with the flow-cell mixers discussed in Section 2.2.3.1 and fast detectors, NSLS-II will also enable time resolved measurements at microsecond time resolution to become routinely achievable.

2.2.2.2 Extension of Solution Scattering to Membrane Proteins

By analogy to protein solution scattering, non-crystalline membrane structures can also be studied with X-ray scattering. Under native conditions, individual membrane protein molecules, and supra-molecular structures such as self-assemblies of membrane-active antimicrobial peptides, diffuse within the confinement of the lipid bilayer. This is much like a two dimensional (2D) liquid, and can be investigated with SAXS by probing the in-plane correlations. Neutron scattering studies on these 2D liquids already exist [7], owing to the use of deuterated components that enhance the contrast in the sample (Figure 2.2.2). X-ray studies have so far been limited to nearly crystalline systems [8] and studies of multiple-layers.

All of the solution scattering techniques used for proteins are equally applicable to the 2D liquid of membrane proteins, including low-resolution shape determination and time resolved measurement. They have the similar advantage that one isn't limited in the quantity of the specimen one can get in the X-ray beam by the size of a crystal. In particular, in the case of the 2D membrane, a glancing-angle beam might illuminate a patch of several square millimeters to produce a significant scattering signal. Just as solution scattering can provide shape and kinetic information to complement protein crystallography, X-ray scattering from single-layered membranes will provide the opportunity to study the structure transitions within membranes.

The high brightness of NSLS-II will enable solution scattering experiments to provide information about these structural transitions, such as the conformation change of receptors upon binding of a ligand. These phenomena are related directly to the function of the membrane proteins, and therefore are central to many branches of life-science research.

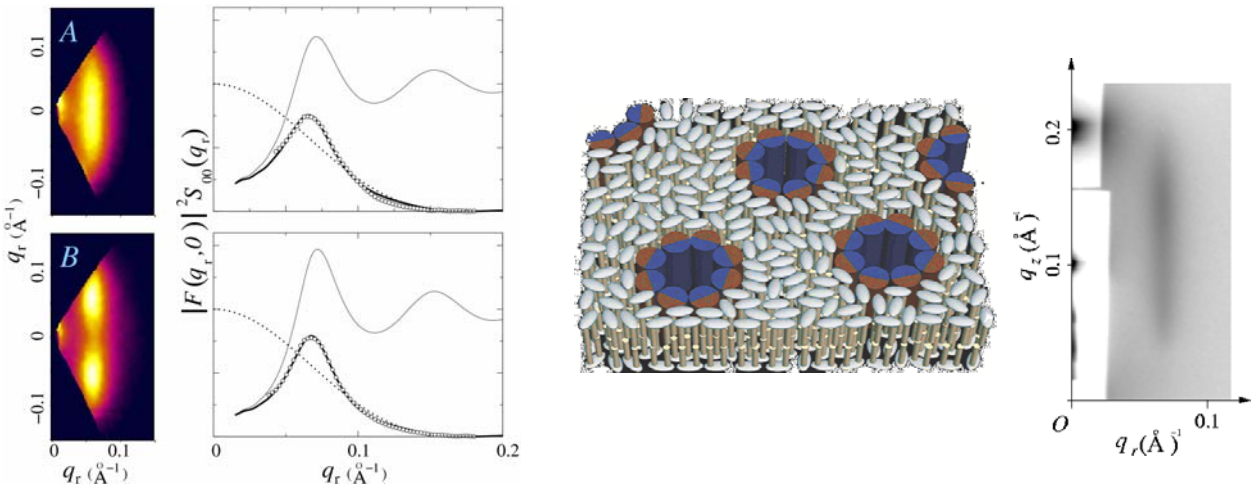

Figure 2.2.2 *Scattering from a two-dimensional liquid of membrane pores formed by antimicrobial peptides (model shown in the middle). Owing to the contrast enhanced by deuteration, neutron scattering can easily detect these structure in multiple-layered model membranes (left), whereas only much more ordered liquids were observed by X-rays (right). The increased beam intensity of NSLS-II will make up for the contrast disadvantage of X-ray scattering. Observation of fluid membrane structure will be possible, even in single-layered membranes.*

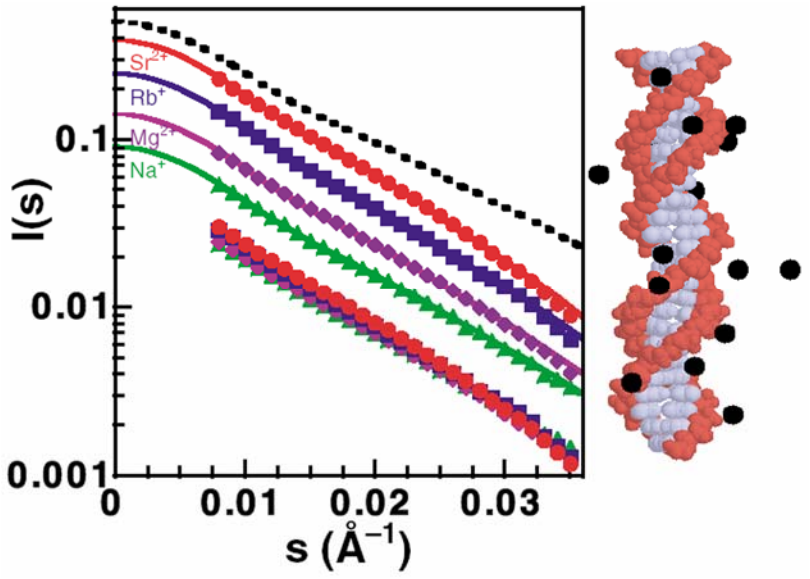

Figure 2.2.3 *Monovalent and divalent counterion clouds around negatively chraged DNA double helices in solution are probed using anomalous small-angle x-ray scattering [9]. The spatial correlation of surrounding counterions to DNA was directly measured.*

2.2.2.3 Counterion Cloud

In their native environment biomolecules are surrounded by water and ions. It has long been recognized that the availability of water and ions is an important factor in protein structure and function but little is known about the structure of "ordered" water and the distribution of counterions around biomolecules. By using synchrotron radiation it is possible to specifically probe the counterion cloud by anomalous scattering while keeping the biomolecules in solution. Multivalent ions are particularly interesting because they are present at much lower concentrations in biology and are often used to trigger biological events, such as opening or closing a channel or enzyme activation. Multi-valent ions are also responsible for DNA condensation inside the cell nucleus, in sperm heads and virus capsids. Recent efforts to employ solution anomalous X-ray scattering techniques to address such questions had to resort to exotic ions such as Rb^{+} and Sr^{2+} with K edges of 15.2 keV and 16.1 keV [9] (Figure 2.2.3).

The high brightness of NSLS-II in the 1 to 4 keV energy range makes it very well suited to use anomalous scattering techniques on biologically relevant ions such as Na (1.07 keV), Mg (1.3 keV), Cl (2.8 keV), K (3.6 keV), Ca (4.0 keV), S (2.5 keV) and P (2.1 keV). Because biological materials including water absorb strongly at these low energies high photon flux is essential and this high flux must be in a small spot to use flow-cell mixers to follow triggered events in time resolved experiments.

2.2.2.4 Study of Metalloproteins with X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) can be used to measure the transition of core electronic states of a metal atom to excited electronic states or continuum states. Spectral analysis near the electronic transition, so-called X-ray absorption near-edge structure, or XANES, provides information on the metal's charge state and geometry. Spectral analysis above the absorption edge (from the edge to 10-15% above the edge in energy), so called Extended X-ray Absorption Fine Structure, or EXAFS, provides complementary structural information, such as numbers, types, and distances of ligands or neighboring atoms. Both spectroscopies are valuable techniques for studying a variety of metal sites in biological systems [10]. Recent experiments where X-ray crystallography and X-ray spectroscopy are used in combination have provided information that was not available from either technique alone [11].

Traditionally, XAS, like most other spectroscopies, has been used as a static probe of structure. NSLS-II provides the opportunity to extend X-ray absorption measurements into the time resolved realm, potentially revolutionizing the study of biochemical and bioinorganic systems. The importance of real-time structural information for mechanistic studies is apparent, and has led to a blossoming of interest in time resolved XAS. Although hundreds of papers have been published on time resolved XAS, until now these have focused mostly on questions of materials-science and catalysis. This is because the best method for measuring time resolved XAS is to use a "dispersive" geometry, in which a polychromatic X-ray beam is focused onto the sample of interest. Unfortunately, the dispersive geometry is limited to relatively high metal concentrations (> 10 mM for modest time resolution; higher for ms time resolution) and is thus not practical for most biological samples.

To study dilute samples such as metalloproteins, one must measure the data as fluorescence excitation spectra. For slow reactions occurring over several hours, time resolved XAS was used as early as 1995 in a study of reaction of the enzyme carboxypeptidase [12]. With recent advances in rapid-scanning monochromators, it has proven possible to measure XAS spectra with scan times as short as 50 ms [13], although typical scan times are several seconds [14]. NSLS-II will allow much faster time scales to be probed.

Since the biomolecular system being studied evolves continuously during the reaction, with many different species potentially being present, one cannot take a literal "snapshot" of intermediates that form. However, use of sophisticated mathematical approaches such as principal-component analysis [15], allows one to come close to this ideal. Combining the information from tens or hundreds spectra, each measured at a different time after mixing, makes it possible for one to deconvolve the component spectra, even for relatively minor components. With the bright X-ray beams provided by NSLS-II, the continuous flow mixing technology discussed above will enable time resolution close to one microsecond.

2.2.2.5 Electron Delocalization in Biomolecules

The wave nature of the electron determines almost all of the properties of simple condensed matter, for example its color, mechanical hardness, electrical resistivity, thermal conductivity, thermal expansion, dielectric constant, melting and boiling points, etc. It is therefore worth investigating the degree to which delocalization underlies protein function, since proteins are, after all, a form of condensed matter. NSLS-II will enable a new class of such phenomena to be studied for the first time.

As an example, consider the light harvesting complex (LHC) protein-chromophore (Figure 2.2.4) of the photosynthetic bacterium rhodobacter sphaeroides. Light is first absorbed by a circular aggregate of bacteriochlorophyll molecules and carotenoids held together by proteins, LH-II. Energy is then transferred to a circular antenna complex, LH-I, surrounding the reaction center, and finally to the reaction center (RC) where it starts the respiratory cycle of the cell. The structures of LH-II and RC are

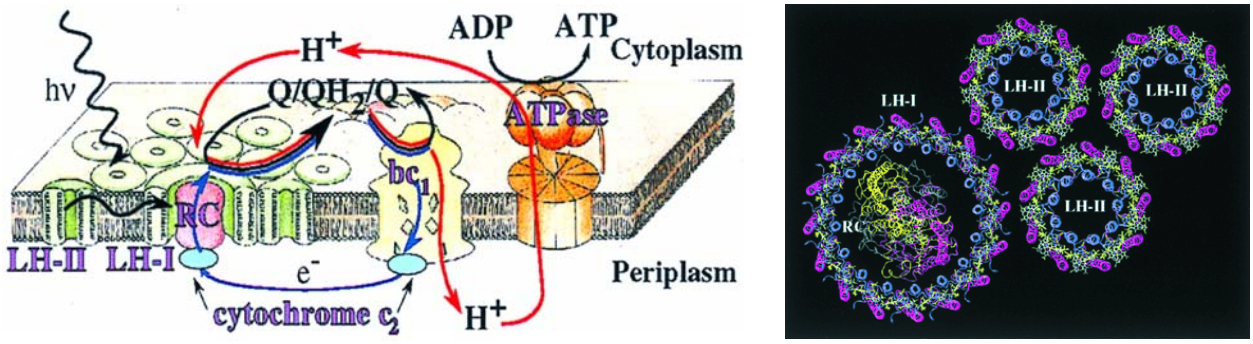

Figure 2.2.4 (*Left) Schematic representation of the photosynthetic apparatus in the intra-cytoplasmic membrane of purple bacteria. (right) A model for the pigment-protein complexes in the modeled bacteria rhodobacter sphaeroides [16].*

known to atomic resolution from x-ray diffraction experiments. However, the mechanism and dynamics of electron energy transfer remains a mystery.

For example, the quantum efficiency of LHC is ~ 95%, raising questions about how it is able to avoid fluorescence losses when transmitting energy over large distances. LHC possesses a high degree of circular symmetry, a property conjectured by Hu *et. al*. [17] to suppress fluorescence by making the lowest excited states of LHC dipole forbidden. For Hu's arguments to be correct, the electronic states must be coherently delocalized over the entire molecule, a prediction with profound implications since it suggests quantum delocalization played a crucial role in the evolutionary history of this organism. So far, efforts to indirectly estimate the coherence length optically, however, have yielded mixed results [18, 19].

Inelastic X-ray scattering (IXS) is a direct probe of quantum coherence. Specifically, the momentum spread of excited states as they appear in the dynamic structure factor $S(\mathbf{k},\omega)$, gives the exciton mean-free-path, i.e. the distance over which it propagates before losing phase coherence. The energy scale is set by the electronic excitations in the photosynthetic unit, the first dipole allowed transition is ~1.4 eV. However, because of the poor quality of these sample, elastic scattering background is going to a severe problem. To overcome this problem, an energy resolution of a few meV will be needed.

The high brightness and flux of NSLS-II, together with new optical schemes, will enable IXS experiments with an energy resolution of a few meV at 8 to 10 keV, and open up a new window into the electronic properties of biomolecules.

2.2.3 Impact of NSLS-II

2.2.3.1 Time resolved Studies in Micro-fabricated Flow-cell Mixers

The development of micro-fabricated lamellar flow-cell mixers (Figure 2.2.5) provides a way to initiate dynamical events in micron-scale jets of solution on microsecond time scales, while requiring only extremely small quantities of specimen [20-22]. These continuous-flow diffusion mixers [23, 24] produce thin laminar flow sheets of solutions and dynamical events are triggered as the solutions mix by diffusion between the solution sheets. They can potentially enable us to watch dynamical events unfold by making measurements at different positions downstream. For instance, to generate a protein-folding

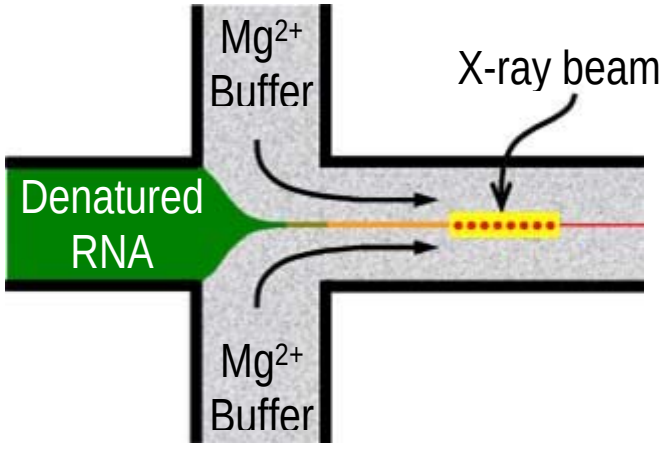

Figure 2.2.5 *Principle of operation of the flow cell, showing a cross section through the center and indicating one possible location of the X-ray beam. In this case, denatured RNA solution was mixed with side-streams of Mg^{++} to initiate folding. Because the time-scale of diffusional equilibrium of the central solution jet with the side-streams varies as the square-root of the central jet width, the time scales for equilibrium can be on the order of microseconds for jets less than a micron wide. The X-ray beam is moved downstream to access later times after the initiation of mixing. The high brightness of NSLS-II will revolutionize mixer experiments.*

event, denatured protein is injected into the central channel, sandwiched between buffer solutions. As the protein and buffer solutions flow downstream, the denaturant diffuses out of the protein layer. Once the denaturant concentration drops below a threshold, the protein folds back to its functional conformation. The solution mixer also could trigger other biochemical reactions by a similar mixing of reactants. The solution-mixer technology can be combined with X-ray solution scattering, spectroscopy, or footprinting techniques to study a wide range of problems in life science.

The high brightness X-ray beams of NSLS-II will have a dramatic impact on mixer experiments. Achieving the ultimate time resolution requires the very small and intense beams that NSLS-II will excel at producing, since, for a given solution velocity the time resolution is directly determined by the beam size. Small beams will also allow smaller overall dimension of the solution layers, reducing sample consumption. Because the solution that is exposed to the X-ray beam is constantly replenished, radiation damage is not a limitation. Finally, the small beams will enable measurements to include as little of the side solution streams as possible, providing enhanced signal-to-noise for the weak X-ray signals from the small volumes.

NSLS-II combined with micro-fabricated flow-cell mixers will revolutionize solution studies in much the same way that earlier synchrotron sources enhanced the possibilities of macromolecular crystallography.

2.2.3.2 X-ray Footprinting

Hydroxyl radicals cleave the phosphodiester backbone of nucleic acids. In sections where the RNA is folded, however, the backbone is inaccessible to solvent, and therefore protected from radical cleavage. X-ray footprinting employs the very intense and ionizing white (polychromatic) X-ray beam to generate hydroxyl radicals. One then analyzes the pattern of fragments after X-ray exposure by gel electrophoresis; the protected sections of the RNA that are not cleaved yield a "footprint", a general illustration of which is in Figure 2.2.6. One can follow the protections as a function of time, showing the tertiary contacts formed as the RNA folds. X-ray footprinting also works for proteins. In this case, hydroxyl radicals modify the amino acid side chains that are exposed to the solvent. The oxidized samples are digested with proteases and analyzed by LC-mass spectrometry to determine the extent and sites of modification.

Time resolved footprinting measurements can be achieved with a solution mixer to induce cleavage after a delay relative to the triggering of a dynamic event. This is an ideal method for gaining insight into dynamic processes of large RNA and protein assemblies. It provides detailed structural information (at the single-nucleotide and single side-chain level) on biologically relevant timescales. Current time resolved footprinting measurements are limited to millisecond time resolution. The high beam brightness provided by NSLS-II will make the time scale that is accessible by this technique significantly shorter, certainly by a factor of ten. This improvement is not only because of the better time resolution of the smaller-scale solution mixers enabled by NSLS-II, but also owing to the shorter X-ray exposure time that is necessary to generate the hydroxyl radicals that cleave the biomolecules. All of this would benefit from use of microcapillary focusing that could produce a 10 μm spot with high intensity. Achieving an understanding of conformational dynamics in macromolecules and their complexes during processes as diverse as ligand binding, folding, catalysis, and macromolecular assembly is a challenging and important step towards providing detailed molecular descriptions of biological systems.

2.2.3.3 High-throughput Characterization of Biomolecules

Whereas the undulator-based beamlines at NSLS-II will offer the opportunity to overcome a number of exceedingly difficult and important problems in life science, the lower intensity bending magnet-based beamlines will contribute by performing relatively simple tasks that are time consuming today. The duration of static measurements will be greatly reduced even on bending magnet beamlines as the source brightness increases. This provides the possibility of high-throughput characterization of large numbers of

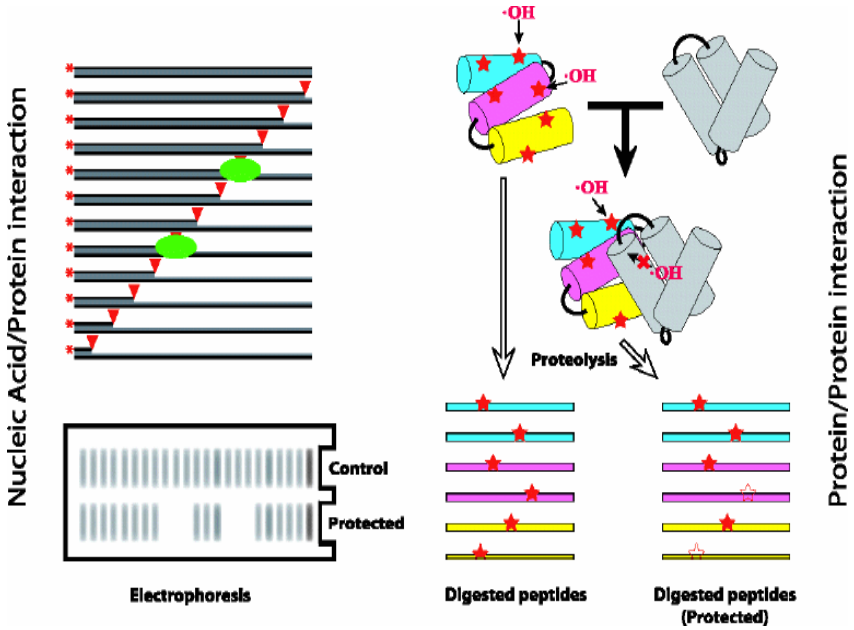

Figure 2.2.6 *Synchrotron X-ray footprinting uses a white X-ray beam to generate hydroxyl radicals to cleave RNA backbone or protein side chains that are exposed to water. Analysis of the cleaved/modified products provides structural information on the single nucleotide/side chain level. This capability is very useful for studying the dynamic processes of large RNA and protein assemblies when combined with time-resolved measurements.*

samples. Automatic sample handlers will be constructed to feed samples, and many, perhaps even hundreds, of samples will be characterized each hour by solution scattering and X-ray spectroscopy.

High-throughput solution-scattering measurements will be useful as a quality-control and diagnostic tool during the genome-scale expression of proteins that accompanies the Structural Genomics programs mentioned in Section 2.1 on macromolecular crystallography. For example, many proteins cannot be expressed in E. coli, or are unable to fold in these bacterial cells. Therefore the quality of the expressed proteins must be monitored, and some of their physical characteristics can be discovered, for example by solution scattering and IR/UV spectroscopy. High-throughput measurement is necessary to match the scale of the whole structural genomics effort.

Another potential application of high-throughput measurements is for crystallization screening. The interaction between individual protein molecules can be measured far before nucleation occurs [25]. Measuring the protein-protein interaction under a spectrum of conditions therefore can serve as a tool for searching for the optimal condition under which proteins can nucleate and continue to grow into large crystals.

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2.3 Biological Imaging

2.3.1. Overview

The high brightness of NSLS-II will make it possible to tightly focus the beam to create very intense nanoprobes for high-resolution cellular imaging and sensitive trace element mapping in biological specimens. The brightness will also provide highly collimated beams of high intensity and large transverse dimensions for novel forms of medical imaging and tomography [1]. In addition to high brightness, NSLS-II will also provide the broadest range of wavelengths to users in a single facility, extending from hard X-rays to the far-infrared and enabling a wide array of analytical techniques, including: X-ray microscopy (hard and soft; scanning and full-field), diffraction imaging, X-ray tomography, X-ray microprobe, diffraction-enhanced imaging (DEI), and infrared imaging. These diverse imaging tools will span the resolution scale from nanometers to millimeters, allowing non-destructive analysis of biological subjects ranging from sub-cellular structures to humans.

Synchrotron facilities worldwide, including the NSLS, demonstrate the value of using a synchrotron for biological and medical imaging. Information that could once be obtained only on pure, spatially homogeneous samples is now obtained from heterogeneous natural and complex biological samples on length scales of tens of nanometers. NSLS-II will extend this to less than 10 nm, enabling studies of nanoscale phases and compositional variations and providing deeper insight into nature (Figure 2.3.1).

The ultra-high brightness of NSLS-II will have significant impact:

- For the highest resolution, radiation with spatial and temporal coherence is required. NSLS-II will increase the coherent flux available by at least two orders of magnitude. Combined with advanced X-ray optics, NSLS-II will make ~10 nm spectromicroscopy routinely available. Higher spatial resolution (~10 nm) for imaging whole cells (>10 μm thick) will enable imaging substructures such as cell membranes, protein complexes (e.g. ribosomes), and cytoskeleton components (microtubules, actin filaments).
- Combined with new techniques in reconstruction of diffraction data, NSLS-II will make sub-10 nm spatial resolution possible, improving the image resolution of subcellular components.
- With NSLS-II, the spatial resolution of X-ray microprobes and DEI will be reduced to below 1 μm. This spatial resolution will enable the imaging of plant and animal tissues on the sub-cellular level, and importantly, in their natural state.

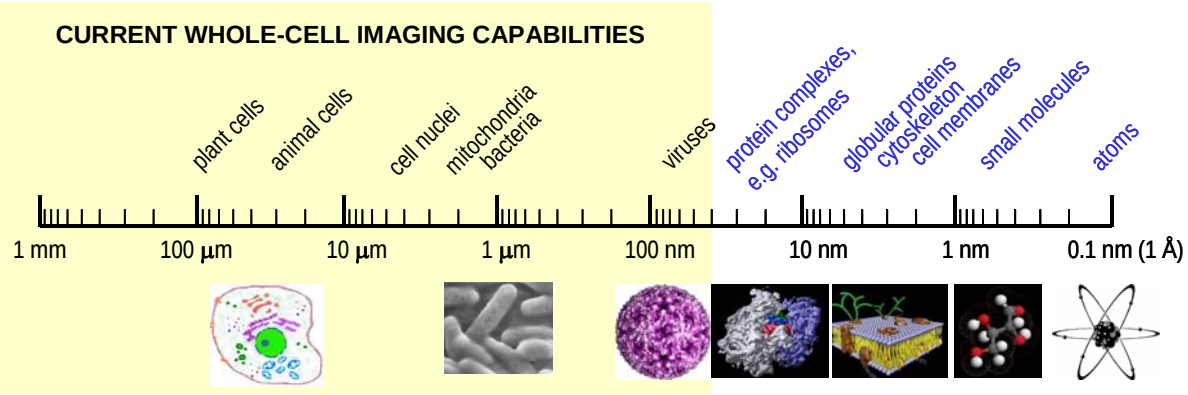

Figure 2.3.1 *The size scale of biological materials. Current visible-light imaging capabilities are diffraction-limited at ~200 nm. Using synchrotron X-rays, imaging is extended to 30-40 nm. With the high brightness and coherence of NSLS-II, this limit will be extended to ~10 nm, permitting intact imaging of subcellular structures such as protein complexes, cytoskeleton components, and cell membranes.*

2.3.2 Scientific Challenges and Opportunities

The requirement for increased efficiencies in the health care system and global trends toward an aging demographic are stimulating investments in biomedical imaging research. NIH and DOE are keenly interested in developing and improving the ability to image macromolecular machines. In 2000, NIH established the National Institute of Biomedical Imaging and Bioengineering, which "coordinates with biomedical imaging and bioengineering programs of other agencies and NIH institutes to support imaging and engineering research." In addition, the first goal of the DOE Genomes-to-Life initiative is to "identify and characterize the molecular machines of life," where "imaging will help define interactions between proteins and other components in the complex interacting networks of living cells."

Recent discoveries in synchrotron X-ray and infrared imaging sciences have spawned the development of new imaging techniques that provide unprecedented resolution of nature's small details. NSLS-II will enable greatly enhanced capabilities for forefront integrated biomedical research that will lead to dramatic breakthroughs in both basic scientific understanding and human health.

2.3.2.1 Imaging Molecular Machines

Biological cells are composed of complex macromolecular assemblies that work together in functional networks that characterize the dynamic life of a cell. These machines execute important metabolic functions, mediate information flow within and among cells, and build cellular structures. Imaging of whole cells, and the macromolecular assemblies within cells, is critical for understanding these interactions.

For example, one of the outstanding problems in cellular biology is the way the mammalian cell packages its genetic material under different conditions. How is the chromosome assembled and organized? How are errors in this organization related to disease? One specific example involves how the organization of genetic material is different in the sperm cell where, instead of histones, protamines are attached to DNA. The ability to image hidden abnormalities in the composition of sperm nuclei, including damaged DNA, impaired chromatin condensation, alteration in the chemical composition and concentration of sperm proteins is important in order to understand how the morphology of the sperm cell affects male fertility.

Recently X-ray microscopy was introduced for the evaluation of a single sperm (Figure 2.3.2). Sperm have a size in the 1-2 micron range, and the structures of interest are typically 30 nm, well matched to the capabilities of soft X-ray microscopes. Soft X-ray spectromicroscopy with a cryo scanning transmission X-ray microscope can evaluate both qualitative and quantitative abnormalities in sperm ultrastructure and composition. The chemical sensitivity of XANES spectroscopy allows the identification of the major constituents (protein, DNA, etc.), and the ability to image frozen hydrated specimens assures that the specimen is as close to its natural state as possible.

The high brightness of NSLS-II will improve the resolution of sperm imaging to ~10 nm. At this size scale, the packaging of genetic material will be imaged. Specifically, the small protamine-DNA complexes will be visualized within the sperm. Chromosomes and abnormalities in chromatin condensation will also be seen. Moreover, spectroscopic imaging of sperm will enable the study of sperm cell chemistry at ultra high resolution, such as the concentration of sperm proteins and nucleic acids.

As another example, the budding yeast, Saccharomyces cerevisiae, has long been a valuable model system for genetic, molecular, and biochemical analyses, and continues to be important for modern proteomics investigations. Hundreds of distinct multiprotein complexes have been identified and new cellular roles for several hundred other proteins, most of which had no previous functional annotation, have been proposed. An important method for gaining insight into the function of a protein is to determine its location in cells. Kumar et al recently conducted a high throughput immunofluorescent localization of tagged gene products in the budding yeast [2]. They concluded that the entire yeast

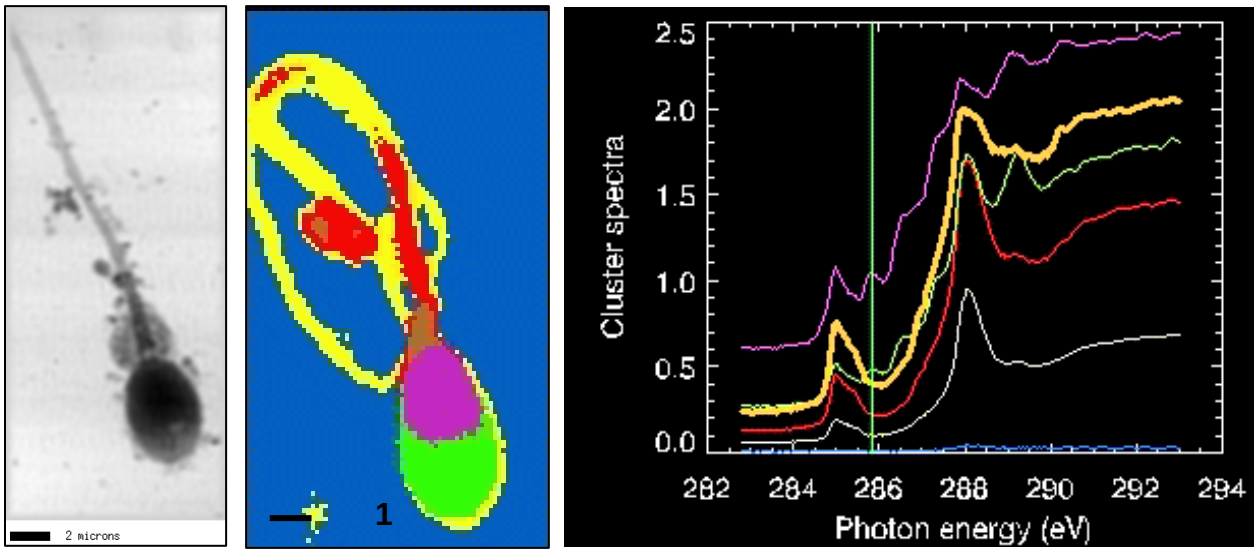

Figure 2.3.2 *Soft X-ray spectromicroscopy imaging of human sperm: wet image (left), and cluster analysis image (center) of spectral data set (right) demonstrating biochemical mapping. Such studies can correlate morphological types with biochemistry.*

proteome encompasses about 5100 soluble proteins and more than 1000 transmembrane proteins. This is a remarkable undertaking that begins to provide insight into protein locations and their associated function. However, if the yeast proteome encompasses 30,000 protein interactions, many of which change during the organism's life cycle [3], more precise information about the location of each protein throughout the cell cycle will be required. This information is beyond the level of resolution of existing light microscopy techniques and is unattainable using electron microscopy, given the time-consuming nature of the requisite specimen preparation.

X-ray tomography has the potential to accomplish these goals and make significant contributions to our understanding of protein function in cells. Using this approach, superb structural information can be obtained from whole, hydrated cells at better than 35 nm resolution. In addition, immunogold labeling techniques similar to those used for TEM can be used to localize proteins in whole cells [4, 5]. These capabilities, combined with tomographic procedures, offer unique three-dimensional views of cells.

Transmission X-ray microscopy has been used to examine whole cells, revealing superb images of cytoplasmic and nuclear structures at 35-40 nm resolution (Figure 2.3.3). The high brightness of NSLS-II coupled with improvements in zone plate technology will enable even higher resolution. This promises to be a remarkably fertile line of research for which NSLS-II is a critical and necessary requirement.

2.3.2.2 Fundamental Basis of Disease

Biological tissues are composed of individual cells and a complex extracellular matrix that holds the cells together to make a tissue. Many diseases involve alterations in the chemistry of the cells and extracellular matrix. For example, cancerous tumors, scar tissue, and atherosclerotic (blood vessel) and neuritic (brain) plaques all form through some combination of irregular cell growth, and breakdown and remodeling of the extracellular matrix around them. Imaging of whole tissues, encompassing the interactions between cells and the extracellular matrix, is critical for understanding these disease processes.

As a prime example, a growing number of neurodegenerative diseases, including Alzheimer's disease (AD), Parkinson's disease, Huntington's disease, amyotrophic lateral sclerosis (ALS) and Creutzfeldt-Jakob disease, involve the misfolding of normal proteins in the brain, which has recently been associated

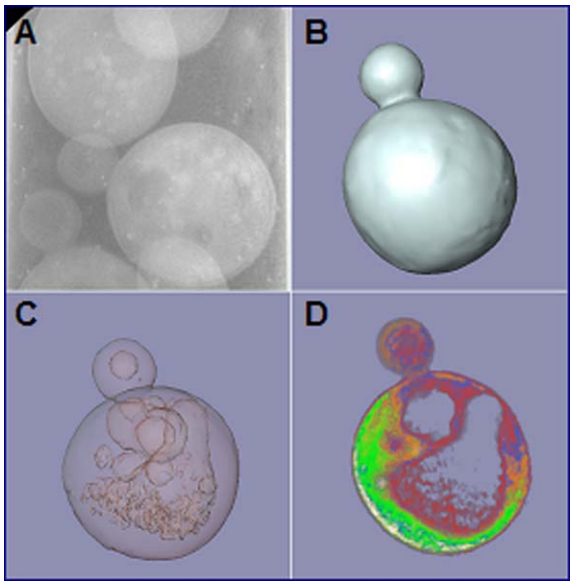

Figure 2.3.3 *X-ray tomograph of the budding yeast, Saccharomyces cerevisia. (A) Projection image of yeast in the capillary; arrows indicate 60 nm gold balls used as fiducial markers for alignment of all images for tomographic reconstruction. (B and C) Computer generated sections from the reconstructed data; X-ray dense lipid droplets (small white circles) are now easily distinguished as distinct organelles and large vacuoles that are less dense appear dark. Yeast cell is 5 microns in diameter.*

with the binding of metal ions such as iron, copper, and zinc. Yet, the functions of these metal ions and the misfolded proteins in the disease process are not well understood.

To date, metal concentrations in brain tissue are generally measured via macroscopic (bulk) techniques that cannot provide any spatial information on localized metal accumulation. Traditional histochemical (staining) methods for localizing metals in tissue are insufficient. Stains and/or fluorescently-tagged antibodies are also used to identify misfolded proteins in tissue, but do not provide direct information on the protein's structure.

Using X-ray microspectroscopy, the metal ion distribution, concentration, oxidation state, and local structure as a function of disease severity can be imaged in intact brain tissue. By combining fluorescence microscopy and infrared microspectroscopy, the location and secondary structure of the associated misfolded proteins are imaged (Figure 2.3.4). By combining these results, it is possible to identify the metal ions that accumulate before, concurrently, or after protein misfolding, in order to develop a possible mechanism for the complex formation and toxicity.

Current limitations for X-ray microprobe imaging of neuritic plaques include spatial resolution and beamtime availability. Although many neuritic plaques are large (e.g. AD plaques are 50-200 microns in diameter), others are much smaller (e.g. ALS) and more diffuse (e.g. mad cow disease and scrapie). The higher brightness and coherence of NSLS-II, including increased insertion device capacity, will enable X-ray microprobe analysis at below 1 micron resolution, and even zone plate microscopy at 70-100 nm resolution. In addition to high resolution, the quantity of beamtime required for X-ray microprobe analysis as well as infrared imaging is also a limiting factor. Large areas of tissue need to be imaged and a large number of samples are necessary for good statistics. With NSLS-II, array-detector infrared imaging will be possible, increasing data collection rates by a factor of at least 20.

NSLS-II will also allow longitudinal in-vivo studies to track disease progression and/or evolution of pathology during treatment of neurodegenerative diseases. For example, DEI and X-ray Microtomography will be able to penetrate the skull of animal models of Alzheimer's disease.

Another important example is that of osteoarthritis (OA), which affects over 40 million Americans. Important questions remain as to the relationship between underlying (subchondral) bone and joint

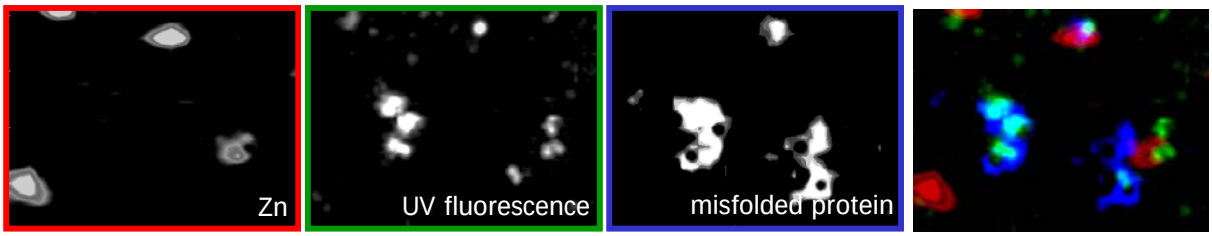

Figure 2.3.4 *Grayscale images of zinc (left), amyloid plaque (left, center), and misfolded protein (right, center) in a single specimen of Alzheimer's brain tissue. The Zn image and the misfolded protein image were collected with X-ray fluorescence microprobe and infrared microspectroscopy, respectively. The UV-fluorescence image of the amyloid plaque identifies their location based on a fluorescence stain, but does not provide protein structural information. (Right) An RGB image containing overlays of the three grayscale images: red = zinc; green = amyloid; blue = misfolded protein.*

cartilage changes in OA, partly because of the difficulty in studying this calcified tissue. DEI is able to simultaneously detect both cartilage and bone changes in the progression of OA (Figure 2.3.5) [6]. The spatial resolution of these images is limited by the present NSLS source size to about 50 microns. However, NSLS-II will extend this to below 1 micron with enhanced sensitivity.

Very little is known about the composition of the mineralized plate beneath the articular cartilage in OA. Presently, infrared microscopy is limited in its ability to examine the chemical composition (e.g. mineralization, carbonate content, collagen structure) of intact sections of joints. Advances in array detector technology will soon enable access to the low wavelength range necessary to image some of the mineral modes in bone, and these detectors will be best suited to a synchrotron source such as NSLS-II with a wide acceptance angle.

2.3.2.3 Early Disease Detection

Challenges remain in clinical diagnostic and screening imaging, despite recent advancements in mammography, MRI, CT, PET, and SPECT. The rate of false negative in mammography is still about 10%; cartilage is difficult to visualize by radiological means; and the contrast of chest X-ray is too low to detect early stages of emphysema and edema. Since early intervention of these diseases is typically life-saving, development of new radiography methods for diagnosis and screening is of great interest.

DEI is advantageous for mammography because its refraction contrast mechanism [7] provides increased sensitivity to soft-tissue contrast. Figure 2.3.6 shows images of breast tissue with invasive lobular carcinoma that extends to the edge [8]. It illustrates the improved visualization of spiculations

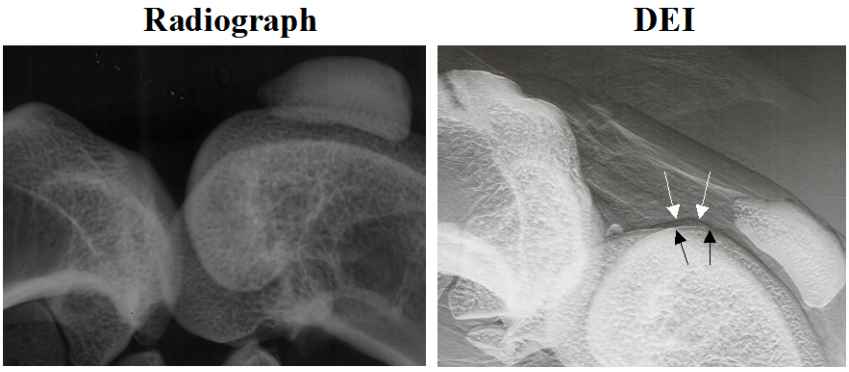

Figure 2.3.5 *Conventional X-ray (left) and DEI image (right) of an intact rabbit knee joint. Notice that even though the DEI contrast allows visualization of cartilage, the resolution of the image does not yet allow detailed study of early stage cartilage damage or the bone-cartilage interface. NSLS-II will extend the resolution from 50 microns today to below 1 micron and make this possible.*

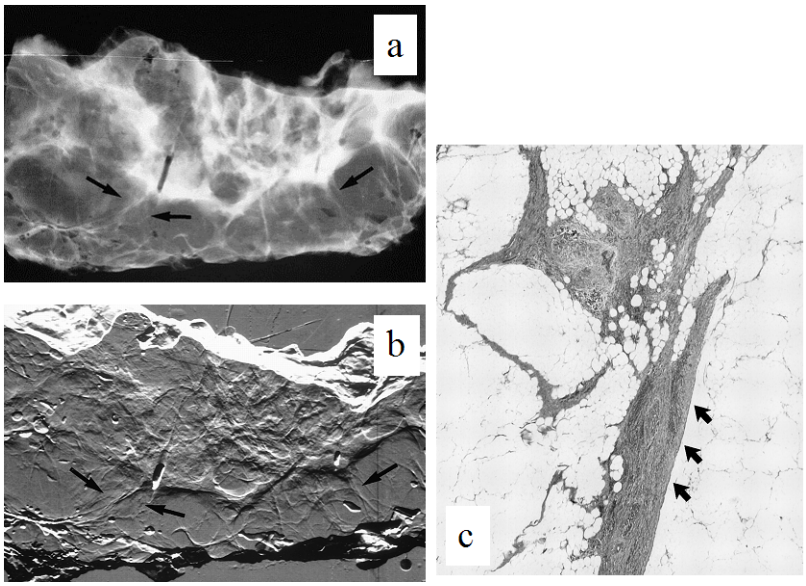

Figure 2.3.6 *Specimen with invasive lobular carcinoma, which typically grows in single files of cells. (a) Digital radiograph of the specimen. Note the vague linear densities along the inferior margin of the lesion. (b) Diffraction-enhanced image of the same specimen. Note the increased prominence and number of lines that extend from the inferior border of the lesion at the arrows. (c) Photomicrograph of the spiculations identified between the two arrows on the left in b shows a band of fibrous tissue with invasive lobular carcinoma.*

representing tumor extension by DEI, compared to standard radiographs. The DEI apparent absorption image was found to have 8 to 33 times greater contrast than that of a normal radiograph [9]. DEI breast images are currently limited to a spatial resolution of about fifty microns and it is important to visualize smaller calcifications and small spiculations. NSLS-II will provide a major advance by extending this to below one micron. The increased resolution and sensitivity allowed by NSLS-II will enable study of the cancer biology and morphological features of animal models of breast cancer and other cancers that are typically too small to be reliably detected by the current DEI resolution and will guide the design of a clinically-relevant DEI system.

As another example, degeneration of joint cartilage in OA is among the leading causes of immobilization and affects 85% of elderly people. Joint pain is one of the first signs of disease, but by the time pain becomes a symptom, successful treatment leading to regeneration of the tissue is too late.

Conventional radiography is the first and most frequently used imaging method to detect joint abnormalities. However, cartilage tissue has little X-ray absorption contrast and cannot be easily seen so that conventional radiography is sensitive only in cases of advanced disease. A high-resolution radiographic method to directly visualize early defects in cartilage is thus desirable.

The ragged face of damaged cartilage produces substantial changes in X-ray refraction as well as small angle scattering. Studies have shown that DEI is able to visualize damage typical of early degenerative disease in cartilage, tendons and other soft tissues in intact joints [10]. Cartilage is thin, especially in animal models of OA, and is usually obstructed by overlaying bone structures in a projection image. Multiple high resolution DEI images, and their reconstruction by CT, are thus necessary.

NSLS-II, with its small source size and top-off filling mode, will allow DEI imaging of cartilage at spatial resolution of less than 1 micron and much better sensitivity to reveal subtle changes in cartilage of animal models. The thermal stability will also allow the longer exposures necessary for routine CT imaging and reconstruction of phase contrast.

2.3.3 Impact of NSLS-II

2.3.3.1 Soft X-ray Microscopy and Nanotomography

Soft X-ray microscopy generates 3-D, quantifiable, structural and molecular information at better than 40-nm resolution. It is fast, relatively easy to accomplish, produces high-resolution, absorption-based images, and is naturally combined with small-spot spectroscopy for chemical identification at high spatial resolution. When operating between the K-edges of carbon and oxygen, it has good intrinsic contrast between organic material and water, and good penetration in micron-thick specimens. By taking images at photon energies near an element's absorbance resonances, regions of high concentration of certain bonding states of the element can be highlighted. Whole, hydrated cells (between 10-15 microns thick) can be examined, eliminating the need for time-consuming, and potentially artifact-inducing, embedding and sectioning procedures, and yet it is possible to localize proteins using simple immunolabeling protocols (Figure 2.3.7).

Obtaining the highest resolution in soft X-ray microscopy requires that the zone plate be coherently illuminated. Hence, the technique is brightness-limited. The high brightness of NSLS-II will provide unprecedented spatial resolution, faster data collection, and improved signal to noise.

The goal of obtaining high resolution 3D nanotomographic images on whole cells is an important one. Electron microscopes are able to obtain 6-8 nm resolution 3D images of regions of frozen hydrated cells but only when the sample thickness is less than 300-400 nm. Soft X-ray tomography demonstrations at the NSLS, BESSY, and ALS have obtained 60-100 nm resolution 3D images of cells up to about 8 microns thick (Figure 2.3.8). To prevent radiation damage, the cells must be rapidly frozen and maintained at low temperatures. Remarkably, cryo-fixation enables collection of hundreds of successive images with no detectable radiation damage. This technique should enable, for the first time, an absolute measurement of the full 3-D structure of small single cells. However, depth of focus decreases as the square of improvements in transverse resolution in microscopes, so that soft X-ray microscopes with better resolution will be limited to even thinner cells.

An important approach to this problem is to use 3-5 keV x rays for phase contrast imaging, where one can push towards 10 nm 3D resolution with good penetrating power and little limit due to depth of focus [13, 14]. The high brightness of NSLS-II at these energies is crucial for phase contrast nanotomography at higher resolution.

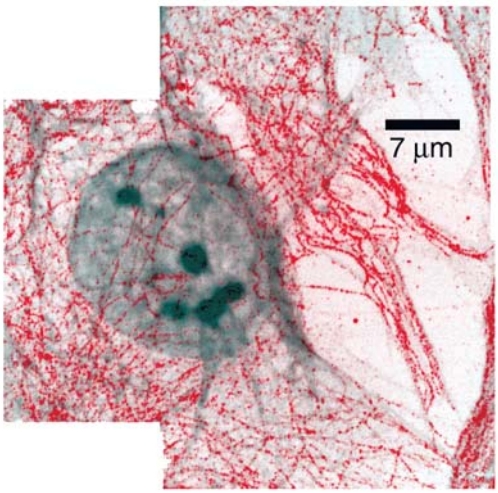

Figure 2.3.7 *STXM image of a fibroblast that has been antibody labeled with gold particles for tubulin (a cytoskeleton component) [11].*

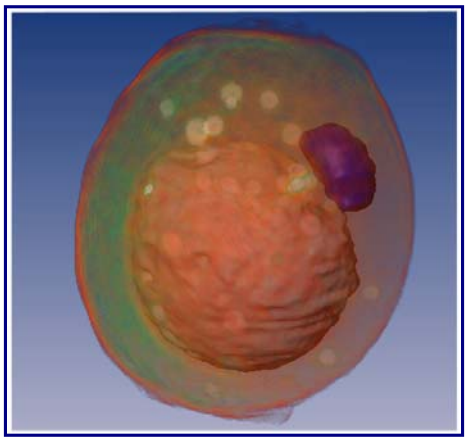

Figure 2.3.8 *Soft X-ray nanotomograph (50 nm resolution) combined with volume rendering of Saccharomyces cerevisiae (a yeast cell). The nucleus is colored blue, lipid droplets appear white, and the surface of a large vacuole in the center of the yeast is color-coded pink. The yeast is 5 microns in diameter. [12]*

Scanning transmission X-ray microscopes are presently quite slow compared to full-field transmission X-ray microscopes (TXMs): it can take several minutes to acquire one high resolution image, several hours to acquire a spectromicroscopy data set, or a day to acquire a 100 nm voxel resolution tomography data set [15]. At the same time, scanning microscopes offer important advantages: the 10-20% efficient zone plate is located upstream of the specimen in the beam path so that its efficiency affects only exposure time but not radiation dose to the sample. Also, the small phase space required for zone plate illumination leads to simpler designs for high energy resolution monochromators, and segmented detectors can be used to simultaneously acquire absorption and phase contrast images in one scan [16]. The NSLS hosts a group from Stony Brook that has pioneered zone plate scanning microscopy, and a large community already uses zone plate scanning microscopy for scientific research in biology and environmental science.

The higher brightness of NSLS-II, combined with laser interferometer position feedback, will enable over two orders of magnitude improvement in spatial resolution and greatly reduced data collection times in TXM measurements.

2.3.3.2 Diffraction Imaging

The resolution of X-ray microscopes is limited by our ability to fabricate high-resolution optics. It was pointed out by David Sayre that one should be able to record the diffraction pattern of small, isolated non-crystalline specimens, such as small cells or organelles, and reconstruct the image at a resolution not limited by optics. The diffraction pattern of such objects is continuous, and can be sampled on a fine raster to obtain the information necessary to retrieve the phase lost in the recording process. Diffraction imaging, illustrated in Figure 2.3.9, was first demonstrated at the NSLS in 1999. The ultimate resolution limit is set by radiation damage to the specimen. A full 3D reconstruction can be performed if diffraction patterns are collected from a complete range of angular orientations.

Scientists using the NSLS pioneered the reconstruction of X-ray diffraction data to yield real-space images of non-crystalline specimens [17], and a development program is nearing completion [18] to allow these experiments to be carried out on cryogenic specimens to minimize radiation damage, and to allow the specimen to be rotated through a 160° tilt range. Experiments underway at the NSLS are using a zone plate to obtain an already-phased image at low spatial frequencies, and collecting diffraction data without the transfer function loss of the zone plate at higher spatial frequencies, and thus extend X-ray imaging beyond the zone plate resolution limit.

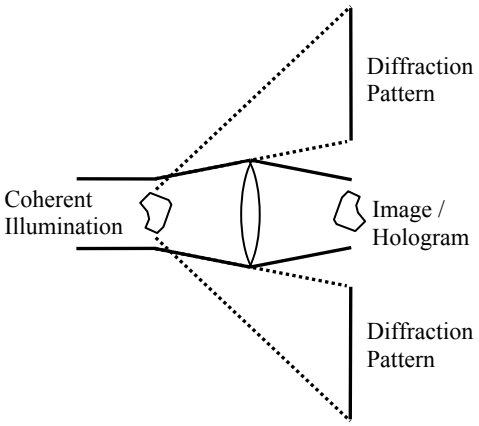

Figure 2.3.9 *Diffraction-based imaging. A zone plate is used to obtain an image at low spatial frequencies, diffraction data yields image at higher spatial frequencies beyond the zone plate resolution limit. NSLS-II provides the essential coherent illumination.*

The diffraction technique depends on coherent illumination, and hence on the brightness of the source. NSLS-II will be the ideal source for diffraction imaging, providing the high brightness required for routine 3D imaging by this technique.

In the push to higher resolution, it is inevitable that radiation damage is increased: one is attempting to illuminate and collect signal from a smaller mass. Scientists using the NSLS have pioneered the development of cryo methods for scanning microscopy [19], and have shown a 10^4 decrease in damage relative to room temperature hydrated specimens, consistent with cryo TXM studies [20]. It is worthwhile noting that timescales play an important role in high resolution imaging: for 10 nm resolution imaging one must either collect the entire dataset in a time much less than 100 fsec to avoid hydrodynamic blurring, or greater than about 1 msec to allow for heat conduction.

2.3.3.3 Hard X-ray Microprobe

X-ray absorption spectroscopy (XAS), including X-ray fluorescence (XRF), has been widely used for probing metal content and structure within biological systems. The XAS spectrum provides information such as metal oxidation state, metal spin state, number and type of ligands bound to the metal, and bond distances. Using focusing mirrors, XAS and XRF imaging can be used to non-destructively provide the distribution of trace element content and structure with a resolution of 1-10 microns and elemental sensitivities in the sub-mg kg^{-1} range. Applications have included the characterization of heavy metal contamination in soils, the uptake of metals in plants (i.e. phytoremediation), and the role of metal ion accumulation in neurological diseases [21]. Analyses can be done on standard microscopic sections, rock fragments, powders, soils, and biological materials; samples can be in solution, liquids, amorphous solids, aggregates, plant roots, surfaces, etc.

The greatly increased brightness of NSLS-II will make it possible to use zone plate focusing optics to improve the resolution to 50 – 100 nm [22]. The resulting nanoprobe will be used for high resolution mapping of trace elements in cells, tissues, and bacteria by XRF, and the mapping of the chemical state of more abundant metals by XAS.

2.3.3.4 Infrared Imaging and Microspectroscopy

Infrared microspectroscopy (IRMS) enables the microscopic chemical distribution in materials to be probed through their vibrational spectra. It has been used to study numerous plant and animal tissues, single biological cells, minerals and soils, etc. For complex samples such as human tissues, an IR

spectrum provides a direct indication of sample biochemistry. For example, as discussed in Section 2.3.2, aggregates of misfolded proteins, i.e. amyloid plaques, have been identified in the brain tissue of Alzheimer's disease patients. Spectral evidence of cervical cancer, heart disease, and bone diseases such as osteoarthritis, osteoporosis, and osteogenesis imperfecta (i.e. "brittle bone disease") have been identified [23-25]. In addition, contaminants in human tissue, such as silicone in breast tissue and narcotics in human hair have also been observed.

The primary advantage of synchrotrons over conventional IR sources is their 100-1000 times greater brightness. This high brightness allows smaller regions to be probed with acceptable signal to noise ratio [26, 27]. Indeed, aperture settings smaller than the wavelength of light can be used, in which case diffraction controls the available spatial resolution [28].

NSLS-II will provide world leading brightness throughout the infrared and will make near-field techniques possible, improving the spatial resolution beyond the diffraction limit to below 1 micron. NSLS-II will provide wide opening angles capable of imaging sixteen or more synchrotron source points onto imaging array detectors, which have not yet been utilized on synchrotron beamlines. This will improve the signal to noise ratio of the data and greatly reduce the data collection time over current, single-point, synchrotron-based microscopes.

2.3.3.6 Diffraction-Enhanced Imaging

Diffraction enhanced imaging (DEI) is a phase-contrast radiography method developed at the NSLS in 1995 that introduces fine selectivity for the angular deviation of x rays traversing an object. It uses collimated X-rays produced by a perfect crystal monochromator, and an analyzer crystal positioned between the subject and the detector. The high angular sensitivity of DEI allows measurement of the gradient of the X-ray index of refraction and ultra-small-angle scattering, as well as the X-ray attenuation. Since the contrast mechanism for DEI does not rely on absorption, it is ideally suited for soft-tissue imaging of biological subjects, where better contrast and lower dose are both important [29], as discussed in Sections 2.3.2 and 2.3.3. And by imaging at higher X-ray energies, the radiation dose is reduced significantly without much degradation of image contrast.

DEI has great potential for high resolution imaging. The gain in contrast in DEI images compared with absorption images increases as the feature size decreases (Figure 2.3.10). However, the resolution of DEI at the current NSLS is currently limited by the source size to about 50 microns. The full advantage of phase contrast imaging can only be realized with a bright X-ray source. The increased brightness of NSLS-II will enable DEI imaging and other phase-contrast X-ray imaging of animals and tissues at a sub-cellular resolution of below 1 micron. This will lead to in vivo investigation of biological processes in small cell populations deep within the tissues of the body [1].

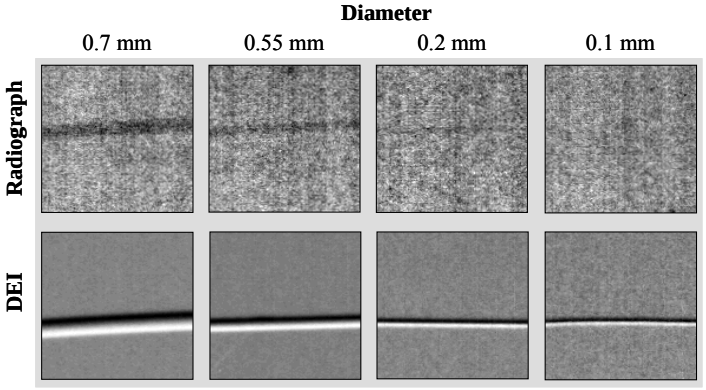

Figure 2.3.10 *Conventional radiograph vs. DEI image (on shoulder of rocking curve) of a nylon fiber, which simulates density variation in soft tissue. With conventional radiography, smaller objects show less contrast, a drawback that is not seen in the DEI images.*

2.3.3.7 User Demand

The number of user groups that use multiple imaging techniques at the NSLS is a rapidly growing user community [22], having approximately tripled in the past few years.

With the broad spectral range available at the NSLS, the wide range of imaging tools can be combined easily to provide complementary information for sample characterization. This is a feature unique to the NSLS; no other facility in the world has such a wide wavelength range available for imaging. Since synchrotron-based imaging techniques are rather new, this complementarity is just being realized.

Despite the success and productivity of the current facility, with a limited number of insertion devices on the existing NSLS storage rings, these imaging techniques are currently brightness-limited. The proposed new facility will provide a significantly brighter source, while maintaining the broad wavelength range familiar to NSLS users.

The NSLS hosts a group from Stony Brook that has pioneered zone plate scanning microscopy and many developments with it, and a large community already uses soft X-ray zone plate scanning microscopy for scientific research in biology and environmental science. In addition, there is also a rapidly growing IR spectromicroscopy, and X-ray microprobe/microdiffraction community for materials, environmental, and biomedical applications. The power of combining the complementary information obtained with all these imaging tools, from IR to hard X-ray, has also begun to be realized.

All these imaging efforts have benefited greatly by a strong collaboration in X-ray optics research, based on advanced electron beam lithography, between Stony Brook University and Bell Labs. The establishment of the BNL Center for Functional Nanomaterials (CFN) will further strengthen this collaboration. In particular, the proposed CFN will house a state-of-the-art electron beam lithography facility that will accelerate the development of a wide range of X-ray focusing optics.

Zone plates act as lenses with a Rayleigh resolution equal to 1.22 times the outermost zone width for incoherent bright field imaging; with a 30 nm zone plate, the Rayleigh resolution is 37 nm while in coherent imaging the contrast transfer has a hard-edged cutoff at a spatial frequency of $1/(2\cdot 30\text{ nm})=17\ \mu m^{-1}$ and in incoherent imaging there is a smooth decline in spatial frequency response to $1/(30\text{ nm})=33\ \mu m^{-1}$. With deconvolution [30], it is quite possible to study structures to spatial frequency at least three-quarters of that limit, i.e., $25\ \mu m^{-1}$, corresponding to a 20 nm half-period width. This is representative of soft X-ray zone plate imaging at the present time, and it is reasonable to expect that zone plates at 5-10 keV will begin to approach this performance level as well [31]. To do so will require considerable research and development, but NSLS is well positioned for this by building upon a collaboration between Stony Brook University and Bell Labs in 100 keV electron beam lithography that has already yielded 20 nm zone width zone plates [32], and ultimately using the e-beam capabilities that will be part of the BNL Center for Functional Nanomaterials building. It is not impossible to foresee zone plates with 15 nm outermost zone width (giving 10 nm structural information), and furthermore waveguide effects may act to improve their efficiency if the zones can be oriented properly [33].

The NSLS has 2 soft X-ray microscopy beamlines, both of which operate on an undulator (X1A1, X1A2). Even with the undulator, the beamlines' brightness is slightly more than a factor of 10 below the brightness of undulators at the ALS. They utilize two of the best zone plates available for soft X-ray microscopy, providing a spatial resolution of about 30 nm. The demand for this very high spatial resolution, despite the lower brightness, makes these beamlines oversubscribed.

The high brightness of NSLS-II, combined with the increased insertion device capacity, will also improve the quality and quantity of X-ray microprobe beamlines. Currently, the NSLS has one microprobe beamline (X26A) and it operates on a bending magnet port, where the spatial resolution is limited to 10-15 μm in order to provide sufficient flux to the sample. Even so, the demand for this beamline is tremendous; it is >200% oversubscribed.

Demand for medical imaging beamlines is strong. Currently there are only three dedicated synchrotron-based medical beamlines in the world, the ESRF in France, the Spring-8 in Japan and the

ELETTRA in Italy. Although one facility is planned for the new Canadian Light Source, currently under construction, no such facility currently exists in North America. The user schedules for the three dedicated medical beamlines are fully subscribed.

NSLS-II allows systematical investigation of the applicability of DEI, pioneered at the NSLS, to clinical imaging, by concentrating on three cases that have been shown by the preliminary studies to be promising: breast, lung imaging and cartilage imaging. There will be substantial expansion of the user base for DEI made possible by the NSLS-II.

The improvement in spatial resolution achieved by using a synchrotron IR source has only been realized recently, and applications to biological systems are growing rapidly. In 1999, the NSLS had one infrared microscope and ~5 user groups. Today, the NSLS has 4 infrared microscopes and over 50 biological/geological/environmental user groups. Each beamline is fully or over subscribed, one by more than 200% (U10B). In addition, only one other DOE-operated synchrotron has IR microspectroscopy capabilities (ALS has 1 IR microscope). Indeed, the NSLS is the premier facility for this type of research in the world. Thus, the NSLS needs to expand its IR microspectroscopy capabilities to accommodate a rapidly growing user community.

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2.4 Nanoscience

2.4.1 Overview

Nanoscience is one of the most dynamic and rapidly developing areas of interdisciplinary research. It addresses the unique physical and chemical properties of nanometer-sized (< 100 nm) materials as well as novel phenomena occurring at the nanoscale. It provides a natural link between physical sciences and life sciences, since nanometer length scales also characterize molecular machines and the basic building blocks in living organisms. The excitement in Nanoscience is driven not only by the potential to revolutionize a wide range of scientific and technical fields, but also the possible economic and societal impact. These can be illustrated by the grand challenges identified by the National Nanotechnology Initiative.

- Nanostructured Materials by Design
- Manufacturing at the Nanoscale
- Chemical-Biological-Radiological-Explosive Detection, and Protection
- Nanoscale Instrumentation, and Metrology
- Nano-Electronics, -Photonics, and –Magnetics
- Healthcare, Therapeutics, and Diagnostics
- Efficient Energy Conversion and Storage
- Microcraft and Robotics
- Nanoscale Processes for Environmental Improvement

In order to understand, and eventually design, the properties of materials at the nanoscale, a full complement of materials synthesis, manipulation, characterization, and theory / modeling / simulation tools need to be developed. In the area of characterization, over the last two decades, a wide range of synchrotron radiation based diffraction, scattering, spectroscopy, and imaging tools have been developed for materials research. These tools have played an essential role in our understanding of bulk materials, thin films, surfaces, and interfaces, by providing atomic resolution structures and unique electronic, chemical, and magnetic information that cannot be obtained otherwise.

There is a compelling need to extend the reach of these synchrotron-based tools to the nanoscale to obtain essential information which is either not accessible with, or is complementary to that provided by, scanning probes and electron microscopy. To do so requires the high brightness of NSLS-II. It will enable these techniques to be applied on nanometer length scales by focusing the x-rays down to ~ 10 nm or below, and by the development of novel full-field x-ray imaging techniques. This unprecedented combination will clearly enable completely new experiments. For example, one can imagine performing in-situ experiments on a single nanometer-sized catalyst in actual reaction conditions (described in section 2.9.2.1); or performing x-ray experiments on a single carbon nanotube while electric current is passing through the nanotube (described in section 2.4.2.1).

2.4.2 Scientific Challenges and Opportunities

2.4.2.1 Nanoelectronics

Today’s microelectronic industry is the result of advances in nanoscale materials research. Gate widths are 45 nm and the equivalent gate oxide thickness is 1.1 to 1.4 nm. The International Technology Roadmap for Semiconductors predicts that gate widths should reach 13 nm and that the gate oxide should reach an equivalent thickness of 0.4 to 0.6 nm in the next decade. However, for many needed device

characteristics, there are no known processes or solutions that will allow us to reach the required dimensions and material properties. As the limits of electronics scaling are pushed further, there are increasingly difficult challenges in silicon technology and an urgent need to develop novel materials with new scaling properties.

For example, as the critical line widths of microelectronics circuits decreased below 100 nm, two new material challenges appeared immediately. First, the feature size became comparable to the size of non-uniformities in polycrystalline materials, which leads to drastic negative effects on device performance due to changes in the material characteristics. Second, the pace of size reduction was reduced (and should reach a limit in the next decade or two), so that size reduction alone is no longer sufficient to maintain the standard rate of improvement that has been observed in past decades (Moore's law).

This led to the introduction of drastic changes in the materials and substrates. After a major research effort, the on-chip interconnections were changed from an Al based metallurgy to a Cu based one. This was shortly followed by an important modification to the original silicon substrate where only a thin semiconductor layer, isolated from the thicker silicon substrate by a buried oxide layer, is used in device fabrication. This technology is known as silicon on insulator (SOI). Recently, to reduce the capacitive coupling between the interconnections and further increase the speed, the standard silicon oxide dielectric was replaced by a low permittivity dielectric.

The NSLS has proven to be an extremely valuable tool for the microelectronics industry in this major materials research effort. Using in-situ X-ray techniques, with particular emphasis on X-ray diffraction, numerous studies crucial to electronics technology have been possible because of the NSLS. Recent examples include studies of copper films [1], silicide formation [2], diffusion barriers [3], contacts to carbon nanotubes [4], and electromigration [5] (Figure 2.4.1). This research addresses fundamental technological questions ranging from conventional silicon CMOS issues such as finding suitable materials for high speed interconnects, materials for contacts, and control of interdiffusion, to the evaluation of new nanoscale materials that will scale beyond the limits of silicon technology.

Finding materials and process solutions to the current and future limitations of CMOS devices will require controlling the properties of materials that are only a few atoms wide. The high brightness of NSLS-II will enable probing material properties on nanometer length scales at higher speed and with increased sensitivity. This will allow us to reach the level of understanding necessary to design the

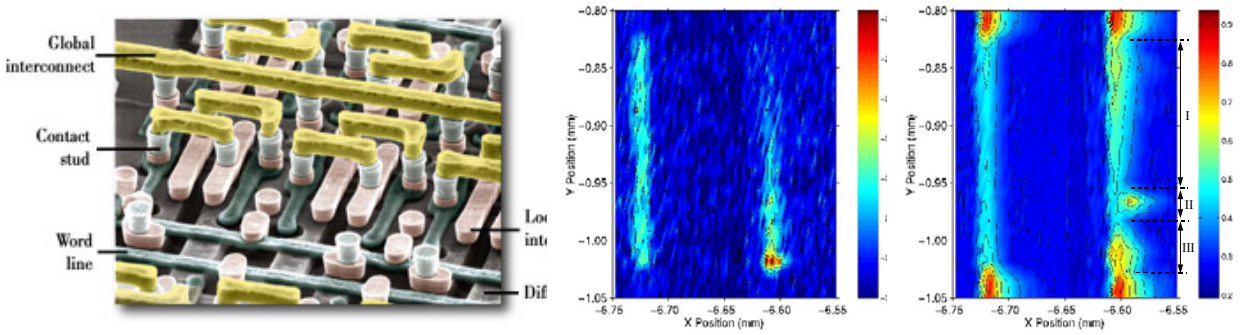

Figure 2.4.1 (*Left) Interconnect in a typical device. To achieve workable devices, a large array of dissimilar materials in very small quantities is used in close proximity. The various processes that are used to deposit these substances can cause very large stresses in very small domains. Such stresses can be due to epitaxial mismatch, phase changes, material densification, and electromigration during device operation. (Right) Real-time in-situ x-ray microbeam diffraction measurements of eletromigration-induced Cu redistribution and the concurrent local stress variation in Al (0.25 at. % of Cu) conductor lines. The lines are 10 μm wide, 200 μm long and 0.5 μm think. (Color) Intensity contours of Cu Kα fluorescence and Si(004) diffraction over an area containing two Al(Cu) wires, with the electromigrated wire on the right and the control sample on the left [5].*

properties of materials having nanometer length scales, control the microstructure and texture of very thin films, control strain and heat transfer in complex structures, and control stresses to avoid generation of dislocations. This is essential if the many materials challenges faced by the microelectronics industry in the coming decades are to be overcome. Examples of essential advanced capabilities enabled by the high brightness and flux of NSLS-II include:

- Nanoscale spatial resolution and elemental sensitivity necessary to enable the study of individual nanoscale structures, devices, and defects.
- Time resolved measurements of material properties during increasingly rapid anneal processing, as the microelectronics industry evolves toward ramp rates of thousands of degrees per second.
- Measurements of the evolution of crystallization and texture, including complete texture maps, during phase formations, as well as phase formation mechanisms, such as nucleation, diffusion, and activation energies, in very thin films at very high temperature (or high temperature ramp rates). One could even imagine following the bonding of a fraction of a monolayer through time resolved x-ray spectroscopy.
- Greatly increased throughput, allowing use of combinatorial approaches to material synthesis in the search for new materials.

2.4.2.2 Nanomagnetics

Nanomagnetics, the study and use of nanoscaled magnetic materials, has undergone tremendous growth over the last decade. It is quite broad, and covers topics such as molecular magnets [6], chemically-synthesized nano-magnets [7], biologically-inspired magnetic materials with nano-scale dimensions [8], and Spintronics. Research and development efforts in Spintronics have been particularly intense as a result of the potential impact in information technology [9]. The most notable example is the use of the giant magneto-resistance (GMR) effect, first observed in 1988 [10], in the current generation of read head sensors. This new technology has already made an enormous impact on ultra-high density magnetic storage, resulting in an increase of storage areal density from 1 Gb/in^2 in 1996 to 100 Gb/in^2 in 2003 [11]. Many more applications and novel concepts are being developed, including Magnetic Random Access Memory (MRAM), active Spintronic devices, spin-injection, manipulating spins in semiconductors, and quantum computing.

The key to all current and emerging devices are intricate magnetic nano-structures (Figure 2.4.2). As the dimension of individual magnetic elements shrink below 100 nm, their magnetic microstructures change from simple multiple domain structures to more complex structures, dominated by magnetization vortices or domain walls, and eventually to single domains for elements smaller than 10 nm. As a result, the physics of the switching mechanisms of the elements, the thermal stability of their magnetization, and interactions between elements must all be re-examined. To achieve this will require new synthesis and fabrication processes, new materials with tailored nanoscale properties, and especially new experimental techniques that are sensitive to the magnetization of nanoscale materials.

The high brightness synchrotron radiation of NSLS-II is critical to advancing the field of Nanomagnetics. NSLS-II will make possible chemical element specific magnetic measurements with nanometer spatial resolution and extremely high sensitivity. It will enable study of the magnetic structure and behavior of individual nanomagnetic elements as well as the interactions among collections of elements. The detection of the magnetic structure of buried interfaces and induced moments in non-magnetic metals and semiconductors will become possible. This will be crucial in understanding interfacial magnetic phenomena such as exchange bias, spin-dependent interface scattering, and spin injection. Time-resolved studies with ~10 picosecond resolution will be possible, allowing study of the mechanism of switching dynamics.

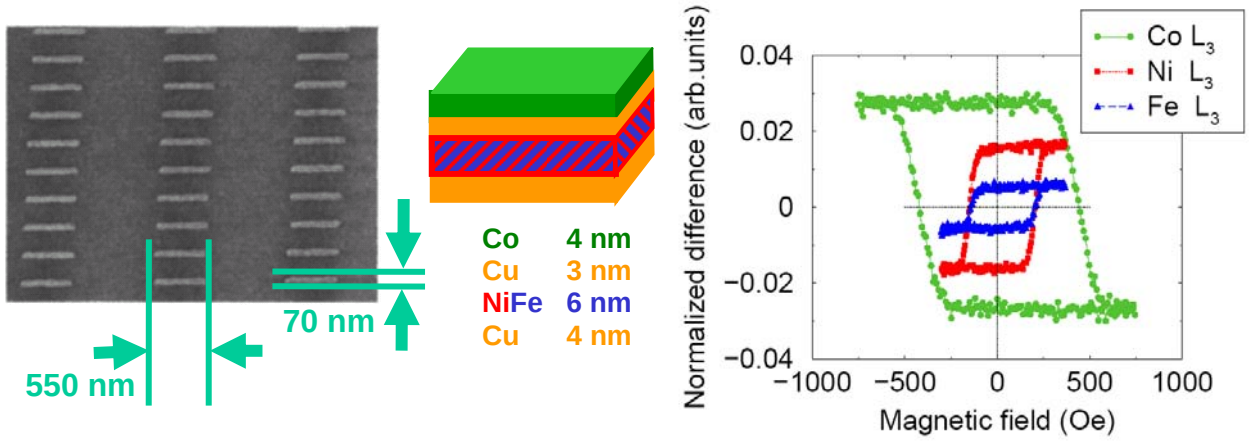

Figure 2.4.2 *Future high-density MRAM devices will require layered magnetic elements with thickness below a few tens of nanometers and in-plane dimensions in the sub-100 nm regime. (Left) SEM image of a large area array of NiFe/Cu/Co pseudo-spin-valves, fabricated using a combination of interference lithography, reactive ion etching, and ion milling. (Center) Schematic of individual spin-valve layer compositions and thicknesses. (Right) Element specific hysteresis loops recorded using x-ray magnetic circular dichroism [12].*

2.4.2.3 Nanoscale Functional Materials

Advances in organic and inorganic synthetic chemistry are providing an abundance of new nanoscale materials that have promising characteristics for a wide array of applications. Perhaps the best known of these are carbon nanotubes, which have remarkable electrical, optical, and mechanical properties and can be functionalized or combined with other materials for novel applications. Perovskite oxide nanotubes have also been synthesized recently [13]. In bulk form, perovskite oxide materials exhibit a wide variety of useful properties, including high temperature superconductivity, colossal magnetoresistance, and ferroelectricity. It is very likely that these will be modified, perhaps even enhanced, in the nanoscale form of these materials.

However, synthesizing novel nanomaterials is only the first step in making functional devices. New fabrication and characterization techniques are needed in order to understand the effect of structure on the properties of these nanomaterials as well as to integrate them into working devices. For example, carbon nanotubes have the ability to carry current densities of 10^9 A/cm^2 [14], much larger than the current densities carried in silicon devices. Moreover, the carbon nanotubes can survive such current densities for a long time, which make them an attractive candidate for future electronic devices. A prototype field effect transistor structure with a single carbon nanotube as the channel material was fabricated recently at the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory (Figure 2.4.3). The crucial element in this structure is the fabrication of ~100 nm separations between the source and drain electrodes so that the nanotube can be contacted. It would be very important to have the ability to characterize the structure of carbon nanotubes under the operating condition of the device to fully understand its performance. For example, the diameter and/or the length of the nanotube might change under operating condition, and affect the transport properties of the nanotubes.

In another example, very small (70 nm x 70 nm) ferroelectric columns were recently fabricated at the CFN from oxide materials using focused ion beam techniques (Figure 2.4.4). Even in these small dimensions, the piezoelectric response of the 70 nm square island is found to be just as large (0.1 nm/V) as that of the 1 mm square island despite its nanoscale dimensions [15]. This nanometer scaling of the piezoelectric properties of the ferroelectric can be combined with nanolithography [16] and oxide based processing of materials [17] to make new structures with integrated electrodes for applying voltages to nanoscale piezoelectric materials (Figure 2.4.4) and achieve nanometer changes in column height with

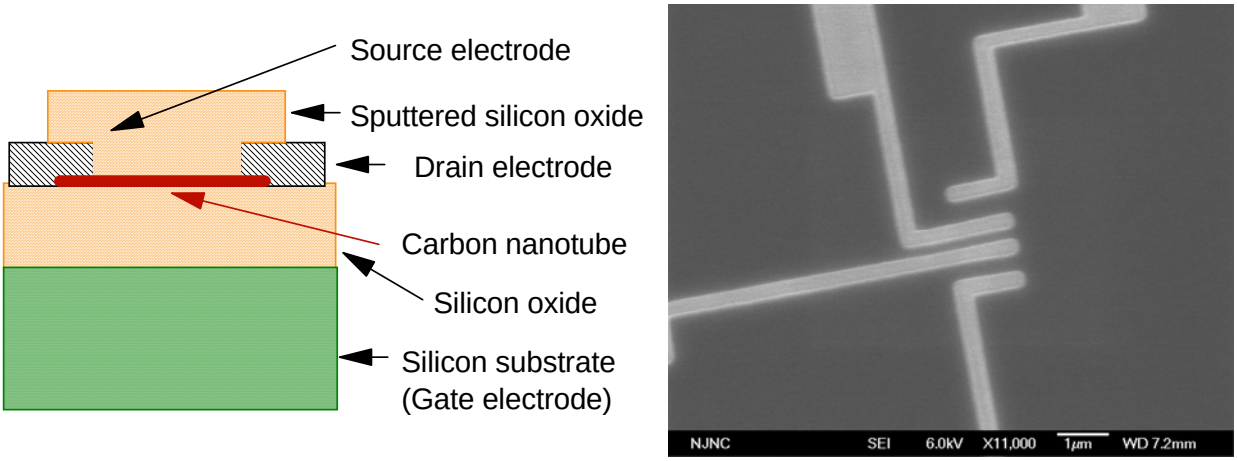

Figure 2.4.3 *(left) Field effect transistor (FET) structure for measuring field dependent electrical transport properties in a single nanotube. The nanotube is dispersed on silicon oxide on a silicon substrate. Metallic source and drain electrodes are evaporated and the tube is optionally encased in a sputtered oxide. (right) Electron micrograph, showing the electrodes with spacings of 300 nm, 100 nm, and 200 nm, which make contact with the nanotube. These lines fan out to larger pads (100 μm x 100 μm) where probe tips connect the device to test equipment. A one micron scale bar is shown at the bottom.*

modest voltages (~ 10 V). The electrical control of the column height on a nanoscale range allows one to place a material, such as a nanotube or nanowire, on the column through standard shadow evaporation techniques and then apply a strain to it. Again, it would be very important to have the ability to characterize the structure of the nanotubes or nanowire, in particular the lattice spacing, using x-ray scattering or spectroscopy, under real device operating conditions to fully understand its performance.

The high brightness of NSLS-II, combined with enhanced focusing capabilities, will, for the first time, allow x-ray scattering and x-ray spectroscopic experiments to be performed on individual nanotube or nanowire. These two examples also demonstrate the synergy between NSLS-II and the Center for Functional Nanomaterials at Brookhaven National Laboratory.

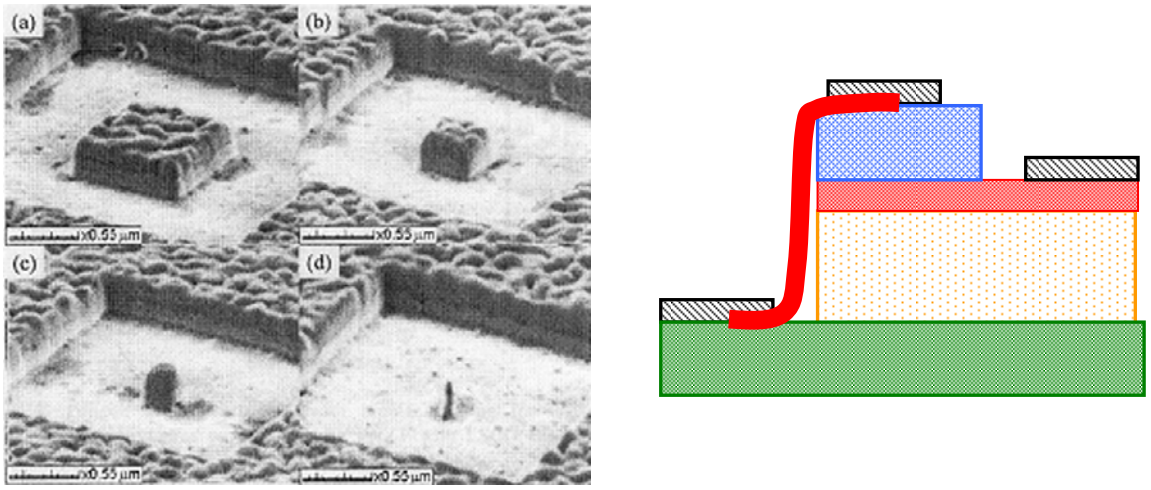

Figure 2.4.4 *(left) Series of focused ion beam fabricated ferroelectric islands ranging from 1 μm x 1 μm base area (a) to 70 nm x 70 nm base area (d). (right) Side view of columnar structure for controllable strain measurements on individual nanotubes (shown in red). The substrate is green, the piezoelectric is orange, the pink layer is a conducting oxide, and the blue layer is a dielectric. Metallic electrodes are gray, allowing for independent application of voltage to the piezoelectric, and simultaneous measurement of the nanotube transport properties.*

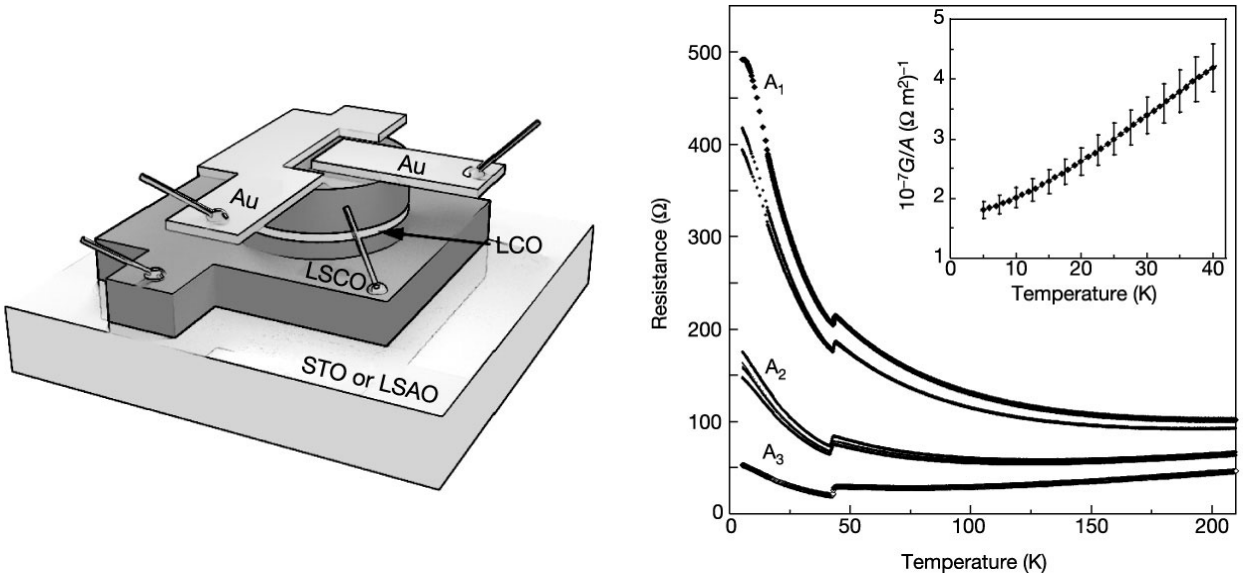

Figure 2.4.5 *The structure of an SIS junction (left) and its transport properties (right). Either $LaSrAlO_4$ or $SrTiO_3$ were used for the substrate. The top and the bottom high T_c superconductor electrodes are made of $LaSrCuO_4$. The barrier, only 1 unit cell thick, is made of La_2CuO_4. The mesa diameter was varied from 10 to 80 μm [18].*

2.4.2.4 Nanoscale Strongly Correlated Systems

The field of artificially nano-structured strongly correlated electron systems, such as transition metal oxides and rare-earth compounds, is one that is presently untapped but holds great promise. Strongly correlated electron systems are intrinsically inhomogeneous, exhibiting spontaneous charge, spin, and orbital correlations on the length scale of a few to a few tens of nanometers. Understanding and manipulating the interplay of the various phenomena on these length scales are outstanding challenges. It is an area in which NSLS-II will have enormous impact. Precisely engineered nano-structured correlated electron systems could provide critical tests for competing theories. New phenomena might occur by confining these systems in one or more dimensions, or due to the presence of surfaces and interfaces.

Strongly correlated electron systems are also characterized by the presence of a range of ground states in a single specimen, including high-T_C superconductivity, charge and orbital ordering, as well as ferro- and antiferro-magnetism. Thus, small changes in composition, extrinsic applied fields, temperature, or pressure make it possible to switch between many of these ground states, and could lead to dramatic changes in their response for device applications. Understanding the interplay between these ground states, their possible coexistence on nanometer length scales, and the effects of strain and compositional inhomogeneities will be an important key in unlocking the mysteries of strongly correlated systems.

In order to realize this tremendous potential, we need to understand the consequences of spatial confinement for strongly correlated systems, and the interplay between the available ground states and external parameters. New methods for artificially fabricating and controlling structures and correlations in these systems will play an important part in these efforts. For example, advanced molecular beam epitaxy was used to fabricate superconductor-insulator-superconductor junction to test the possible mixing of superconducting phase and antiferromagnetic phase in a high T_c superconductor (HTS), see Figure 2.4.5. The authors found that even one unit cell thick of the barrier layer, 1.3 nm of La_2CuO_4, is sufficient to completely block the supercurrent, indicating that these two phases do not mix. The ability to fabricate the structure with precise chemical composition and atomically smooth interfaces is critical for the success of the experiment.

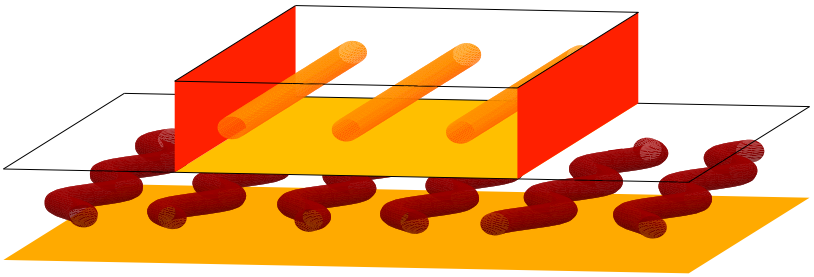

Figure 2.4.6 *Could nano-engineered layer boundaries (indicated in red) induce static stripe order in a material that would otherwise be a metallic stripe liquid?*

New nanofabrication techniques will allow lateral nanopatterning of strongly correlated systems with resolution approaching the same length scale as their relevant electronic correlations, i.e., a few nm. This might involve controlling the physical dimensions of the sample, as suggested in Figure 2.4.6, or nanopatterning provided by, for example, variations in the doping levels or some other parameter. A promising approach is shown in Figure 2.4.7, where the polarization of piezoelectrics is used to pull charge into or out of a transition metal oxide. Writing a voltage onto the piezoelectric with an STM tip will allow nanopatterning of the doping levels. Such structures have the potential to enable direct manipulation of the correlations that are responsible for the exotic, and potentially useful, behavior of these systems. Examples of such correlations include the charge and magnetic stripes in the cuprates (1.2 nm periodicity) and the nanoscale charge/orbital correlations responsible for the high resistance phase in the colossal magnetoresistance manganites. This will provide a whole new avenue of research in patterning correlations in strongly correlated systems.

Progress in this field will depend critically on the availability of experimental probes that can quantitatively characterize the structure, strain, composition, and magnetic order with nanometer scale resolution and high sensitivity. With the high brightness of NSLS-II together with advanced x-ray optics,

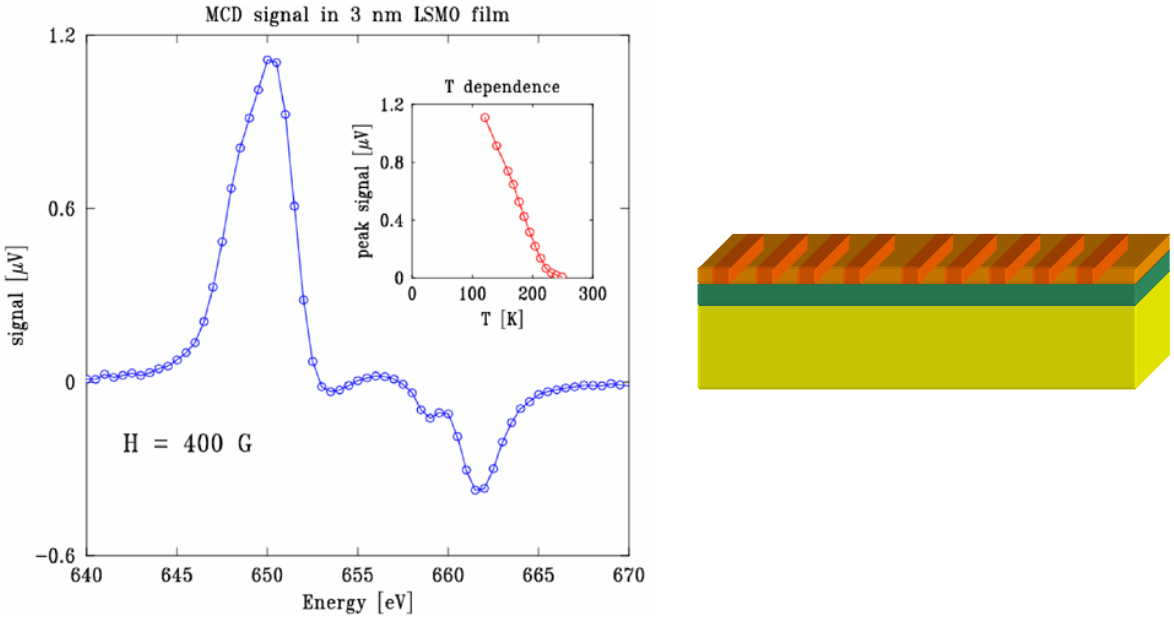

Figure 2.4.7 *XMCD signal measured at NSLS beamline X13B on a 3 nm film of $La_{1-x}Sr_xMnO_3$ (LMSO). Schematic of the film is shown above with the LSMO layer in green on a STO substrate (yellow). Future experiments will allow the decoration of such films with a piezoelectric, PZT, (orange). Applying a voltage to this PZT (i.e., with an STM tip) "writes" changes of doping into the LSMO below. NSLS-II will enable measurement of the effects of such nano-engineering in manipulating the correlations in strongly correlated systems.*

it will be possible to measure charge, magnetic and orbital ordering on a 10 nm length scale and thus to directly probe the effects of applying boundary constraints or patterning induced modulations. This will likely require soft X-ray resonant scattering techniques for which the wavelength is well matched to these length scales and the strong resonances help in providing the required sensitivity. For non-periodic structures, imaging techniques are required, either direct microscopy or inversion of coherent scattering patterns. In both cases, the high-brightness of NSLS-II will play a crucial role in extending the state-of-the-art in this promising new field.

2.4.2.5 Polymer Nanocomposites

Nanocomposites are a broad family of materials consisting of two or more component phase, at least one of which has dimensions between 1 and 100 nm. Polymer nanocomposites represent a special class of materials, consisting of a soft condensed matter matrix (such as synthetic and natural polymeric or biological templates) and nanoscale inorganic particles. These materials can exhibit markedly improved mechanical and other properties compared to the neat matrix materials or conventional composites, and they may supplant more traditional materials for many applications where high strength-to-weight or high surface-to-weight ratios are required to satisfy extreme conditions.

Recently, polymer nanocomposite materials have attracted a great deal of interest because many new and innovative preparation techniques have been demonstrated that generate novel inorganic/organic hybrid materials. These methods can be divided into several categories: (1) the dispersion of nanometer-scale inorganic particles or molecular clusters (such as layered silicates and carbon nanotubes) in the polymer matrix [19] , (2) the growth of inorganic crystals in synthetic nanostructured templates (such as block copolymer/surfactant micelles and structured gels) [20], and (3) the in-situ biomineralization in natural or biomimetic superstructure templates (such as collagen) that can simulate the process of bone growth [21].

The nanoscale structures in polymer nanocomposites can be thoroughly characterized by microscopic means, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). However, the sample preparation schemes for these techniques are often tedious and difficult. In-situ determination of the structure that develops during material preparation and processing, which is critical for optimization of the properties, is particularly challenging using these microscopic techniques.

The high brightness of NSLS-II will enable time-resolved SAXS/WAXD experiments [22] with a small beam size (~ 1 μm) on very small specimens to be carried out. This will significantly advance the development of these unique materials.

2.4.2.6 Biomimetic Devices

Biomimetic systems that implement self-organization principles encoded in biomolecular structures – with biomacromolecules or synthetic supramolecular complexes as building blocks for a nanoscopic construction set – will play an overwhelmingly important role in the design of functionalized interfaces and the self-assembly of molecular machines. The biochemical, pharmaceutical, sensoric or catalytic properties of such nanoscopic systems integrated in devices are naturally controlled at the molecular level. Utilizing such systems, solid-state surfaces will be functionalized with adsorbed lipid/protein membranes whose optimization requires a deep and detailed comprehension of their structure and dynamics, as well as the molecular-level interactions between their constituents.

The potential of the molecular construction set approach for surface-functionalization is demonstrated in Figure 2.4.8 (left), which shows only a limited set of possibilities on the basis of merely one particular biomacromolecular species, bacterial S-layer proteins (which has been particularly well studied in the recent past). Once the construction of biomimetic membrane structures based on S-layer technology has

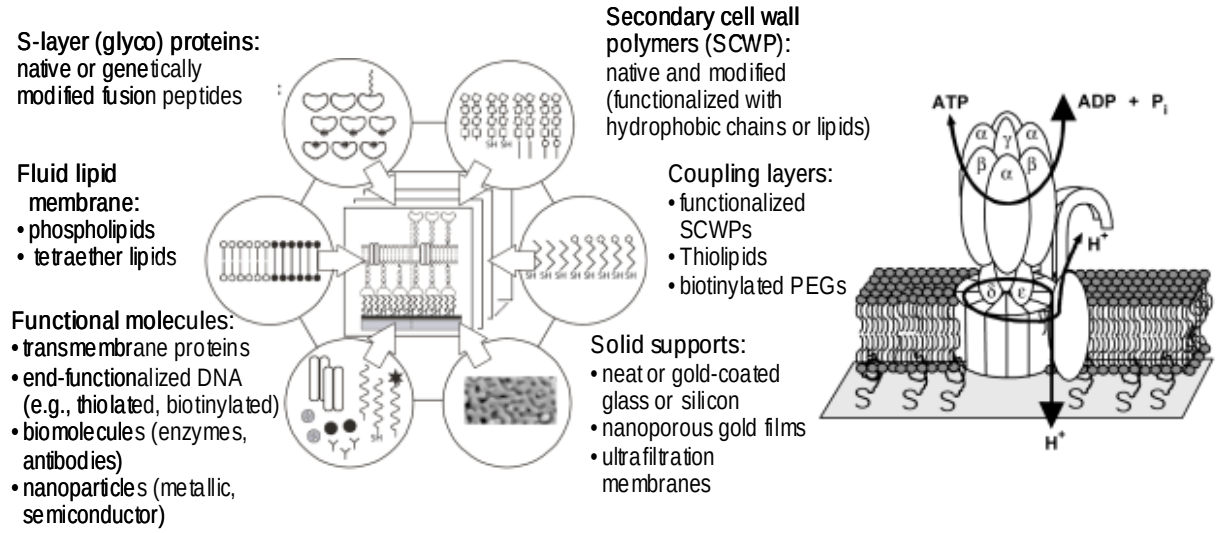

Figure 2.4.8 *A supramolecular construction set for interface functionalization based on bacterial S-layer proteins. A molecular machine based on an ATPase might be reconstructed in an interfacial membrane mimic (right). The ability to implement these concepts requires the high brightness of NSLS-II to enable molecular-level surface characterization (left) [23].*

matured, functionalization with membrane proteins as 'molecular machines' is the next logical step, again resulting in a plethora of different possibilities as illustrated in Figure 2.4.8 (right).

The X-ray characterization of a miniscule amount of biomolecules on an infinitely large background of bulk molecules is achieved with well-established techniques in which the excitation of radiation fields is confined at a surface or interface. Challenges in the next decade include the surface-sensitive diffraction from μm-sized monodomains of 2D protein crystals, as well as their in-situ micro-manipulation and handling; the measurement of form factors of membrane-bound peptides, proteins and supramolecular complexes in a laterally disordered state; determination of the location and spatial distribution of specific atomic constituents via anomalous scattering; or the sequential preparation of complex hierarchical structures as flexible matrices in which biomolecular processes such as signal transduction and amplification may be studied at the molecular length scale. Examples of future device applications may include the electrogenic sequencing of DNA in molecular pores suspended in interface-stabilized membranes or the implementation of stochastic sensors.

To exploit the possibilities in this field, new experimental capabilities are needed that permit surface-sensitive scattering, both in horizontal or vertical scattering geometry (beam directed down toward a horizontal fluid sample surface at a grazing incidence angle), together with micro-focusing of the x-rays for in-plane diffraction from micron sized monodomains of 2D crystals. This capability is also required for surface-sensitive characterization of samples in micro-fluidic applications, e.g. in high-throughput screening. X-rays with energy of 20 keV will permit the characterization of buried interfaces and there is also an urgent need for a tunable, low-energy (E = 2 - 8 keV), highly monochromatic ($\Delta E \sim 1$ eV), high brightness beam in this sample geometry for the species-specific interrogation of surfaces in anomalous scattering experiments. NSLS-II is needed for these experiments.

2.4.3 Impact of NSLS-II

The high brightness of NSLS-II will offer the scientific community a unique opportunity to develop a wide range of novel experimental tools for nanoscience and nanotechnology by combining the detailed structural and spectroscopic information obtained from x-rays with nanometer spatial resolution. In this section, several exciting developments are outlined.

2.4.3.1 X-Ray Nanoprobes

Synchrotron-based X-ray microprobes, with micron and sub-micron spatial resolution, have proven themselves to be extremely valuable research tools. However, by further improving the spatial resolution to 10 nanometers or below, X-ray nanoprobes will, for the first time, allow the characterization of individual nanoparticles or nanometer-sized grains in complex nanomaterials by their density, elemental composition, elemental oxidation state and spin-state, strain, texture, magnetization, and atomic and electronic structure and dynamics. This exciting prospect has stimulated x-ray optics development efforts worldwide, with four main types of x-ray focusing optics attracting the most attention. All of these approaches require the high brightness of NSLS-II to provide a high flux of x-rays in the resulting small focal spot.

2.4.3.1.1 Reflective Optics

Sub-micron diameter X-ray beams have been made using single hollow tapered capillaries, with the greatest performance obtained using parabolic or ellipsoidal shaped capillaries. A decade ago [24], 50 nm beams at energies of 5-8 keV were produced. Recently, Bergmann et al [25] performed a full wave optics treatment of the confinement of an X-ray beam within narrowly tapered capillaries and suggested that there is a theoretical minimum beam size on the order of 10 nm (FWHM). Although the theoretical minimum is still controversial, there is a general consensus that ~10 nm focus is within reach.

The Kirkpatrick-Baez (KB) mirror system focuses hard X-rays using grazing incidence reflecting surfaces and consists of two orthogonal crossed mirrors. One mirror focuses the X-ray beam in the horizontal plane while the second focuses it in the vertical plane. At the European Synchrotron Radiation Facility (ESRF) on beam line ID19, spot sizes of 100 x 100 nm^2 have been measured at 20.5 keV [26]. There are several promising approaches, including novel polishing techniques and adaptive optics, which suggest that the figure error of these mirrors can be improved to 0.1 μrad in the near future. Combing the extremely low figure errors and the superior source properties of NSLS-II, ~10 nm focus with substantial x-ray flux will be possible.

2.4.3.1.2 Refractive Optics

Snigirev, et al [27] have shown that cylindrical and crossed cylindrical X-ray lenses based on X-ray refraction can be made with a focal length in the meter range and a focal spot size in the micrometer range. More recently, parabolic lens have been shown to provide superior focusing. As a consequence of the very weak refraction by matter of hard X-rays one needs to make a stack of many lenses. The focal length of such a parabolic compound refractive lens (PCRL) is given by $f=R/2N\delta$, where N is the number of stacked lenses, R the radius of curvature at the apex of the parabola and δ the real-part decrement of the index of refraction ($n= 1 - \delta - i\beta$). The limits on resolution of a PCRL are due to the absorption limited, finite aperture of the lens, and by the surface roughness of each individual lens. Therefore choosing a more transparent material such as lithium, beryllium, boron or diamond should improve the resolution. However, to fabricate lenses with extremely small radii of curvature, nanofabrication techniques, such as electron-beam lithography and deep trench reactive ion etching, need to be used. Schroer et al [28] demonstrated that horizontal and vertical FWHM beam sizes of 380 nm and 210 nm, respectively, with a parabolic refractive lens made of silicon. Extrapolations using a Be lens suggest that a lateral size of 70 nm x 70 nm could be obtained.

2.4.3.1.3 Diffractive Optics

In the soft X-ray spectral region zone plates with a focal spot size close to 20 nm are under development using electron-beam lithography fabrication techniques. Figure 2.4.9 shows a SEM image of a soft x-ray zone plate fabricated through collaboration between Christopher Jabobsen (SUNYSB and

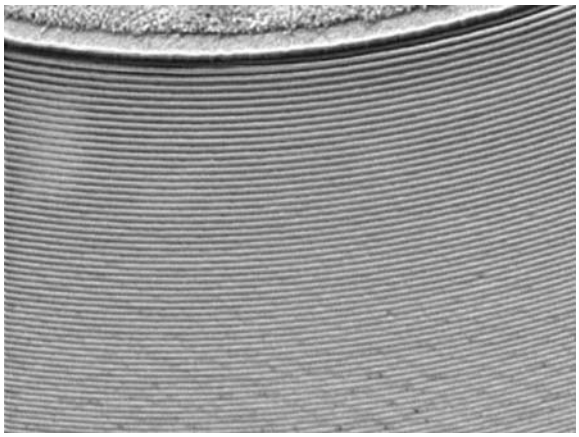

Figure 2.4.9 *Soft X-ray zone plate.*

BNL/CFN) and Don Tennant (Lucent/NJNC). For hard X-ray applications, Xradia, a new Silicon Valley Start-up, has developed a technology to provide zone plates that currently achieve a focus of 50 nm. We anticipate significant improvement in this technology in the near future with the availability to researchers of new advanced electron lithography facilities through DOE funded nanoscience centers, such as BNL CFN. With these advances, sub-10 nm focus beam size will be achieved by using higher orders of these zone-plates.

2.4.3.1.4 Hybrid Optics

One way around the limited aperture of purely refractive optic is to fabricate a hybrid optic that one can think of as zone plate with the analog profile of a refractive lens. By choosing to work at a fixed wavelength, and removing material that contributes to multiples of 2π phase shifts while maintaining the lens shape, the optical focusing properties of the lens are maintained. In exchange for working at a fixed wavelength, absorption is no longer a limitation on the lens aperture, and hence no longer a constraint on the lens resolution. Using the e-beam and etching facilities of Lucent/NJNC, Evans-Lutterodt, et al [29]

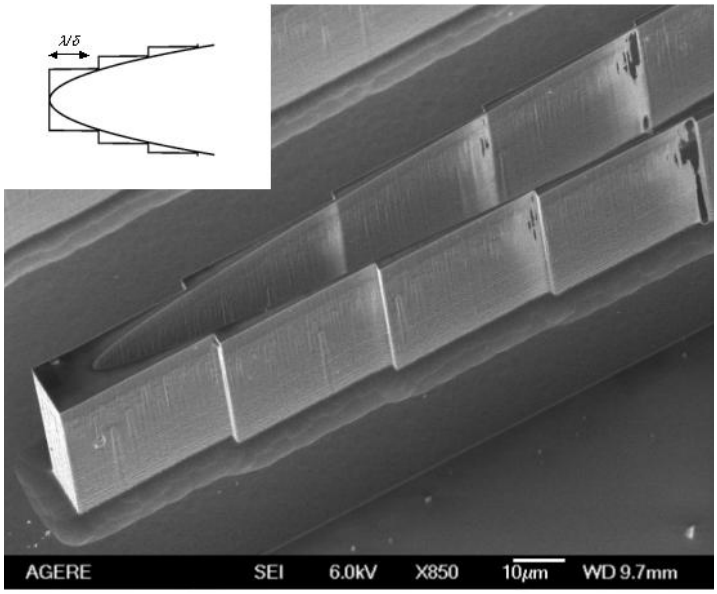

Figure 2.4.10 *Single element kinoform lens with elliptical profile for 12 keV X-rays. Steps are seen where materials was removed which originally contributed to 2π phase-shifts [28].*

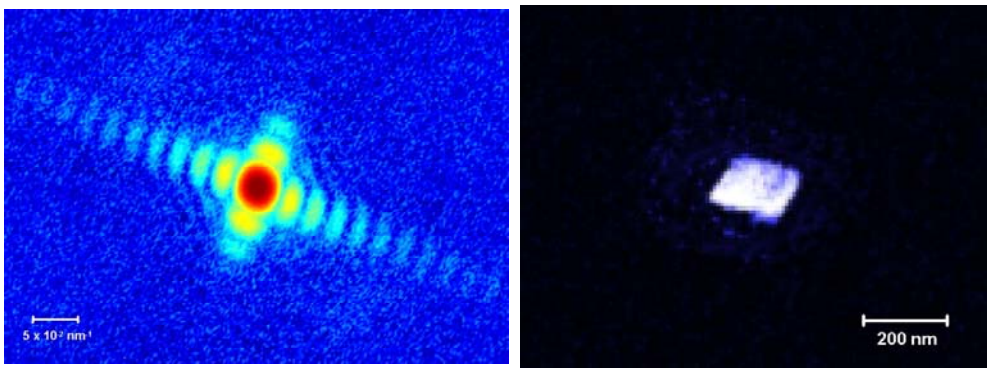

Figure 2.4.11 *Left -- CXD diffraction pattern of a 160 nm Ag nanocube. The experiments were carried out at the ID-34-C beamline at the APS. Right -- Image of the reconstructed nanocrystal obtained from the diffraction pattern using a variant of Fienup's hybrid input-output inversion algorithm [33].*

recently fabricated a single element kinoform lens in silicon with an elliptical profile for 12 keV X-rays (Figure 2.4.10). This novel approach holds promising for providing sub-10 nm X-ray focusing.

2.4.3.2 Full-field Imaging

With NSLS-II, X-ray imaging with nanometer spatial resolution can be achieved straightforwardly by scanning the sample under the nanometer-sized x-ray probes outlined in the previous section. In addition, there are two classes of full-field imaging techniques that show great promise to provide sub-10 nm spatial resolution. Full-field imaging techniques also offer researchers the opportunity to follow fast dynamic processes in time-resolved imaging experiments.

2.4.3.2.1 Diffraction Imaging

It was first pointed out by Sayre in 1980 that with the advent of synchrotron radiation sources, it might be possible to sample the continuous diffraction pattern of non-crystalline specimens to provide the oversampling necessary for solving the phase problem [30]. After two decades of development, Maio, Charalambous, Kirz and Sayre recently succeeded in recording and reconstructing the diffraction pattern of an artificial microstructure with 75 nm resolution [31]. This pioneering work was followed by a demonstration of three-dimensional imaging of Ag and Au nano-crystals using hard X-rays by Robinson et al [32], where subtle internal structure was revealed (Figure 2.4.11).

Since this is diffraction-based lensless imaging, the ultimate achievable resolution does not depend upon developments in optics. The highest resolution achieved to date is already 8 nm in 2D and 50 nm in 3D [34]. For non-biological samples, where radiation damage is not a concern, 2-4 nm resolution for 3D samples should be achievable with NSLS-II. It is also possible to combine this technique with chemical and magnetic contrast unique to x-rays to provide 2D or 3D chemical and magnetic imaging with similar resolution [35].

2.4.3.2.2 Low Energy Electron and Photoelectron Microscopy

Synchrotron-based Low-Energy Electron Microscopy and Photoelectron Emission Microscopy (LEEM/PEEM) generates high image contrast between sample regions having different chemical composition and/or atomic order in the topmost atomic layers (Figure 2.4.12). In LEEM mode, the imaging contrast is provided by the interaction and diffraction properties of the low energy electrons (0 – 100 eV) with the surface. In this energy range, the technique is highly sensitive to the surface crystal structure and surface morphology. Furthermore, with the use of spin-polarized electrons, magnetic domain imaging can be achieved. In the PEEM mode, secondary electrons or photoelectrons are imaged

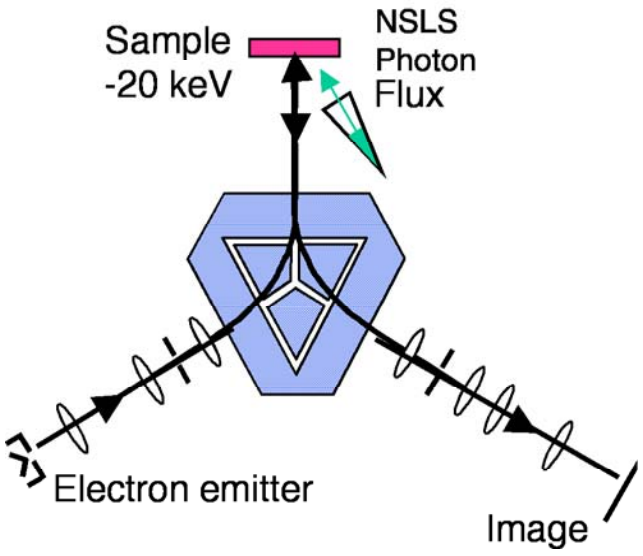

Figure 2.4.12 *Schematic illustration of low-energy-electron microscope and photoelectron emission microscope (LEEM/PEEM). Images are formed using electrons reflected from the surface. Contrast comes from surface morphology, crystal structure, and chemical composition.*

in a variety of chemically sensitive modes. It is a uniquely versatile tool with the potential to provide an unprecedented combination of spatial (~10 nm laterally and atomic vertically), temporal (~10 msec), structural (short range ordering or amorphous), and compositional (element and oxidation state) information. It can be designed to image at variable temperatures (170 to 1870 K) and during processes such as material deposition and gas phase chemical reactions. As a result, it can revolutionize our understanding of problems as diverse as surface-assembly, in situ pattern formation, and catalysis. The versatility of LEEM/PEEM is especially crucial for catalysis, since the complex nature of catalytic systems demands simultaneous acquisition of data characterizing the catalyst and the catalytic process in a complex multi-parameter space.

At present there is only one working synchrotron-based LEEM/PEEM instrument in the world, located at ELETRA in Trieste, Italy. Aberration corrected instruments are being developed at BESSY-II in Berlin, Germany and at the present NSLS. The ultra-high brightness of NSLS-II is crucial if the instrument is to achieve its ultimate spatial and temporal resolution as well as take full advantage of the chemical information available.

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2.5 Soft Matter and Biomaterials

2.5.1 Overview

Soft matter, such as polymers, complex-fluids, liquid-crystals, and colloids, are materials that readily respond to perturbations, from mechanical stress to applied electric and magnetic fields, can be solution-processed utilizing self-assembly into thin, conformal coatings, and form nanoscale ordered structures that can serve as templates or porous membranes. In the related and increasingly important field of biomaterials, the hard tissues (composites of biopolymers and minerals) created by living organisms provide structural support, protective shells, magnetic sensing, and chemical reservoirs that store nutrient. These serve as an inspiration to the design of new functional materials and synthetic biocompatible materials that either do not stimulate host reaction (e.g. in the case of implants) or can trigger a specific cellular reaction (e.g. controlled drug delivery systems). Both classes of materials have hierarchical structures, where the molecular building blocks assemble into supramolecular structures, which in turn form microscopic structures with multiple length scales from a few nanometers to tens of microns.

The study of soft materials has been one of the most rapidly developing areas of condensed matter science. Despite the diversity of their constituents, they share many of the same physical and chemical features: a large number of internal degrees of freedom, relatively weak interactions between the structural elements, hydrocarbon-based building blocks, and substantial entropic contribution to the free energy. These properties give rise to a broad multiplicity of forms, large thermal fluctuations, sensitivity of the equilibrium configuration to external boundary conditions, macroscopic "softness" and different metastable states.

Soft materials are opening exciting new directions in the fundamental physics and chemistry of materials, and provide a wide variety of novel technological applications, such as flexible displays, photonic devices, information storage media, anisotropic properties, biomedical materials, drug delivery, electronics and optics, membranes, porous materials, superior blends, and nanostructured templates. The challenges in soft materials studies include incorporating multiple components to tailor properties, overcoming thermodynamic immiscibility, tuning dimensions from nanometers to microns, utilizing both equilibrium and metastable structures, controlling interfacial properties, prescribing a distribution of functionality, and utilizing self assembly to create hierarchical structures.

The increasing sophistication and successes achieved in soft materials research in recent years promises dramatic progress in the decade ahead. However, progress will require currently unavailable enhanced structural analysis capabilities, the need for which is being felt even now. Application of these materials requires understanding of their kinetics, which often plays a determinate role in how they form.

The ultra-high brightness of NSLS-II is required to effectively address many of these challenges. The high brightness and well collimated beam is absolutely required for measuring the scattering from ultra-small samples such as those in confined geometries and from materials with large intrinsic length scales (0.1 to 1000 nm); for imaging of microstructures especially for systems containing weak scattering contrast or at the initial stages of different forms of phase transitions; for measuring fast processing kinetics, typically on time scales from seconds to microseconds; and for determining the structural evolution in relevant processing conditions, such as shear and elongation flow. The proposed SAXS, USAXS, coherent and surface scattering beamlines at NSLS-II, spanning the nanometer through micron scales (i.e., overlapping the optical regime), and enabling dynamic scattering and effective microscopy, will provide essential tools in the study of soft matter and biomaterials. The high brightness and flux of NSLS-II is absolutely essential to achieve a fundamental understanding of the behavior of these highly complex and technologically important systems.

2.5.2 Scientific Challenges and Opportunities

The research opportunities that NSLS-II will open to the soft matter and biomaterials research communities are described in this section. We first describe scientific opportunities in polymers. Because polymer films are self-supporting and robust, applications abound. We next describe the scientific opportunities in materials based on colloids, liquid-crystals and related composite soft systems that exhibit the anisotropic properties of a solid while retaining the processing advantages of a fluid. We conclude by describing the exciting scientific opportunities that result from using biosynthetic techniques to engineer new organic-inorganic complexes that exhibit tailored functionality. The complexity of the processing intermediates and final composite structures, often in the form of thin films or fibers with only partial order, provide a considerable challenge for achieving the X-ray characterization crucial for technological advances.

2.5.2.1 Hierarchical Structures in Polymers

Many synthetic block copolymers have distinct hierarchical structures. The phase behavior in these structures is of great scientific and technological interests. For example, an effective way to construct well-defined and uniformly oriented nano-environments uses diblock copolymers as templates. Diblock copolymers are well known to form various ordered phase morphologies, such as lamellae, double gyroid, cylinders and spheres, on a length scale of a few tens of nanometers. These ordered structures are formed because of microphase separation of the dissimilar components below the order-disorder transition temperature (T_{ODT}) and they are well suited as the template to provide the nano-scale confinement.

For example, recent studies have been carried out at the NSLS based on a series of poly(ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymers with different molecular weights and different compositions as the confinement templates (Figure 2.5.1) [1]. After the PS component was vitrified, the subsequent crystallization of PEO was completely confined within the ordered nano-environments. Using simultaneously time-resolved synchrotron SAXS and WAXD techniques, path-dependent PEO crystal orientations with respect to the lamellar surface normal were observed on the oscillating shear-aligned sample and the lamellar morphology of the block copolymer was found to be perfectly aligned with their lamellar layers parallel to the shear plane.

This phenomenon has also been observed in other nano-confined environments and raises important questions. What is the formation mechanism of mechanical shear to generate different phase morphology

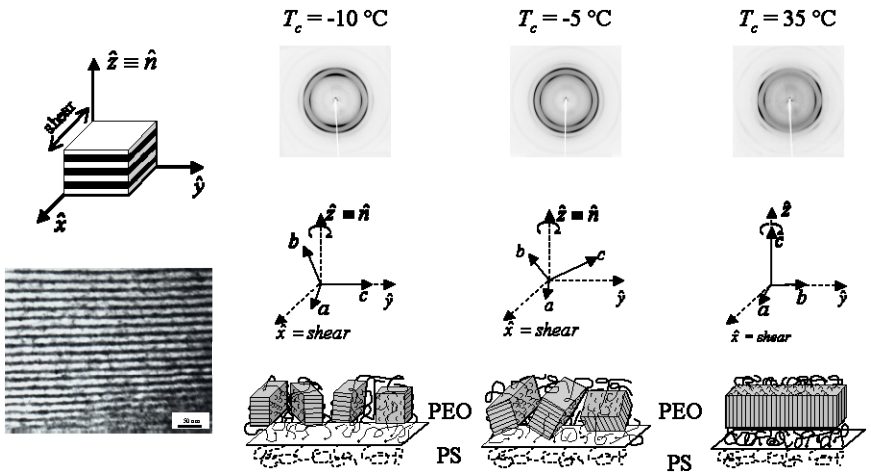

Figure 2.5.1 *PEO blocks crystallized in a lamellar confined environment. At the low T_C, the c-axis of the crystals are perpendicular to the $\hat{n}$. With increasing the T_C, The c-axis is tilted with respect to the $\hat{n}$. At the high T_c, the c-axis of the crystals are parallel to the $\hat{n}$.*

on the nanometer scale? Why do the crystals formed in these nano-confined environments behave so differently from those crystallized in unconfined bulk samples? Solving these questions is practically important since these nano-phase structures are potentially useful in photonic band gap materials.

The high brightness SAXS facility at NSLS-II will be ideal for investigation of these and related important fundamental questions.

2.5.2.2 Complex Phases in Block Polymers

Multiblock copolymers, such as ABC triblocks, offer unprecedented opportunities for preparing nanostructured materials with high degrees of internal organization. For example, recent experiments have shown that small variations in composition (e.g., by homopolymer dilution) can provide access to several three-dimensionally tri-continuous network phases from a single parent polymer. Such structures provide a means to incorporate several different functionalities into one material. For example, in ionic conductivity applications, such as fuel cell membranes, one block could provide mechanical integrity, another the transport pathway, and the third a regulatory or buffering role. However, with increasing complexity in both the ingredient molecules and the resulting phase structures, the challenge of morphological characterization becomes acute. Even in "pristine" ABC copolymers, for example, it has sometimes taken 2-3 years of combined painstaking scattering, microscopy, and calculation just to be able to assign the correct space group! Over 30 different structures have already been identified for ABC copolymers, with no obvious limit in sight, so "process of elimination" is not a viable strategy. Add in further ingredients, the inevitable kinetic effects, spatial heterogeneity, distorted unit cells due to processing or previous stress, etc., and it becomes clear that progress will be painstakingly slow without substantial advances in technique.

Although theory and microscopy will continue to play key roles, the SAXS facilities proposed at NSLS-II will offer the greatest potential for significant improvements. In particular, the ability to gain high signal-to-noise scattering from ever-smaller sample volumes will lead to the ability to access single crystal patterns from macroscopically polydomain samples. Furthermore, it will be possible to gain rapid information on sample structural uniformity/heterogeneity and the presence of defects, as well as response to external fields (especially flow); both will play key roles in the future applicability of such complex phases.

2.5.2.3 Liquid Crystals and Colloids

The self-assembly of nanometer sized organic and inorganic molecules can lead to exotic hierarchical structures on very long length scales, often extending to thousands of times the molecular size (Figure 2.5.2). A variety of methods for assembling colloidal nanoparticles, phase segregating composites, or liquid crystals into mesoscopic two and three-dimensional structures are producing an exciting new class of photonic bandgap-based optical materials. Examples include Bragg switches, or self-organized organic nanostructures with controlled optoelectronic properties [2], and a variety of self-assembly schemes that are being explored [3] to produce tailored, defect-free materials. Liquid crystals provide an ever-broadening palate of fascinating systems that self-organize on multiple length scales, serving for example as templates for making novel mesoporous catalysts [4], and spontaneously organizing nanoperiodic structural elements over micron length scales, as in the twist grain boundary phases [5], and polarization-modulated smectics [6]. Exploring the meso/micro range is also of crucial importance for understanding and controlling “disordered” behavior, such as the flocculation of colloids, the gel forming process exploited in manufacturing such products as diverse as cheese, cosmetics, and ceramics.

To effectively study these and other such hierarchical structures, it will be necessary to integrate scattering and multiple microscopies into beamline instrumentation in completely novel ways. Microprobe SAXS, for which the high brightness of NSLS-II is essential, will be required for decisive studies. The study of the delicate intrinsic local structure in such systems, crucial to understanding their most basic properties, such as elasticity, will benefit from fast ultra-high resolution dynamic SAXS, as

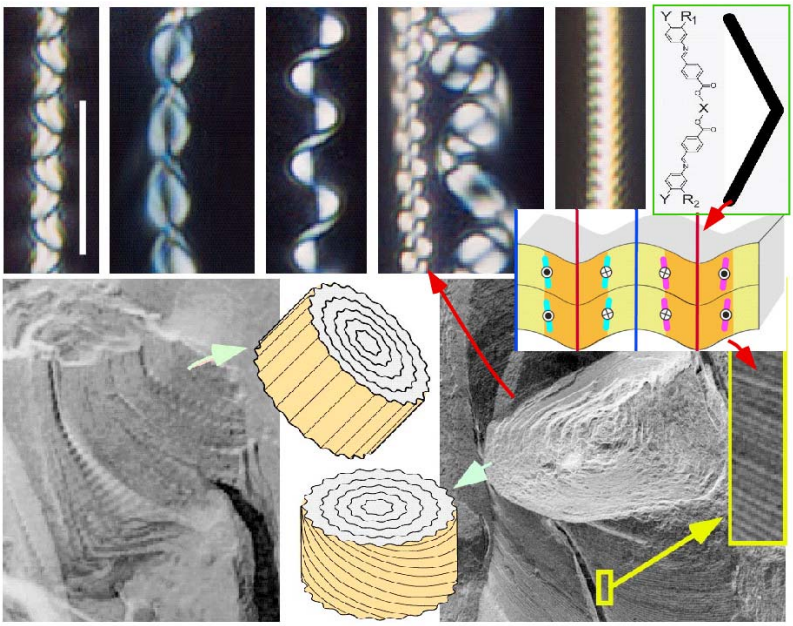

Figure 2.5.2 *Hierarchical filamentary liquid crystal structures formed by the smectic layering of bent-core molecules. The layers are periodically undulated on the 100 nm length scale (yellow box) by polarization modulation and the resulting two dimensional ordering forms micron scale helical filaments.*

well as the ability to carry out X-ray PCS on weak scatterers. The rapidly developing research pursuing the use of hierarchical colloidal and liquid crystal organization employing biomolecular components, such as complexes of DNA with cationic lipids [7] or dendrimers [8], will have similar instrumentation needs.

2.5.2.4 Liquid and Soft Matter in Confinement

An important and challenging problem in interfacial science is the behavior of liquids in the vicinity of both hard and soft walls, specifically how the structural properties differ from that of the bulk liquid. For molecular liquids and liquid metal, the broken symmetry imposed by the wall modifies the structure of liquid relative to the underlying bulk [9-11] and in the case of liquid metals gives rise to surface layering [9, 10]. Further, in binary or tertiary liquids, one component may preferentially wet the wall while other components are repelled. Understanding the nanoscale behavior of liquid interfaces is relevant to many fields of science and technology, including sensors, biological interfaces, liquid crystal displays, electrochemistry, and wetting phenomena.

Technical advances, such as very thin, submicron liquid channel cells [11, 12] and the use of high-energy (20 keV), penetrating X-rays allows one the possibility of exploring a new class of problems by reducing the otherwise strong diffuse scattering signal. Sinha and coworkers have demonstrated the technique at the APS for the organic liquid, octamethylcyclotetrasiloxane under confinement [12]. For this system, they have shown that the gap and the number of molecular layers decreased in a quantized fashion with increasing pressure, from a gap size of 25.2 Å containing three close-packed layers to a gap size of 19.9 Å at the highest pressures containing two non-close-packed layers.

Using this approach, it may be possible to study the structure of single membrane bilayers in-vitro. Such studies will greatly benefit from the ultra-focused, micron sized beams provided at NSLS-II. A significant biological problem that would benefit from this advance is that of cholesterol rafts and the micro-phase separation of membrane proteins that occurs at the interface of cells due to the rafts formation. Using the confined geometry it should be possible to study the detailed structure and composition of individual rafts within the biomembrane.

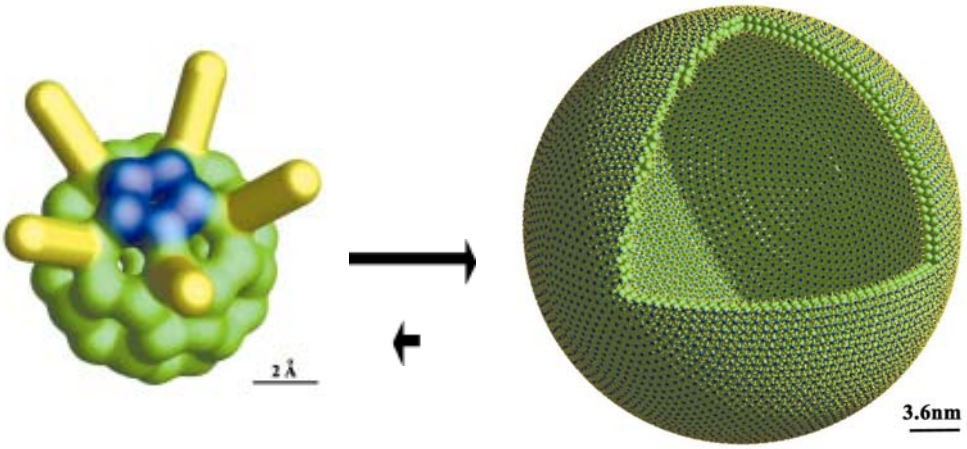

Figure 2.5.3 *Left: Polymer-Surfactant Complexes (PSC's) such as this $Ph_5C_{60}^-$ molecule can form highly ordered superassemblies due to the interplay of electrostatic and hydrophobic interactions, which can be fine-tuned by the degree of hydration. The phenyl group, represented as a stick, reduces the constraint on the inner bilayer curvature. Right: Simulated image of a spherical bilayer vesicle of fullerene surfactants $Ph_5C_{60}^-K^+$, with a cutaway view showing the inner layer packing.*

2.5.2.5 Complex Solutions

Polyelectrolyte-surfactant complexes (PSCs) are microphase-separated systems containing hydrophilic domains (surfactant head groups and polyelectrolyte charges) and hydrophobic regions (surfactant tails and hydrophobic parts of the polyelectrolyte) [13]. The interactions of polyelectrolytes with oppositely charged surfactants are quite strong and can generate complexes having highly ordered structures. The two most important driving forces for the self-assembly of surfactant molecules in PSCs are the electrostatic interactions between the charged components and the hydrophobic interactions between the polymer backbone and the alkyl chains of the surfactant. The well-defined supramolecular structures have unusual properties that may find application in gene therapy, cosmetics, food, paints, coatings, enhanced oil recovery, and other technologies.

For example, as shown in Figure 2.5.3, a PSC in the form of a modified fullerene molecule has recently been described: $Ph_5C_{60}^-K^+$, with Ph denoting the phenyl group, self-assembles into bilayer vesicles, with a radius of 17 nm and an aggregation number of close to thirteen thousand modified fullerene molecules [14]. These well-defined and relatively non-toxic fullerene-based surfactants have a distinct feature, i.e., instead of flexible hydrophobic chain(s), the $Ph_5C_{60}^-$, or the hydrophobic part of the "surfactant", is a rigid hydrophobic ball. Furthermore, organic chemistry permits rational design of the chemical nature of these functionalized fullerenes, resulting in the establishment of a new class of surfactant systems. These differ not only in hydrophobicity and geometrical constraints (size and shape) from existing surfactants, but can also control the charge (cationic, anionic, or neutral; univalent or multivalent) as well as the spacing between the charges and the hydrophobic C_{60} ball.

Improved SAXS capabilities, as promised by NSLS-II, enabling higher intensities measured in small detection volumes, are required for further progress in properly characterizing newly developed PSCs.

2.5.2.6 Hierarchical Biological Systems

Understanding the structure of hierarchical biological systems is not only of fundamental importance but can also have substantial medical consequences. Biomineralization processes lead to particularly interesting hierarchical biological systems that can be considered as composite materials consisting of an

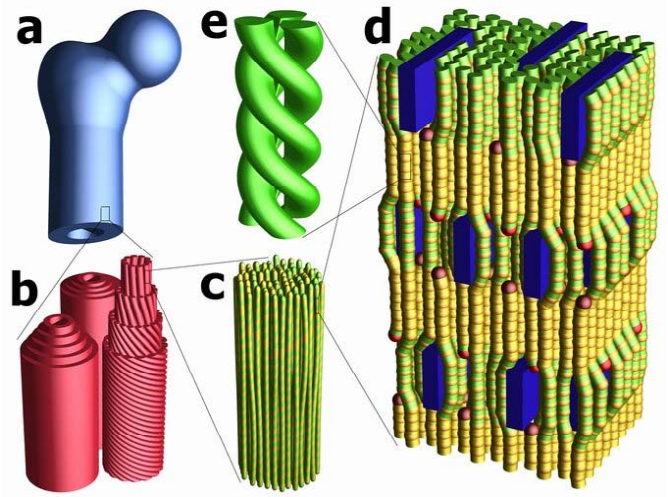

Figure 2.5.4 *Schematic representation of the hierarchical structures in bone: (a) Macroscopic bone. (b) Osteons (~100µm) with circular arrangements of differently oriented collagen fibers. (c) Collagen fiber (~5µm lateral) consisting of bundles of collagen fibrils (~500nm lat.). (d) Striped collagen fibril (period ~68nm longitudinal) consisting of a staggered arrangement of collagen molecules (~1.5nm lat.) with embedded mineral crystals (~ 2...20 nm lat., 30nm long.). (e) Collagen molecule triple helix.*

organic matrix embedding a nanoscopically dispersed inorganic phase. The mechanical properties, especially the toughness, of such natural composite materials are still unparalleled in the synthetic world.

An important example is given by bone (Figure 2.5.4). The central challenges are to understand the dynamics of the mineralization process, from nucleation to the final stages of mineralization, the localization, size, shape and orientation of mineral crystals, as well as their effect on the order of the collagen matrix, the redissolution of mineral crystals when acting as a calcium ion reservoir, intrafibril versus interfibril mineralization; and the role of non-collagenous proteins.

Synchrotron techniques such as wide-angle scattering, small-angle scattering, and ultra-small-angle scattering, can contribute significantly to the structural analysis on several of the length scales over which these hierarchical structures extend. Imaging techniques and micro-focus scanning probes can be used to investigate structural heterogeneities on even larger length scales. The combination of poor order with poor contrast and strong background scattering that characterizes these materials, makes a highly brilliant source necessary, especially when employing multi-wavelength measurements for anomalous scattering studies. Studying the local dynamics of biomineralization will be photon flux driven and will require the development of a beamline that can span USAXS to WAXS measurements, using a micron size parallel beam to scan across the samples. NSLS-II will make such measurements possible.

2.5.2.7 Signal Transduction, Neuron Plasticity and Structural Changes in Membranes

Biological membranes contain rafts of proteins that act as critical elements in many biological processes. For example, in bacteria such as E. coli there exists a “nanobrain” consisting of a 100 nm x 100 nm ordered raft containing 5 different chemoreceptor proteins. Due to chemical-mechanical changes in the receptor structure, binding of a signaling agent to one receptor changes the response of adjacent receptors. An even more important example is the puzzle of neuron plasticity. Neuronal plasticity is the activity-dependent structural and functional changes of dendrites, axons, and synapses that plays an important role in the brain function under both physiological and pathological conditions. One of the great challenges is to be able to probe the local protein structural organization and changes in such signaling complexes. A combination of X-ray microprobe scattering coupled with labeling of the receptors and proteins using high-Z multivalent ions could help us untangle this sophisticated and vital signaling path on the membrane.

2.5.2.8 Synthetic Biomolecular Systems

Many polypeptides, consisting of a sequence of hydrophobic and hydrophilic amino acids, fold into specific protein shapes when dissolved in water. This is a consequence of the fact that water is an incompatible solvent for the hydrophobic units and the folding is a way in which the polymer acts to shield the hydrophobic units from exposure to water. There is growing evidence that many polymers, consisting of a sequence of monomers that are soluble in incompatible solvents, will spontaneously fold into a specific 3-dimensional shape when inserted into one of the solvents. This is true for polymers that are not based on amino acids and for solvents other than water. The synthesis of such polymers is a tremendous challenge, but we can foresee a day in the not so distant future when such syntheses are more common. It is now well recognized that the 3-dimensional shape of a folded polypeptide is the key to enzymatic activity. For example, the protein might form a channel that is specific to the shape of one end of a specific substrate molecule with a reactive atom, such as a strained-bond transition metal atom, at the bottom of the channel. In this way the protein creates tremendous specificity for chemical reactions at the end of the substrate molecule. The continued progress of polymer synthetic chemistry and of the protein-folding problem will some day allow the creation of "artificial enzymes" with very unusual chemistries. For example, one can envision such artificial enzymes made of polymers that are stable in pH or temperature environments that would destroy proteins. This would open an era of synthetic chemistry of materials using "artificial enzymes" that is vastly greater than now possible. Such developments would have a huge impact on our world. Determination of 3-dimensional structure will be important to understanding artificial enzymes, and it is quite likely that initial quantities of test polymers will be very small. In these circumstances, it will be necessary to perform crystallography on very small crystals of complex macromolecules. The high brightness of NSLS-II will be invaluable for this task.

There also exist strategies to design artificial peptides, based on both α-helical bundle and β-sheet structural motifs, so as to incorporate biological cofactors, compounds that confer function to many biological proteins, including catalysis [15]. The design of artificial peptides with synthetic non-biological cofactors could lead to peptide-based systems with novel properties not exhibited by biological systems. For example, extended π-electron systems can now be designed and tailored, with appropriate donors, acceptors and constituents, to exhibit selected nonlinear optical responses and light-induced electric charge separation over large distances. Importantly, the interior of the artificial peptide scaffolding can be used to control the solubility, position, orientation, and indeed the properties of the cofactor within the peptide (Figure 2.5.5).

The exterior of the artificial protein scaffolding can be used to control the peptide's supramolecular assembly into sufficiently ordered nanophase materials whose macroscopic behavior arises from such novel properties. The protein scaffold can thus be employed to control the degree of interaction/non-interaction between neighboring cofactors in the ordered nanophase material [16].

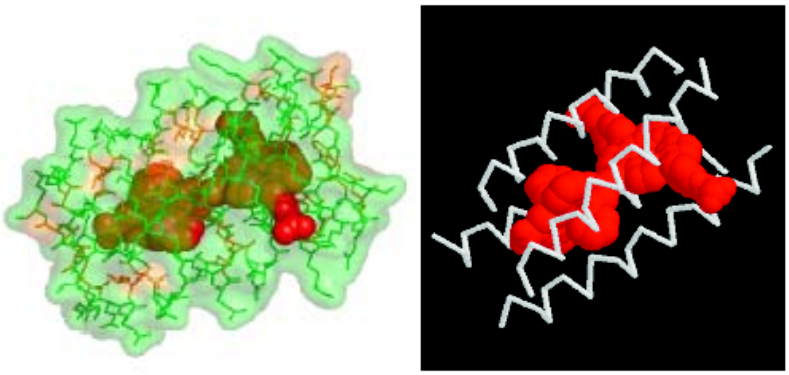

Figure 2.5.5 *Model of statistically designed 4-helix bundle peptide (green/white) to incorporate a novel, non-biological extended π-electron system (red) – an enlarged rendition is shown to the right.*

The structural motifs chosen for the artificial peptides can be significantly more stable than the natural protein. However, the interior of the scaffold may not be so stable to the supramolecular assembly process that is required to form a sufficiently ordered material. Thus, it is important to monitor structurally the various stages of the self-assembly process starting from the designed peptide, e.g. a particular α-helical bundle, to the incorporation of the non-biological cofactor, through to the supramolecular assembly of the peptide-cofactor complexes to a material ordered on a macroscopic scale. Since the desired material properties need not require long-range periodic order, as opposed to orientational order, in one, two or three dimensions, structural determination in the absence of such "crystallinity" is essential.

The high brightness of NSLS-II will enable advances in techniques that are critical for these studies, including X-ray absorption spectroscopy, inelastic X-ray scattering and both non-resonant and resonant elastic X-ray scattering.

2.5.3 Impact of NSLS-II

The NSLS-II facility will incorporate a suite of beamlines optimized to implement the X-ray techniques crucial for addressing the scientific challenges in soft matter and biomaterials research described in the preceding section. The X-ray scattering-based techniques utilized in soft matter and biophysics research include X-ray photon correlation spectroscopy (XPCS), time-resolved SAXS and GISAXS, and X-ray resonant scattering. The most dramatic enhancements in capabilities enabled by the high brightness and coherence of NSLS-II will involve coherent X-ray techniques such as XPCS and X-ray focused-beam techniques such as SAXS or GISAXS applied to small samples or used to probe spatial inhomogeneities. The high X-ray flux provided by NSLS-II will benefit flux-limited techniques such as time-resolved SAXS and GISAXS. NSLS-II will also have high brightness and flux at the lower X-ray energies (1-4 keV), which are difficult to access at higher energy synchrotron sources. This will enhance the application of resonance x-ray techniques at the Si, S, P, and Cl k-edges that are of interest in soft matter and biomaterials research. In the following sections, the impact of the enhancements in these X-ray techniques is illustrated by specific examples, and strategies are described to handle the radiation sensitivity of soft matter and biomaterial systems.

2.5.3.1 X-Ray Photon Correlation Spectroscopy - Fluctuations

One of the most exciting scientific opportunities offered by the unprecedented brilliance of NSLS-II is its revolutionary impact on our capability to carry out XPCS experiments. XPCS experiments at NSLS-II will yield exciting new insights into the dynamics of equilibrium fluctuations in soft condensed matter, occurring on shorter length scales than can be reached in light scattering and longer time scales than can be reached with the neutron spin echo technique. Specifically, by illuminating the sample under study with a partially coherent X-ray beam, XPCS reveals the characteristic times of the sample via autocorrelation of its (speckled) scattering pattern [17-20]. The resultant intensity-intensity autocorrelation function [$g_2(Q, t)$] is related to the intermediate scattering function (ISF) [$S(Q, t)$] of the sample via $g_2(Q, t) = 1+ \beta[f (Q, t)]^2$, where β is the optical contrast, $f (Q, t) = S(Q, t)/S(Q)$ is the normalized ISF, and $S(Q) = S(Q,0)$ is the static structure factor. The ISF is a key quantity of interest for any condensed matter system, but as for any method, the issue for XPCS is the range of length and time scales over which it may be applied. In this regard, the crucial aspect of an XPCS experiment is the signal-to-noise ratio (SNR), and, to maximize the SNR, the source should be as brilliant as possible.

Figure 2.5.6 shows representative correlation functions, plotted versus time on a logarithmic scale. They were obtained at the APS for a block copolymer-homopolymer blend at 140^o C that forms a so-called sponge (L3) phase, in which amphiphiles self-assemble into extended, random, multiply-connected bilayer membranes [21]. These data extend over 4 decades from a minimum delay time of 17 ms to 200 s. They represent the current state-of-the-art, i.e., 10 millisecond time scales and length scales to 60 nm.

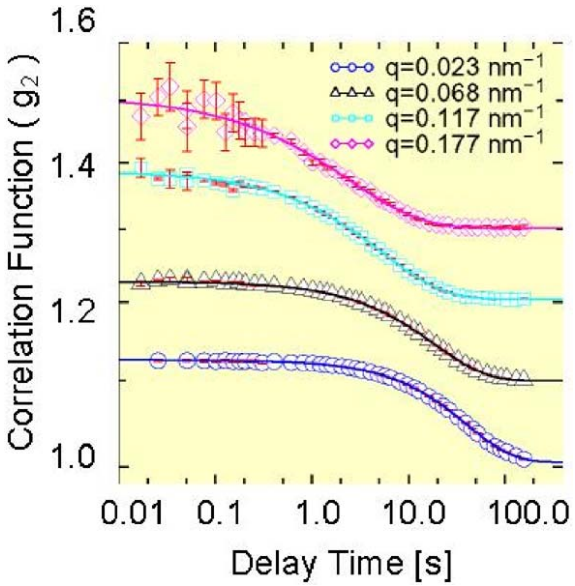

Figure 2.5.6 *Intensity-intensity autocorrelation functions (g_2 vs. delay time for an L_3-phase sample of P(SEBS) triblock copolymer in short-chain PS homopolymer at 140° C at wavevectors of 0.023, 0.068, 0.117, and 0.177 nm^{-1}. For clarify, the g_2s are displaced by 0.3, 0.2, 0.1, and 0.0, respectively.*

Improvements in vertical beam focus, X-ray window quality, and use of a wider energy bandpass would provide at least a 10-fold increase in coherent flux at existing facilities; coupled to the 30-fold enhancement in source brightness at NSLS-II (see Figure 3.3.4), this will yield a net gain of 300. Because of the way XPCS signal-to-noise depends on intensity and accumulation time, a factor of 300 in coherent flux enables the study of processes 10^5 times faster! This will revolutionize XPCS, permitting measurements with a time resolution in the hundred nanosecond range, vastly increasing the diversity of kinetic processes to which XPCS may be sensibly applied.

Beyond studies of the dynamics of bulk complex fluids, grazing-incidence scattering at NSLS-II will also permit studies of the dynamics of complex fluids confined in thin films at comparable time scales. In part, this is because of the large increase in sample dimension along the beam direction that occurs at grazing incidence. In addition, there exists the opportunity for an additional enhancement in the scattering signal when studying thin films, due to wave guiding [22].

2.5.3.2 Resonant X-Ray Scattering - Orientational Order

In soft matter systems, orientational order plays a crucial role since it impacts the electro-optic anisotropies that are utilized in device applications. Resonant X-ray scattering is a unique probe for measuring these orientational correlations when they occur on nanometer length scales [23]. As an example, Figure 2.5.7 illustrates the nanoscale interlayer and intralayer orientational correlations that can develop in tilted, layered, smectic-C liquid-crystal phases. When the incident X-ray beam is tuned in energy to the resonant edge of one of the atoms in the core of a constituent molecule, the off-diagonal components in the tensor X-ray structure factor become significant and orientational periodicities will diffract X-rays and can change the polarization state. Since the molecules in soft matter systems often contain atoms like S, Si, P, and Cl, with K-edges in the 1 to 4 keV range, this technique requires a soft X-ray beamline.

The high brightness of NSLS-II in this energy range offers the potential to use focused beam to measure orientational periodicities within liquid-crystalline fibers, helical ordering of biomolecules in solution, and an extension of XPCS to the study of orientational fluctuations.

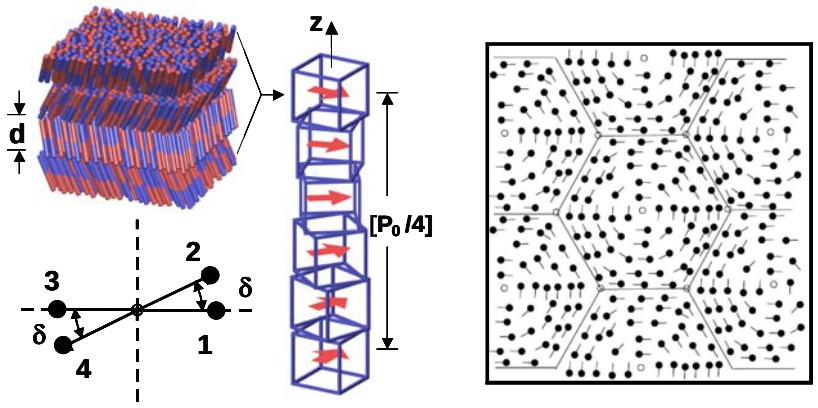

Figure 2.5.7 *Orientational periodicities in tilted, layer liquid crystal phases. Left: a phase with a uniform in-plane molecular tilt direction, which varies between layers exhibiting a 4-layer unit cell of size 1.2 nm. This unit cell helically rotates with a 1.5 μm pitch (P_0) – both periodicities can be observed by RXRD [23]. Right: a proposed phase with an in-plane periodicity of the molecular tilt direction [24].*

2.5.3.3 Time-Resolved SAXS - In-Situ Processing

Over 80% of the polymers produced in the world are crystalline polymers. It is well known that during polymer processing, the crystallization kinetics and the final morphology are deeply influenced by molecular orientation induced by flow (in the molten state) and deformation (in the solid state). Understanding and quantifying these effects is extremely important, both scientifically and technologically. Synchrotron X-ray scattering techniques can play a key role in investigations of the molecular orientation in the deformed melt and the resultant morphological changes during the rapid crystallization process under processing flow.

For example, in-situ synchrotron SAXS and WAXD techniques were recently carried out at the NSLS to study the effects of shear and elongational flow fields on orientation and crystallization of polymer chains in undercooled melts [25]. Results suggest that a scaffold (or network) of primary nuclei can be induced by flow at the very early stages of crystallization and that this dictates the morphology of the crystallized polymer. A stable network structure forms, consisting of microfibrillar "shish" with extended chain conformation along the flow direction (form first) superimposed by the crystalline layered structure of "kebabs" with folded chain conformation perpendicular to the flow direction (form second) (Figure 2.5.8). However, the exact nature of the shish-kebab structure (crystalline, mesomorphic and amorphous) remains elusive.

With the present NSLS, information on these precursor structures can only be obtained with a time resolution of seconds (the scattering contrast is quite weak). The high brightness and flux of NSLS-II together with high speed area detectors will allow obtaining structural information with submillisecond or, for stronger scatterers, even microsecond resolution. The proposed NSLS-II SAXS facility will be particularly suitable to explore new insights into the subject of flow-induced polymer crystallization during processing.

2.5.3.4 Time-Resolved GISAXS – Nanostructured Organic Films

The high brightness and high flux of NSLS-II will enable grazing-incidence SAXS (GISAXS) on supported polymer thin films (order 100 nm thick) that are themselves nanostructured. Examples include block copolymer thin films (Figure 2.5.9), where the phase-separated domains can act as templates for surface patterning or for the growth of nanoparticles [26, 27] and organic optoelectronic devices (Figure 2.5.10), such as the elements of electroluminescent flat-panel displays, where the distribution of the carrier-transport and luminescent species governs the device performance [28]. The use of a high-

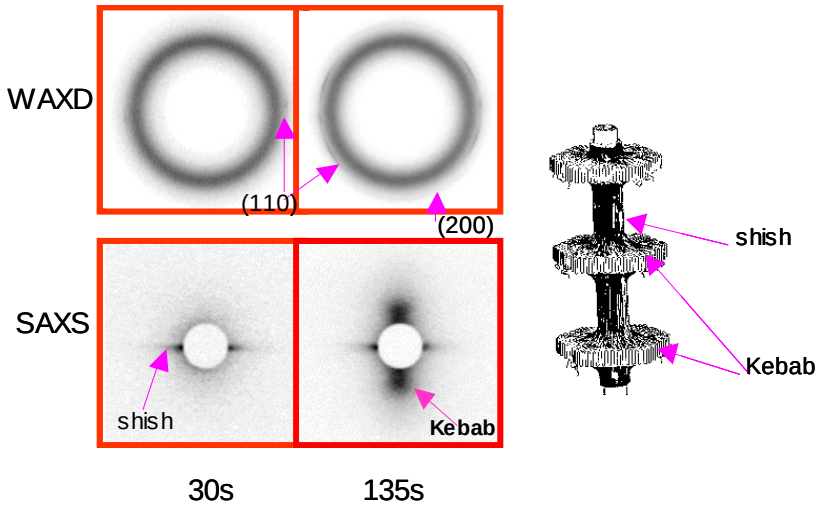

Figure 2.5.8 *Microfibrillar "shish" with extended chain conformation along the flow direction (form first) superimposed by the crystalline layered structure of "kebabs" with folded chain conformation perpendicular to the flow direction (form second) prior to full scale crystallization.*

brightness beam and area detection will produce a modest beam footprint on the sample while enabling the simultaneous collection of data over a wide range of scattering and azimuthal angles, in a time-resolved fashion (e.g., during annealing of a block copolymer film, or during the operation of an electroluminescent device).

Small spot size will enable microbeam SAXS/WAXS in a scanning probe mode that will be particularly useful for composite materials. It could, for example, resolve the structure that develops around reinforcing fibers, including ones that nucleate particular structures in the matrix [29]. By decreasing the probe size below 1 micron (e.g., 100 nm), this approach could be extended to nanocomposites, e.g., with layered or exfoliated silicates, that also strongly influence the structure of semi crystalline polymer matrices; and to composites incorporating advanced nanofibers produced through electro spinning. In addition, continuous energy tunability will permit "anomalous reflectivity" measurements on supported polymer thin films. Tuning the X-ray energy to slightly below the absorption edge of one of the constituent elements will permit the direct location of a particular element within the structure from the electron density (index) profile.

2.5.3.5 Strategies for Studying Radiation Sensitive Materials

It is evident from the annual reports of the ESRF, APS, and Spring-8 that the high brightness of third

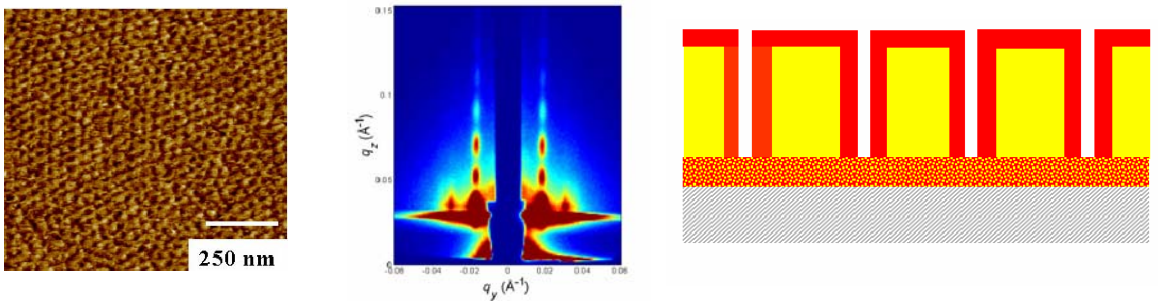

Figure 2.5.9 *A thin polymer film of P(S-b-MMA) deposited on a silicon substrate, modified with random copolymer. After rinsing in an acetic acid solution, a local hexagonal pattern emerges as shown in the AFM image (left). The GISAXS spectrum (middle) supports the hexagonal structure and establishes that the film is porous with pores extending the entire depth of the film (right).*

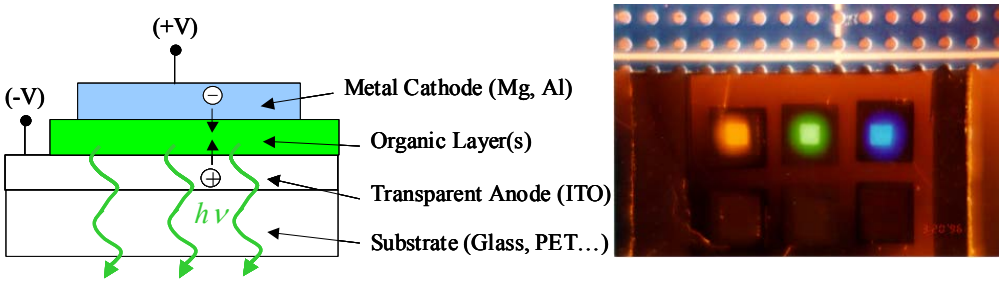

Figure 2.5.10 *Left: schematic of an organic electroluminescent device, where the thickness of the active organic layer is typically 100 nm. Right: photo of an integrated three-color organic device based on dye-doped polyvinylcarbazole; individual subpixels are 2 mm on a side.*

generation sources is being widely applied to the study of soft matter systems. Nonetheless, from unpublished comments at synchrotron workshops, it is equally clear that there were a number of cases where attenuation was required to prevent radiation damage. Hence, it is fair to ask whether the substantially higher brightness of NSLS-II can be fully utilized in studies of soft matter.

Clearly, the avoidance of radiation damage at NSLS-II will require careful attention. Researchers who have succeeded in studying soft matter at current third generation sources invariably applied a few of the following strategies. When possible, samples were selected that were composed of radiation robust constituents such as cyclohexane, benzene, biphenyl, rather than constituents known to be susceptible to radiation damage such as COOH, $-SO_2-$, NH_2, and C=C. Since there is considerable evidence that radiation damage is due to cumulative dose, care must be taken to make every photon count, for example, through parallel detection or on-the-fly scans. In some cases, the X-ray beam was rastered and data taken from equivalent sample areas or, when in solution, samples were flowed through the X-ray beam (see the very exciting development of flow-cell mixers in Section 2.2.3.1). Samples were usually kept in vacuum or an inert gas environment. In some cases, samples were freely suspended to avoid interaction with photoelectrons ejected from a substrate and kept thin and studied at grazing incidence to avoid heating from X-ray absorption.

When such precautions are taken, the full range of soft matter and biomaterials applications described in this section will be open for exploration with the ultra-high brightness beams at NSLS-II.

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2.6 Strongly Correlated Electron Systems

2.6.1 Overview

Understanding the electronic behavior of strongly correlated electron systems is one of the most important problems in condensed matter physics – one that is driving a revolution in the prevailing paradigm of Fermi-liquid behavior of solids. As their name suggests, it is their electronic degrees of freedom that give rise to their exotic properties. In materials with poor screening properties, such as the doped transition metal oxides, the interaction energy between valence electrons can overwhelm their kinetic energy, giving rise to a strongly coupled many-body ground state. As a result of this strong electron correlation, these materials display a range of exotic and useful behaviors, including high-temperature superconductivity, colossal magnetoresistance and a general extreme sensitivity to external perturbations. An example is shown in Figure 2.6.1.

However, in these materials the independent electron framework of solid state physics is not applicable. In our effort to understand the physics of, for example, high T_c materials, there is thus more at stake than simply the mechanism behind superconductivity – the language we use to discuss condensed matter is itself at issue. J. R. Schrieffer has said: "When high temperature superconductivity is solved we will have to rewrite the textbooks on solid state physics." This monumental theoretical task is one of the "Grand Challenges" in physics today.

Of particular relevance in this field is the need to go beyond the conventional picture of ordered ground states with weakly interacting (linear) excitations to identify and understand more exotic phases, which may be characterized by unusual correlation functions (orbital currents, topological order, etc). Identifying and characterizing these new phases will require extended phase space in which to search (ultra-low temperatures, high-magnetic fields and high-pressures) closely coupled with materials synthesis (including especially nanoscale structures) together with X-ray techniques (scattering, imaging and local probes) to fully elucidate the electronic behavior.

The high-brightness of NSLS-II will drive advances in energy and real-space resolution of these techniques that, when coupled with the extremes of sample environment and novel materials synthesis, will dramatically advance the field of strongly correlated electron systems, announcing a new era in condensed matter physics.

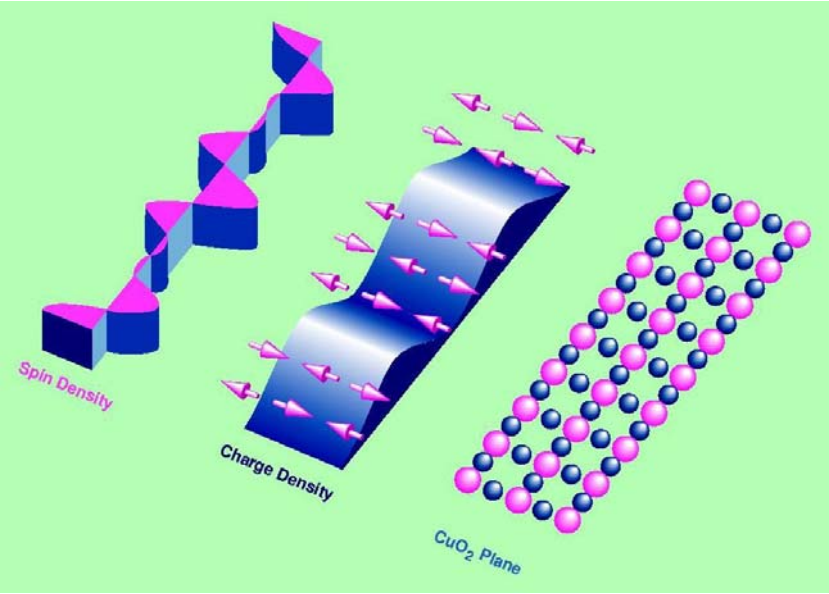

Figure 2.6.1 *Schematic of charge and spin stripes in a high T_c superconductor. Such exotic electronic orderings, frequently observed in strongly correlated electron systems, remain poorly understood.*

2.6.2 Scientific Challenges and Opportunities

Correlated Electron Materials Science is a frontier field, currently dominating hard-condensed matter physics. Yet it is far from mature and surprising new phenomena appear on a regular basis, such as the recent discovery of superconductivity in cobaltate materials. While it is believed that the possible phases of one-dimensional electronic systems have been completely classified and characterized theoretically, no such characterization is available for two- and three-dimensional systems. We have recently learned that 'spin liquids' exist in well-defined, non-artificial theoretical models. It has been proposed that they can occur in real metallic systems. The key to finding new phenomena will be a strong effort in materials synthesis, in characterization, and in measurement techniques, including more and better spectroscopies.

To illustrate the importance of this problem in the coming decades, a number of emergent directions that open new avenues for exploration and raise new challenges to present measurement and calculation abilities are highlighted. It is clear that this topic will remain amongst the most fertile and surprising in physics for the foreseeable future.

2.6.2.1 Surface Science

The surface science of correlated electron systems is a crucial but surprisingly little-studied issue, practically begging for attention. The motivations are both practical and fundamental. On the fundamental side, the issue is this: correlated electron materials exhibit a multiplicity of interesting electronic phases. It is natural to ask: how do the electronic phases at surfaces or interfaces differ from those in the bulk? On the practical side, one hopes to exploit the interesting electronic properties (such as superconductivity, 'half-metallic' or 'colossal' magnetoresistance) of strongly correlated systems. However, most applications involve getting electrons into or out of a device, and therefore necessarily involve a surface or interface, whose electronic properties are vital to the performance of the device. Very little is actually known about changes in electronic properties near surfaces and interfaces.

Traditional surface science focuses on where the atoms are and why they are there. Correlated electron surface science will focus on the properties of the electrons, asking “what is the electronic phase, and why”. This is basic science for possible future correlated electron devices.

Key probes will include photoemission, X-ray Magnetic Circular Dichroism (XMCD), grazing-incidence X-ray scattering, and X-ray resonant scattering. High quality sample preparation will also be crucial, including fabrication of near-ideal interfaces and nano-scaled architectures.

2.6.2.2 Fluctuating Order

Fluctuating Order and its consequences are a key open area. One of the traditional questions in materials theory has been the effects of long ranged order on the electronic spectrum (i.e., ordering of atoms into a lattice, ordering of electrons into superconducting or magnetic states). However, we are now learning that many materials exhibit wide regimes in which substantial short-ranged (in space and time) correlations exist that dramatically affect physical properties.

For example, the physical mechanism underlying the magnetic field induced insulator-metal transition and the associated large change in the electrical resistivity in perovskite manganites has been the subject of intense experimental and theoretical investigation since its discovery in 1993. A recent diffuse x-ray scattering study found a strong correlation between the presence of nanoscale charge/orbital ordered regions and the increased electrical resistivity in the paramagnetic phase of these materials, suggesting that nanoscale inhomogeneity plays an essential role in these phase transitions (Figure 2.6.2)

Our ability to detect, normalize and interpret these fluctuations lags far behind our ability to detect, normalize and interpret the Bragg peaks associated with long ranged order. Taking the next step in understanding materials properties will require great improvements in our spectroscopic abilities. In particular, correlation functions beyond the usual two-point correlation functions may be central to the

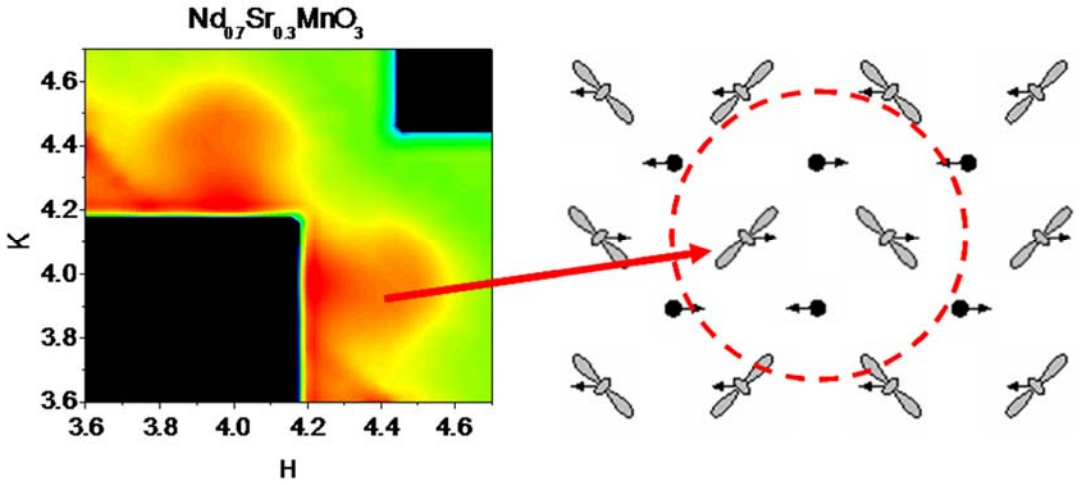

Figure 2.6.2 *Diffuse x-ray scattering (left) in a perovskite manganite resulting from nanoscale charge/orbital ordered regions, shown schematically on the right [1]*

problem (i.e., beyond the usual density-density correlations). New scattering experiments will need to be devised to probe such objects, perhaps using resonances or the enhanced coherent properties of the beam.

2.6.2.3 Dynamics

Density functional-based band theory has revolutionized our understanding of materials. We are now able to calculate with great accuracy, for a very wide range of systems, anything that can be related to static, ground-state properties. For dynamics we are in much worse shape: for example, even for moderately correlated materials, density functional methods over-predict quasiparticle velocities by factors of two or more. This of course does not cast doubt upon the successes of the methods: the theorems on which the methods are based make no guarantees about excited state properties. However, it does show that additional methods are needed. Recent developments (i.e., the development of the "dynamical mean field method" and its marriage to band theory) suggest that progress is now possible on these issues. The challenge will be to compute dynamical response functions (transport coefficients, single-electron dispersions and linewidths, dynamical structure factors, etc) and to refine our ability to measure these quantities using emerging techniques such as inelastic X-ray scattering and X-ray correlation spectroscopy and advances in more well-established techniques such as angle resolved photoemission spectroscopy.

2.6.2.4 Quantal Correlations

Although nature is inherently quantum-mechanical, most of what is measured, calculated, or thought about is fundamentally classical: particle positions, velocities, two-particle correlations, etc. However, we know that the combination of quantum mechanics and interactions leads to correlations that are subtle and surprisingly long ranged in space and time. A well-known example is the phase correlations of superconductors. A very recent example is provided by the work of Rosenbaum, Aeppli and co-workers on the diluted $LiHo/YF_4$ system in which quantum entanglement was observed in the spin system. The challenge is to measure the quantal correlations more directly, and to find ways to exploit them. Resonant scattering techniques will be able to make unique contributions here.

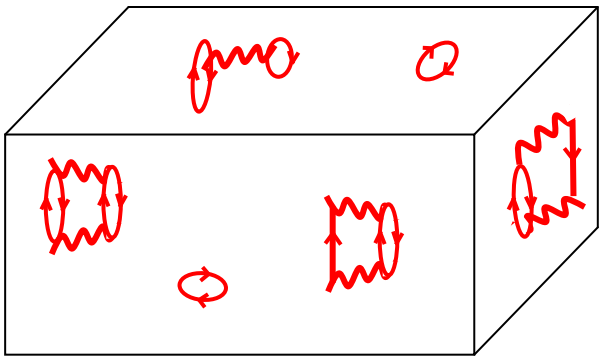

Figure 2.6.3 *A given system consists of the ground state and its excitations. The excitations "dress" the particles. To completely understand a system one needs to understand the excitations of that system. It is these excitations which determine the response of the system to perturbations.*

2.6.3 Impact of NSLS-II

The controlling degrees of freedom in strongly correlated electron systems are electronic in nature and therefore probes that couple directly to the electrons are uniquely suited to their study. Furthermore, these systems are characterized by competing interactions and frequently display inhomogeneous ground states. Thus, probes on a number of different length, energy, and time scales are required to fully elucidate their behavior. As a result, the full gamut of synchrotron techniques has impact in the study of strongly correlated electron systems.

In recent years, progress has been made in characterizing the unusual electronic ground states of these materials, such as stripe order in high-temperature superconductors and charge and orbital order in the manganites. Of particular importance have been basic structural studies, such as X-ray powder diffraction, electronically sensitive local probes, including EXAFS and XANES, and diffraction probes of electronic correlation, including especially resonant X-ray scattering.

However, for complete understanding, the excitations must also be understood (Figure 2.6.3), and it is in measurements of the electronic excitation spectrum where the greatest opportunities lie. The scientific challenge will be to understand the charge dynamics in the vicinity of the gap, which are the prime signature of a strongly correlated electron system. Phenomenon such as spin-charge separation and holon dynamics, charge dynamics associated with striping behavior, charge Goldstone modes (symmetry breaking collective modes), effects of orbital degeneracies as well as charge dynamics in new emergent classes of Mott compounds all remain poorly understood due to a lack of relevant experimental data.

There are two main probes of electron dynamics in the energy domain: inelastic X-ray scattering (IXS) and angle-resolved photoemission spectroscopy (ARPES). IXS measures a two-particle correlation function, $S(k,\omega)$, and is bulk sensitive. However, it is presently limited to fairly moderate energy resolution (~ 0.3 eV), even at today's third generation synchrotron sources. Thus, the technique is constrained to study the high-energy physics of the electrons. Conversely, ARPES measures the single-particle spectral function $A(k, \omega)$, with resolutions of ~ 1 meV, but it is intrinsically surface sensitive. ARPES has had an enormous impact in probing the excitations of high-temperature superconductors, in particular in the vicinity of the Fermi surface.

All of these techniques will continue to be of vital importance in addressing this and related problems and all will benefit dramatically from NSLS-II. In the following, we highlight a few areas where the impact will be particularly great.

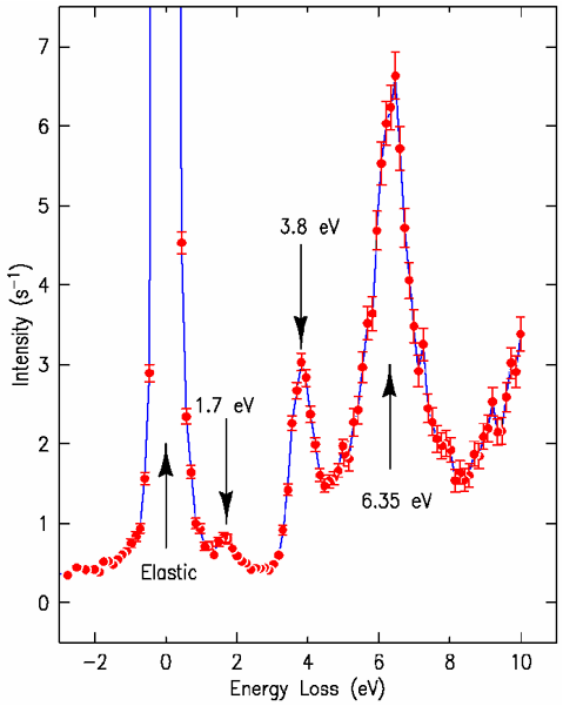

Figure 2.6.4 *Inelastic X-ray scattering spectrum from $CuGeO_3$, a 1D cuprate. These data were taken at the hard X-ray Cu K-edge with 0.4 eV resolutions at CMC-CAT at APS. With NSLS-II, such experiments will have ten times greater signal strength and improved energy resolution.*

2.6.3.1 Hard X-ray Inelastic X-ray Scattering

Over the past few years, IXS has begun to establish itself as a bulk-sensitive, momentum-resolved probe of charge dynamics. Pushing the resolution of IXS down to ~100 meV is presently underway at several different synchrotron facilities. In the past decade, enormously improved resolution and experimental geometries have elevated angle-resolved photoemission from a band mapping tool to an important many-body spectroscopy. Inelastic X-ray scattering holds a similar promise.

Hard X-ray inelastic scattering studies of charge dynamics are performed near the transition metal K-edges for 3d transition metals, to take advantage of the large resonant enhancements (Figure 2.6.4). For such edges, the perturbation on the d-orbitals is relatively weak but a large momentum transfer is possible, allowing measurement of dispersion relations. The anisotropy of the Mott gap and studies of holon dynamics are two recent examples of such studies [2-4]. This pioneering work has provided a new window into these strongly correlated systems. However, the large quasielastic scattering in the hard X-ray regime tends to mask out the interesting low-energy physics and it is not possible to separate the valence electron contribution from that of diffuse scattering with the current resolution. Improving the resolution of hard RIXS to the sub 50-meV level would allow it to play a key role in elucidating the charge dynamics of these systems.

For IXS then, the challenge is to reach energy resolutions such that excitations of direct relevance are accessible, namely $\Delta E \sim 10$ meV. Such resolutions, and better, are presently accessible only by working at high incident photon energies. However the flux is such that one is only able to study collective dynamics of the ion cores (i.e., phonons). While important in the study of electron-phonon effects, this precludes the study of electronic excitations. The ability to obtain meV type resolution at medium incident energies (5-10 keV) would transform this field, making accessible the transition metal resonances (K-edges) that

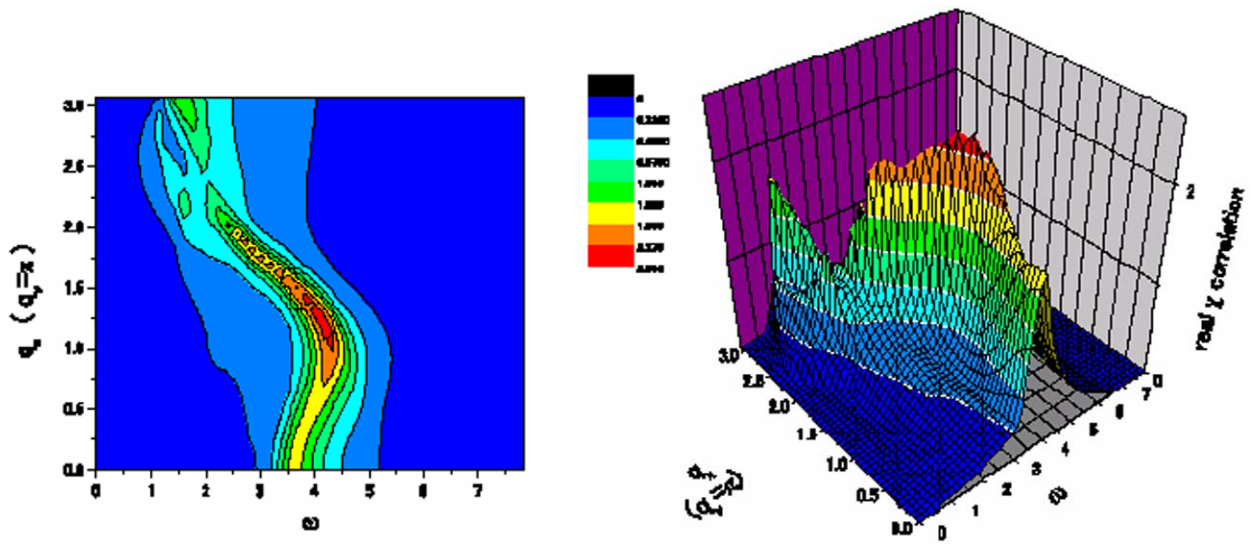

Figure 2.6.5 *Spectral function predicted for the correlation of the kinetic operator in a recent theory of dynamics in a high-T_c superconductor [5]. With NSLS-II, such a correlation function will be measurable by inelastic X-ray scattering at the Cu L-edges, and the validity of the model determined. Energy units (ω) are 3/8J ~ 60 meV.*

greatly enhance the inelastic scattering, and allowing one to probe the electron dynamics with unprecedented resolution.

This will require both very high brightness beams, and the development of new analyzers. The latter is presently underway at the Advanced Photon Source (APS), with preliminary work being performed on sapphire. The former will be provided by NSLS-II. Compared to existing beamlines at APS, NSLS-II will be 35 times brighter in the 5-10 keV range (see Figure 3.3.4), providing more than a factor of 10 more photons in the same bandpass. Presently, it takes about 6 hours to take a single scan. This will be reduced to less than 30 minutes at NSLS-II, transforming what will be possible and making studies of the charge dynamics in strongly correlated systems routine. Comprehensive studies as a function of doping, temperature, and momentum transfer will become possible.

Important experiments will include probing the charge dynamics of stripe order in cuprates, searching for dynamic, hidden order parameters of the type recently proposed in high-temperature superconductors (Figure 2.6.5), probing orbital excitations ("orbitons") in manganites, and investigating the superconducting gap in transition metal oxide superconductors. There are also a number of significant mysteries in the "mid-gap" states as revealed by infra-red (IR) studies, where changes in spectral weight appear to violate sum rules [6] and shed light on the condensation energy. NSLS-II will enable enhanced momentum-resolved IXS studies, which will be tremendously important in understanding these results.

Finally, it is important to stress that the same inelastic techniques would have immediate applicability in a variety of other scientific disciplines, including for example organic semi-conductors, heavy fermion systems, quantum critical points (e.g., V_xCr_{1-x}) and essentially all other hard condensed matter systems. In addition, geophysics (systems under pressure), biology (protein and membrane dynamics, electronic charge transfer in photosynthetic compounds) and soft condensed matter (polymer dynamics, thin film dynamics etc) all benefit in similar ways.

2.6.3.2 Soft X-ray Inelastic X-ray Scattering

Soft X-ray (0.5-2 keV) inelastic X-ray scattering at the L-edges of transition metal compounds complements hard X-ray IXS in probing electronic excitations (Figure 2.6.5). Valence excitations exhibit enhancements of several orders of magnitude near an L-edge and the quasielastic scattering is relatively

low (in many cases lower than the inelastic signals). This would allow studies of the low-energy electron physics of many systems.

Another exciting prospect offered by the use of L-edges is to take advantage of the strong spin-orbit coupling present in the 2p core-hole created in the intermediate state to gain access to magnetic excitations. By changing the helicity of the photon (on an elliptically polarizing undulator (EPU) beamline) one can couple to such excitations. Magnetic inelastic X-ray scattering will open up an entirely new window on spin dynamics that will complement existing neutron scattering techniques. Together, these techniques will allow studies of the magnetic and charge dynamics with the same probe for the first time.

While the use of soft X-ray energies limits the available momentum transfer, near the Cu-L edges (950 eV) there is enough momentum to reach the zone boundary. This is sufficient, for example, for both cuprates and manganites where the pseudogap has its maximum value near the zone boundary. It is also sufficient for studying dynamic charge-stripe correlations for which the ordering vector is small. A big advantage of L-edge resonances is that they involve the d-states directly and are thus highly sensitive to the orbital fluctuations. Mott systems, such as colossal magnetoresistance (CMR) manganites, where orbital degrees of freedom play a role would thus be a perfect match for such a scattering technique. The CMR effect itself is a field effect and hence one needs to have a momentum-resolved probe of electronic structure in the presence of a magnetic field, which is not possible in an ARPES experiment. Inelastic X-ray scattering at the soft edges will be the perfect match for this.

However, in order to achieve these capabilities, the energy resolution must be improved by at *least* an order of magnitude [7, 8]. The current state-of-the-art is 0.25 eV at 500 eV. NSLS-II will be a factor of 60 times brighter than the ALS at 500 eV (see Figure 3.3.4). The extreme brightness of NSLS-II in this spectral range will make it possible to achieve 10 meV at 500 eV and will revolutionize soft X-ray measurements. With such resolution, soft X-ray IXS will directly complement ARPES, which has been so instrumental in advancing our understanding of the very low energy phenomena in these systems.

2.6.3.3 Angle Resolved Photoemission Spectroscopy

Dramatic improvements in the photoemission technique have allowed it to become a powerful probe of condensed matter in general and strongly correlated systems in particular. Very high energy resolution (1 - 5 meV) combined with excellent momentum resolution (0.01 $Å^{-1}$) have allowed the study of the electron interaction with phonons, CDWs, and spin fluctuations. Such studies have, for instance, had an important place in the overall discussion of the mechanism behind high-T_c superconductivity. In the latter materials, the magnitude of the superconducting gap is approximately 8 kT_c and has proven relatively easy to observe with existing resolutions. The gap of about 3.5 kT_c in the traditional phonon mediated superconductors puts more demands on the experiment, but even so there have been reports of its observation. However, at the typical photon energies used for these studies, the technique is very surface sensitive.

The challenge is to use higher photon energies where the escape depth would be larger: At 1000 eV, 86 % of the electrons come from the first 15 layers, rather than the first 4 layers at 20 eV. How feasible is the possibility of doing angle resolved photoemission at the higher energies? Clearly it is possible to design an instrument with high-energy resolution at high energies but because the momentum resolution, $\Delta k_{||}$, reflects the kinetic energy according to $\Delta k_{||} = 0.5123\ \Delta E^{1/2}\ \Delta\theta$, where $\Delta\theta$ represents the angular resolution, it requires a dramatic improvement in the angular resolution to maintain the same momentum resolution. For example, increasing the kinetic energy from 10 eV to 1000 eV requires an order of magnitude increase in the angular resolution. This is difficult to imagine in the large hemispherical analyzers used at the present time but may be possible in time-resolved instruments where the energy resolution, $\Delta E/E$, equals twice the time resolution, $2\Delta t/t$.

As discussed in Section 3.4.4, NSLS-II will have a bunch length of only 11 psec (rms) in fast timing mode. The slower the electrons in the drift tube the better the resolution. However, the drift tube should not be too long since stray fields then make it more difficult to retain the angular information. Retarding

the electrons from 1 keV to 1 eV and allowing them to drift down a 1 meter length tube leads to an achievable energy resolution of 10 meV, which matches the current "state of the art" achievable in photon monochromators. A similar instrument in the form of a photoelectron microscope has in fact already been built and tested. It has the possibility of switching its mode of operation from microscopy to spectroscopy and will be well matched to the time structure of NSLS-II.

If the electrons are retarded, it becomes necessary to take phase space considerations into account in considering the angular resolution. Assuming a source size on the sample of 0.1 mm and an acceptance angle of 10 degrees, retarding the photoelectrons to 1 eV with a 1 degree divergence in the drift tube leads to a required spatial resolution of 10 microns in the detector to give an angular resolution of 0.01 degrees. The latter would be an order of magnitude better than currently available.

Such an instrument operated at higher photon energies offers the possibility of more bulk sensitive measurements in the spectroscopy mode or the possibility of examining much smaller samples in the microscope mode. The high brightness of NSLS-II will make such an instrument possible and will enable ARPES experiments to be carried out at high photon energies with the energy and angular resolution required for strongly correlated systems for the first time.

2.6.3.4 Anomalous Soft X-ray Scattering

In weakly interacting electron systems, the dominant length scales are the lattice parameter, a, and, under some circumstances, the inverse Fermi-momentum, $1/k_F$. In correlated systems, however, a variety of spontaneous symmetry-broken ground states may occur, with characteristic length scales determined, in general, by a competition between interactions and geometric frustration.

To learn about such ground states one requires a probe that can detect ordering in the carrier liquid directly, even in cases where such ordering is not accompanied by a structural (lattice) distortion. In general if translational symmetry is broken by many-body interactions, rather than for example the electron-phonon interaction as in a charge density wave material, there is no reason to expect the crystal structure to reflect this, except perhaps passively.

The magnetic aspect of such ground states has been studied extensively with neutron diffraction. An example is the "stripe" correlations seen in nickelates and cuprates, which are sometimes accompanied by a crystallographic distortion [9, 10] but more often are not [11-13]. A good probe of the charge

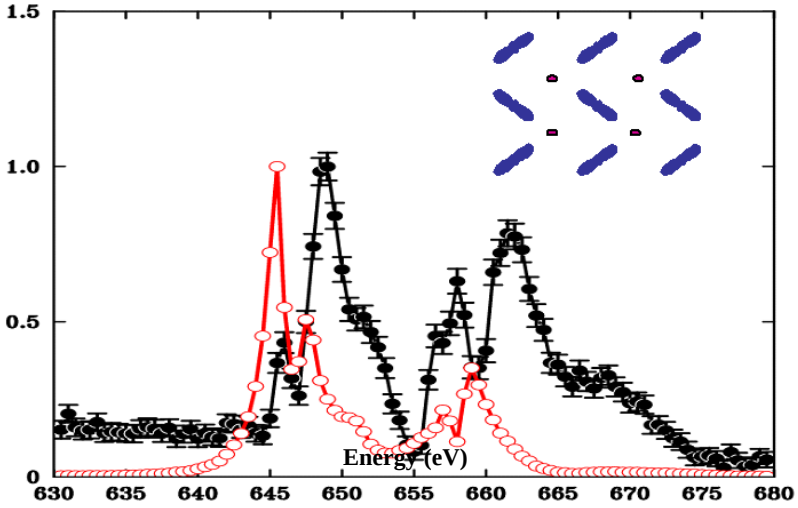

Figure 2.6.6 *Soft X-ray resonant scattering in a doped manganite, $Pr_{0.6}Ca_{0.4}MnO_3$. Red data is magnetic scattering, black data are due to orbital order. Inset is an idealized schematic of the orbital and charge order. These data were taken at NSLS beamline X1B. NSLS-II will be 1000 times brighter at this energy and will radically transform such studies.*

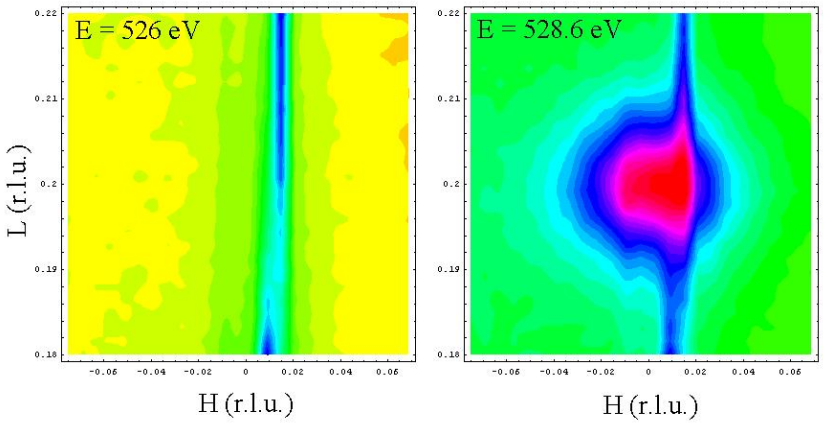

Figure 2.6.7 *Appearance of charge-density wave superstructure reflection from the spin ladder material $Sr_{14}Cu_{24}O_{41}$. This feature is visible only on-resonance as it forms from many-body effects rather than via the electron-phonon interaction. The vertical rod at $H \approx 0$ is the specular reflection from the surface.*

component of such phases has been lacking as charge sensitive probes such as X-rays or electrons couple mainly to the core electrons in the former case, and to both the core electrons and the nuclei in the latter.

It was recently demonstrated that the charge channel can be accessed by exploiting anomalous scattering factors in the soft X-ray regime, so called anomalous soft X-ray scattering (ASXS) [14]. In addition, magnetic scattering at transition metal L-edges is known to be extremely strong. Recent experiments at NSLS beamline X1B demonstrate the ability to measure spin and orbital correlations in the same sample at the same time (Figure 2.6.6). Being able to study such correlations simultaneously will be crucial in unraveling the interactions and competing behaviors of these important degrees of freedom.

Soft X-ray resonant scattering has also proved fruitful in studying valence modulations in $YBa_2Cu_3O_{6.5}$ [15], La_2CuO_{4+y} [16], $La_{2-x}Sr_xNiO_4$ [17], and $Pr_{1-x}Ca_xMnO_3$ [18]. For example, Figure 2.6.7 shows a scan through a superlattice reflection from $Sr_{14}Cu_{24}O_{41}$. This peak occurs at [0,0,0.2], very close to $4k_F$, and demonstrates the existence of a Wigner crystalline state in the spin ladder plane of this material. This feature is visible only on resonance, as it forms via many-body effects rather than through the electron-phonon interaction and can only be studied with ASXS.

With the increased brightness and flux of NSLS-II, it will be possible to tackle significantly more challenging problems, such as searching for dynamic stripes in high-Tc superconductors, i.e., charge stripes whose positions with respect to the crystal lattice are fluctuating in time. This problem is particularly difficult because the superlattice peaks corresponding to the ordered state are very weak already. However, with NSLS-II, dynamic stripes should be observable.

2.6.3.6 Coherent X-ray scattering

Coherent X-ray scattering is a powerful tool for the study of domain structure because of its sensitivity to the exact spatial arrangement of the domains. Upon illumination by a coherent beam, a sample composed of a mosaic of domains introduces a set of different phases into the scattered beam. The interference of these phases, which are related to the position of individual domains, gives rise to a "speckle" pattern. In principle, this speckle pattern can be inverted to obtain a real-space image of the domains. Such a reconstruction is quite challenging, but has been accomplished in a number of systems.

Another promising use of coherent X-ray scattering is in the study of dynamics. If the spatial arrangement of the domains changes with time, the phases of the scattered beam will be affected and the speckle pattern will also change. Measurements of these changes can therefore be used to study the dynamics of fluctuations.

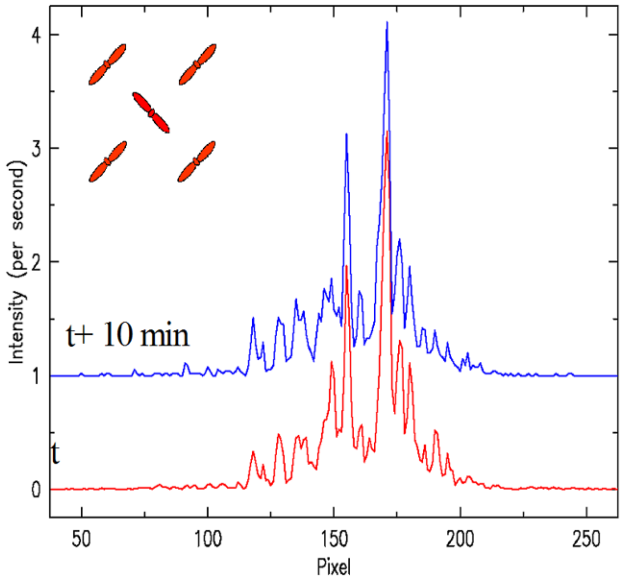

Figure 2.6.8 *"Speckle" pattern resulting from orbital order in $LaMnO_3$ [19]. The two curves, taken ten minutes apart, demonstrate that the orbital order is static. The high brightness of NSLS-II will enable speckle experiments to probe the dynamics of orbital domains.*

One example where such techniques will profitably be applied is the study of the dynamics of orbital domain walls in the manganites. Domain walls are observed on a number of length scales in these systems, but there is no understanding of the origin of these domains. Elucidating the dynamics of such structures would be an important step in approaching an understanding of this apparent glass-like behavior. Demonstration experiments performed at the Mn K-edge revealed static orbital speckle patterns in a test system, $LaMnO_3$ (Figure 2.6.8). However, these experiments, performed at the ESRF, lacked sufficient coherent flux to study the formation of orbital domain walls.

The greatly increased coherent flux at NSLS-II, combined with the large resonant enhancements at the L-edges, as shown in Figure 2.6.9, will allow entirely new classes of experiments to be performed for the first time, including the statistics of orbital and magnetic domains, imaging in real space of the inhomogeneous state and the study of nanostructured materials. It is also possible that in certain temperature ranges, orbital dynamics will be accessible with this technique.

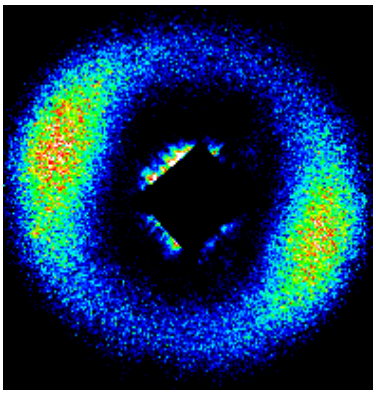

Figure 2.6.9 *Magnetic speckle pattern from a magnetized CoPt multilayer taken with the incident X-ray energy tuned to the Co L-edge at 780 eV. Such images provide microscopic real space information on the magnetic state of a sample with nanometer spatial resolution. With the increased coherent flux available at NSLS-II, these techniques will be able to explore both the statics and dynamics of magnetic domains.*

2.6.3.7 Infra-Red Studies

Infrared beamlines at NSLS-II will have world leading brightness throughout the near to far IR, as discussed in Section 3.4.13. This will be a tremendous advantage in high-resolution IR microscopy utilizing near-field techniques, as well as in ultra-high pressure studies on solids. To achieve the highest-possible working pressures generated in diamond anvil cells, very small gaskets are required, which necessarily entails the ability to focus down to extremely small spot sizes of 100 microns or less. The high IR brightness of NSLS-II will translate directly into more photons on the sample and will make it feasible to look for metal-insulator transitions in highly-correlated systems and for metallic hydrogen. Another area ripe for investigation will be time-resolved spectroscopy of collective excitations in highly-correlated electron systems. The short bunch length at NSLS-II will allow systems with very fast relaxation times to be studied using pump-probe techniques. This will be particularly useful in some of the cuprate materials, where there is considerable evidence for dynamically-fluctuating stripes and infrared anomalies have been observed.

2.6.3.8 Materials Synthesis

Strongly correlated electron materials are often doped compounds and synchrotron facilities can improve materials growth by advancing in situ studies of crystal growth in tools such as floating-zone furnaces or high-pressure ovens. The growth of crystals in the former apparatus has been tremendously successful and of considerable impact in the correlated electron field. Yet growing large, single-grain, homogeneous crystals often remains a "trial and error" activity. The ability to track grain growth, phase evolution, and growth orientation in situ would bring a new level of scientific understanding to this crystal growth process.

The study of small (~micron size) samples, and in particular the exploration of magnetism of small samples, would be a tremendous advance for the field. In the growth of doped crystals, composition gradients are inevitable, and indeed an essential aspect of the zone-melting process. Studying small samples will obviously reduce the impact of such distributions. Furthermore, it may be possible to exploit the natural composition gradient of the zone-refining process to map out properties diagrams in a compact, efficient way akin to "combinatorial" studies in thin films. In the case of crystals grown at high pressure, large crystals of the kind required for neutron scattering experiments will be impossible and X-ray scattering techniques will be the only ones of utility.

In the particular case of transition metal oxides (TMOs), the condensed matter field has concentrated on the effects of cation substitution, e.g., $La_{1-x}Sr_xMnO_3$ while trying to minimize the impact of nonstoichiometry on the anion sublattice. Modification of this oxide sublattice is known to have dramatic impact on electronic and magnetic states of TMOs, for instance the Y-123 superconductor and the cobaltite $RBaCo_2O_{5+}\delta$ (R=rare earth). However, large, homogeneous crystals are extremely difficult to come by (the nickelates are a notable exception that require considerable precision in the control of T, pO_2 in their synthesis and cooling to generate homogeneous oxygen distributions).

NSLS-II will enable researchers to fully characterize small single crystal samples in ways comparable to neutron scattering in large, cation-doped materials, opening a new realm of possibilities in TMOs.

2.6.3.9 High Pressure

When pressure is applied to matter, atoms are brought closer together, ultimately altering a material's structural, electronic and mechanical properties in radical and often unexpected ways. There are countless examples: metal-insulator transitions occur; some materials reach their yield strength while others become superhard; phase transitions, such as ferroelectric, magnetoresistive, and superconducting, occur; normally unreactive transition metals form alloys with alkali metals; electronic, magnetic, structural and dynamical properties of materials can be determined and tuned for a wide range of technological, defense,

and energy applications; both the highest temperature superconductivity on record and entirely new superconductors have been produced under pressure.

Variations in composition and temperature also change the structural state and the properties of materials. However, changes in these variables are not "clean" since they may be difficult to model (temperature) or reproduce from one synthesis to the next (composition). Isochemical changes of the unit cell volume at high pressure provide unparalleled tests of fundamental theory.

To understand the complex nature of materials, it is essential to observe their response under pressure. With the development of next generation pressure cells, many of these measurements will be extended to higher pressures. Structural studies by X-ray diffraction are an essential starting point for characterizing materials under high pressure (> 100 GPa). Inelastic X-ray scattering can explore in detail the concomitant changes in electronic structure and bonding. EXAFS and XANES measurements can provide local information to beyond the second coordination shells. An understanding of local structure is seen, for example, as the key to understanding the behavior of complex materials such as the oxide superconductors and CMR materials.

The advanced facilities for high pressure research at NSLS-II, described in Section 4.2.1, will provide the combination of local and long range structural probes together with measurements of electronic structure and bonding that are essential for advancing our understanding of these materials in new domains of pressure and temperature.

2.6.3.10 High Magnetic Field

A steady-state high-field magnet will be another essential component of the core set of extreme condition facilities at NSLS-II, as described in Section 4.2.2. Magnetic field represents a thermodynamic variable, in addition to temperature and pressure, with which to tune the balance of the competing degrees of freedom in these systems and can therefore often provide vital clues as to the nature of that balance. Many of the properties of correlated systems will only be understood through investigation in an applied magnetic field. Most X-ray techniques are equally applicable in an applied field and it is expected that they will be implemented at the high magnetic field beamline.

The high magnetic field beamline at NSLS-II will be invaluable for studies of an extremely wide range of systems, including charge and orbitally ordered states (manganites, ruthenates, titanates, etc.) and field-induced transitions in these compounds; mixed-valent compounds; magnetic semiconductors; materials with quantum critical points; heavy-fermion materials; high-T_c superconductors, including the normal state at high fields; Mott transitions; oxide and sulfur based compounds (BEDT-TTF based organics, etc); one dimensional magnets such as spin-Peierls compounds ($CuGeO_3$) and field-induced density waves in the TMTSF-based compounds; materials with commensurate-incommensurate transitions; rare earth compounds; frustrated magnets (spinels, pyrochlores, etc); multiferroic compounds ($YMnO_3$, $BiMnO_3$); and Jahn-Teller systems (manganites).

2.6.3.11 Ultra-low Temperature

The final essential component of the extreme conditions facilities at NSLS-II will be ultra-low temperature facilities, as described in Section 4.2.3. Ultra-low temperatures are crucial for a number of reasons, including providing expanded regimes in which to search for novel phases, the ability to test for quantum critical behavior, and as a test bed for theoretical calculations, which may be rigorous in the zero temperature limit. As with high magnetic fields, most X-ray techniques are equally applicable at ultra-low temperatures and it is expected that they will be implemented at the low temperature beamline.

An example of the impact of ultra-low temperature capabilities at NSLS-II is that of frustrated magnetism. Long-range ordering in magnetic systems is generally well understood when a unique ground state exists. When multiple ground states compete at low temperature, however, novel physics emerges from the spin degrees of freedom and is far from understood. The physical systems of interest can be broadly classified into two categories, quantum critical and geometrically frustrated.

Quantum criticality arises when two different magnetic phases, e.g. antiferromagnetic and spin liquid, meet at zero temperature as a physical parameter is varied. Theoretical understanding of quantum criticality is quite advanced and model experimental systems are being studied.

Geometrical frustration arises when a thermodynamically large number of possible ground states compete at temperatures well below the two-spin interaction energy scale. There are empirical rules that govern frustration in materials and several attractive model systems have been identified. Examples include the compounds $Gd_3Ga_5O_{12}$, $Gd_2Ti_2O_7$, and $Dy_2Ti_2O_7$, which display fascinating spin-liquid and spin-ice ordering. These magnetic states appear at temperatures below 1 K and therefore require dilution refrigeration. It is important to note that neutron scattering cannot be employed to study these systems, since both Gd and Dy have enormous neutron capture cross-sections. X-ray magnetic scattering is the only route to probe the full physics of their geometrical frustration and the ultra-low temperature facility at NSLS-II will be crucial for this.

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2.7 Magnetism

2.7.1 Overview

Magnetism continues to play an important role in fundamental physics as well as in technological applications. In magnetic materials, superimposed on the spatial charge-order (the crystalline lattice), there is a second spontaneous spatial ordering of the magnetic moments. Why the atomic magnetic moments survive and how they arrange in the solid is the subject of magnetism. Research in magnetic materials can be divided into three principal areas: the study of the microscopic electronic interactions that give rise to the local magnetic moments (the exchange interaction); the study of the long-range interactions of these moments with the resulting formation of macroscopic magnetic domains (the spin-orbit interaction); and finally, the study of the interaction between magnetic domains, which tend to arrange in macroscopic ordered structures to minimize the total energy of the system, including the magnetic energy stored in its surroundings (micromagnetic interactions).

The past 20 years have shown a steady progress in all these three areas. Synchrotron radiation is playing an increasingly important role in this activity, spurring the development of a number of unique spectroscopic techniques especially designed for the study of magnetism.

Initially the high photon-flux was the main motivation for the use of synchrotron radiation; as a result, new techniques such as spin-resolved photoemission suddenly became possible. More recently, the possibility of creating both linear and circular light polarization via extensive use of advanced insertion devices in third generation rings has driven the application of synchrotron radiation in the field of magnetism. Traditional synchrotron-based techniques such as absorption, reflection and light scattering have been adapted to take full advantage of the light polarization control. This has permitted the observation of large magnetic dichroism effects, now routinely employed in magnetic studies.

Synchrotron radiation techniques have become indispensable tools for the investigation of the properties of magnetic materials. For example, spin-polarized electronic band dispersions, magnetic moments (in bulk and/or at surfaces), magnetic anisotropies and susceptibilities, Curie temperatures and critical behavior at phase transitions are routinely determined at synchrotron beamlines.

The extension of spectroscopic methods that are sensitive to the orientation of magnetic moments to the field of microscopy, with nanometer length scale resolution, will permit the simultaneous observation of magnetic-domain and topographical structures with element sensitivity. Application of the time structure of synchrotron radiation to magnetism will allow investigation of the dynamics of magnetic phenomena. The high brightness, short pulse length, and broad spectral coverage of NSLS-II together with advanced insertion devices with full polarization control will dramatically advance our understanding of magnetism.

2.7.2 Scientific Challenges and Opportunities

2.7.2.1 Low Dimensional Magnetism

The possibility of direct manipulation of the electronic wavefunctions in artificially engineered materials has opened new and exciting vistas on all aspects of solid state physics. This wavefunction engineering modifies the magnetic properties to such a degree that these nano-engineered systems can be considered entirely new classes of magnetic materials. Much of this fundamental work has been possible because of increased abilities in the preparation and characterization of “exotic” magnetic structures and because of the extremely sophisticated probing capabilities realized at synchrotron radiation facilities.

The fundamental difference between a material in film form rather than bulk is the quantization of electronic levels induced by the film geometry (Figure 2.7.1). The study of the properties of discreet energy levels (Quantum Well States) in two dimensional systems has been crucial in understanding the indirect exchange interaction recently discovered in metallic magnetic multilayers [3]. Magnetic

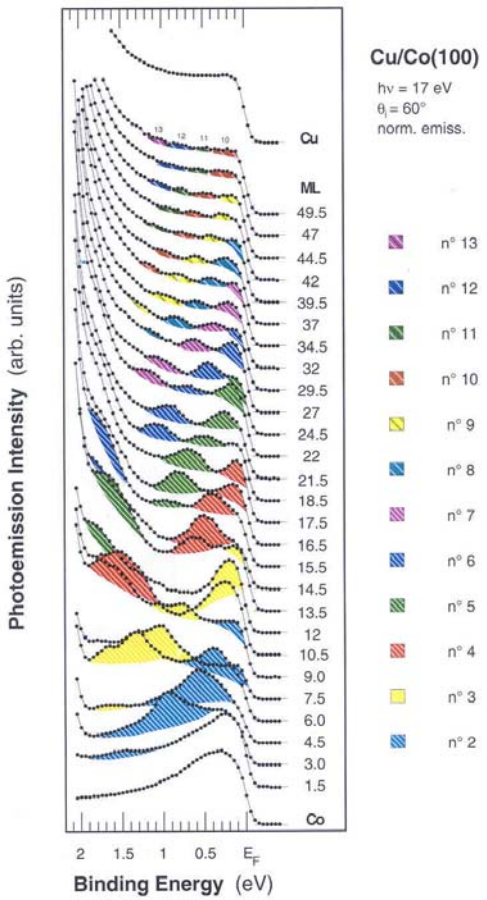

Figure 2.7.1 *Angular-resolved photoemission experiments performed with synchrotron radiation allow the direct sampling of discreet energy levels (colored peaks) in ultra-thin films of Cu (thickness indicated in monolayers units), epitaxially grown on a Co(100) single crystal. The ability to control the light polarization (linear in this case) as well as the photon energy proved essential for this type of experiments [1]. The study of the quantization of states in ultra-thin films not only allows the experimental determination of the bulk band structure with unprecedented precision but it also serves in measuring essential properties of quasi-particles such as lifetime broadening, interfacial reflectivity and phase-shift [2].*

multilayers are artificial structures that are prepared by alternate superposition of layers of magnetic and non-magnetic (spacers) metallic materials. The interest in these systems stems from their peculiar physical properties that have no counterpart in bulk: i.e. their properties do not correspond to the superposition of the properties of the constituent materials. Among these - and of great relevance for technological application - are the electronic transport properties (Figure 2.7.2).

The two-dimensional film geometry is clearly the simplest possibility of confining electronic wave-functions. Modern material science technologies however allow the preparation of structures such as atomic chains and clusters in which electrons are confined in two or even in all three-dimensions. This further confinement has been shown to have spectacular effects in magnetic materials. For example the orbital moments that are effectively quenched in the formation of itinerant magnetic metals can be considerably restored in these lower dimensional systems. At third generation light sources, the high photon flux enables the detection of extremely small quantities of material. Single atomic monolayers and even one dimensional chains become measurable with element-specific magnetic spectroscopy techniques such as magnetic circular dichroism (Figure 2.7.3).

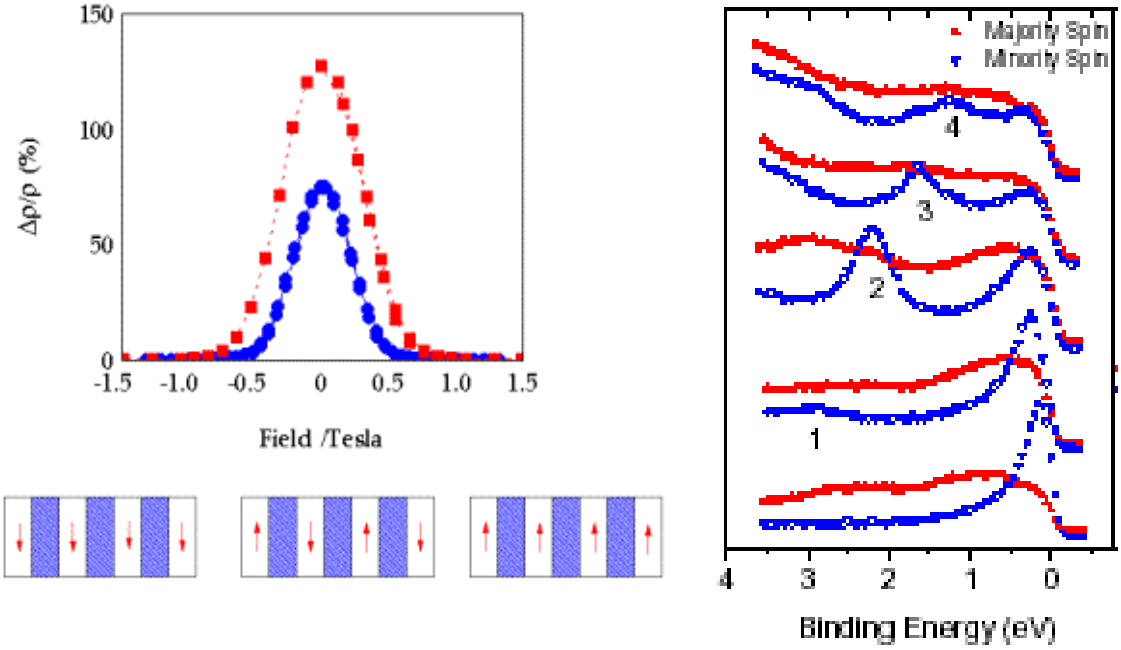

Figure 2.7.2 *In magnetic multilayers with spontaneous anti-parallel alignment, the relative resistance decreases with increasing magnetic field: a conspicuous magnetic phenomenon aptly called Giant Magneto Resistance (left panel). This connection between magnetic and electric properties is technologically significant because it can be used to convert magnetic signals in electrical ones. Magnetic field sensors based on GMR effects in films a few nanometers thick are nowadays routinely employed in industrial application in read-out heads for magnetic memories. The spontaneous alignment, which makes the GMR effect possible, is explained by the existence of spin-polarized QW States in the non-magnetic layers. These states effectively transport the magnetic information from one magnetic layer to the next, thereby enabling the long-range coordination of the single-layer magnetization. An example of these states is shown on the right panel; here quantum well states from 1, 2, 3 and 4 monolayers of Ag grown on an Fe substrate are monitored using Spin-Resolved photoemission. The QW States displays an extremely high degree of (negative) spin-polarization (blue curves: minority spin) [4].*

Quite apart from electronic confinement effects, another aspect of low dimensional magnetism has very important technological implications. It is related to the intrinsic anisotropy of these systems. The property that makes magnets so useful in applications is the magnetic anisotropy energy (MAE). MAE describes the tendency of the magnetization to align along specific spatial directions rather than randomly fluctuate over time (Figure 2.7.4).

The quantitative study of this kind of phenomena is usually difficult because the energy differences between competing macroscopic configurations are very small. Nevertheless, low dimensional structures such as films, chains and dots are all highly anisotropic and significant effects on the MAE are expected and are actively investigated in these systems. For example easy-magnetization directions different from those of the bulk materials have been successfully stabilized by MBE deposition of epitaxial films. Even more importantly, perpendicular magnetization in thin film samples has been observed in a number of cases. These systems have the prospect of very high bit-density in magnetic storage memories.

For these reasons the effects of low dimensionality on the anisotropy properties of materials are an important topic of current research in magnetism. These studies require a careful characterization of the system to be investigated (which is a difficult material science research project in itself) and intense radiation sources due to the small amount of material being sampled. For example, recent work at high-flux beamlines at ESRF has demonstrated the possibility of detecting MCD signals from single isolated

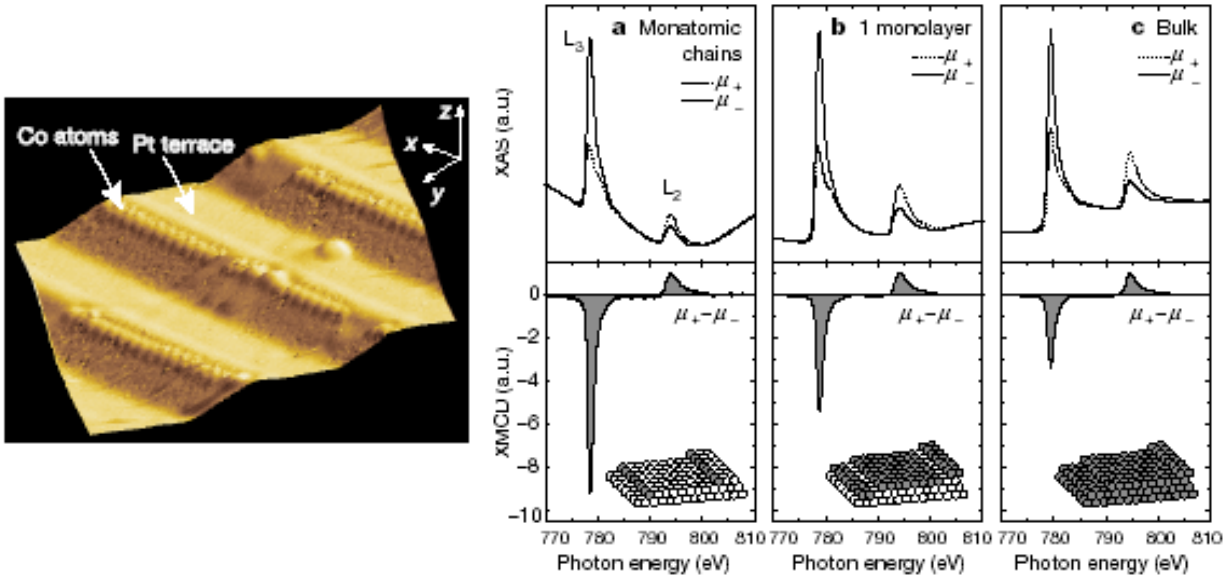

Figure 2.7.3 *Left panel: STM images. Long atomic chains of magnetic material (Co) are obtained by "step-decoration" of a vicinal Pt (111) surface. Right Panel: Corresponding to higher and higher confinement, the Co orbital moment increases substantially, as seen in the MCD spectra of Co on Pt (111) [5].*

clusters consisting on the average of only 3 atoms! These results are indeed spectacular and indicate the importance of high brightness, high flux synchrotron radiation for research in magnetism.

The examples of studies on magnetic-multilayers, magnetic films, magnetic chains and magnetic dots just described demonstrate that the opportunities for fundamental as well as applied research in the area of the magnetism of low dimensional structures are vast and still largely unexplored. In this area, synchrotron radiation based spectroscopies constitute unique tools that will continue to be of extreme value in the foreseeable future. Indeed, the high brightness and high flux of NSLS-II are crucial for enabling continued major progress in this field by greatly enhancing the ability to detect small signals from a diminishing number of atoms.

2.7.2.2 Complex Magnetic Materials

The notable improvements in sample preparation and characterization techniques over the last 10 years has caused a considerable shift of research in magnetism toward the study of complex materials, often in artificially engineered structures. Spintronic applications, which combine the exquisite control of charges in traditional semiconductor based electronics with the direct manipulation of electronic spin, will have a revolutionary impact on technology.

In a recent article, Wolf and co-authors summarized the potential of new technologies but also pointed out a number of issues that must be understood and overcome before the technology can mature: "*It is envisioned that the merging of electronics, photonics, and magnetics will ultimately lead to new spin-based multifunctional devices such as spin-FET (field effect transistor), spin-LED (light-emitting diode), spin RTD (resonant tunneling device), optical switches operating at terahertz frequency, modulators, encoders, decoders, and quantum bits for quantum computation and communication. The success of these ventures depends on a deeper understanding of fundamental spin interactions in solid state materials as well as the roles of dimensionality, defects, and semiconductor band structure in modifying these dynamics. If we can understand and control the spin degree of freedom in semiconductors, semiconductor heterostructures, and ferromagnets, the potential for high-performance*

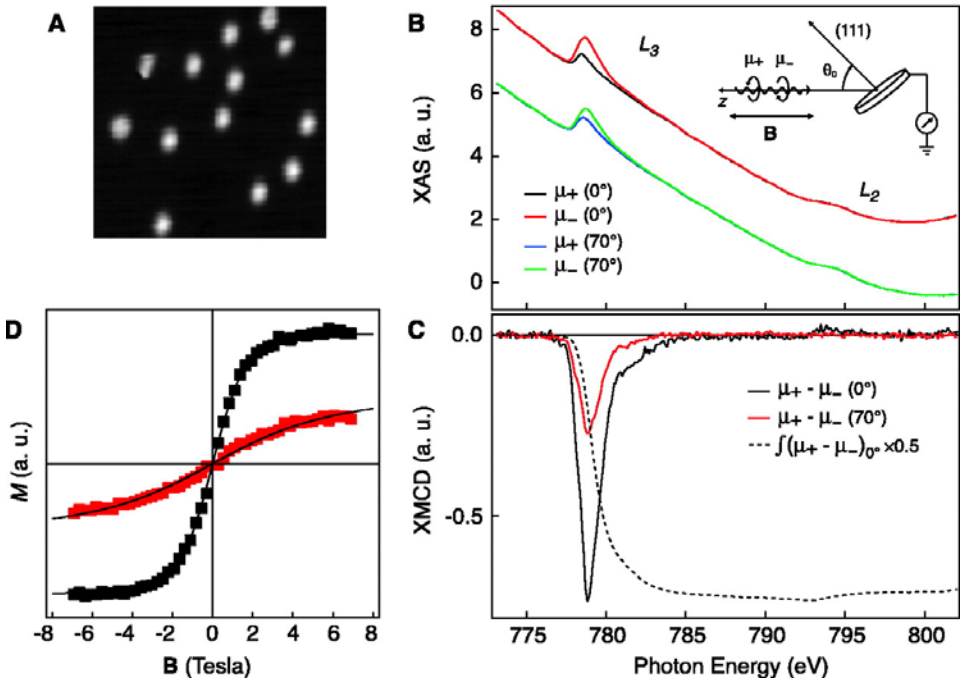

Figure 2.7.4 *Isolated Co atoms deposited on a Pt (111) surface are monitored with MCD techniques using synchrotron light. The MAE is extremely high in this Co atoms: external fields as high as 7 T are not quite enough to align the moments along the substrate plane (panel D: red curve in plane magnetization, black curve out of plane magnetization) [6].*

spin-based electronics will be excellent. The most interesting devices will probably be those that we have not even contemplated here!" [7]

At the moment, diluted magnetic semiconductors (DMS) constitute one of the most promising classes of new magnetic materials for spintronic applications. Their principal interest stems from the possibility of (relatively) easily integrating magnetic degrees of freedom in traditional semiconductor technologies. DMS combines its transport and/or optical properties with magnetism, and thereby carries an enormous potential for opening up a path to entirely new devices.

Up to now, $Ga_{1-x}Mn_xAs$ has been a representative DMS with a moderately high Curie temperature (T_C) ~ 100 K. Therefore, an essential task is to find a DMS with T_C above the room temperature. Recently, a few DMS based on wide gap II-VI and III-V semiconductors have been reported to have such high T_C. However, the reproducibility of T_C is somewhat questionable. More fundamentally, the origin of ferromagnetism in DMS materials is still very much an open question. Synchrotron-based spectroscopies are indispensable tools in unraveling the detailed mechanism that governs the magnetic behavior in DMS.

In DMS, the doped magnetic ions can be either 3d transition metal ions or 4f lanthanide ions, and the typical doping levels are the order of a few percent. Element specific X-ray absorption combined with magnetic circular dichroism (XMCD) provides unique tools to probe the spin and valence states in these systems and to clarify the ferromagnetic origin in DMS [8]. Furthermore the impurity band induced by the Mn-doping in GaAs was recently successfully detected in an angle-resolved photoemission spectroscopy study. As predicted by the theory, the impurity band is localized very near the Fermi level, confirming that the charge carriers in Mn-doped GaAs are governed by this impurity band (Figure 2.7.5).

The efficiency of spintronic devices depends closely on the value of the spin polarization (the imbalance between spin-up and spin-down charge carriers) near the Fermi level. Theoretical predictions for $Ga_{1-x}Mn_xAs$ indicate that it may be a half-metallic ferromagnet (i.e., fully spin polarized) and thus would be a very efficient material for use in spintronic devices. A measurement of the spin polarization of the near-Fermi level states can confirm the half-metallicity as well the ferromagnetic nature of Ga_{1-}

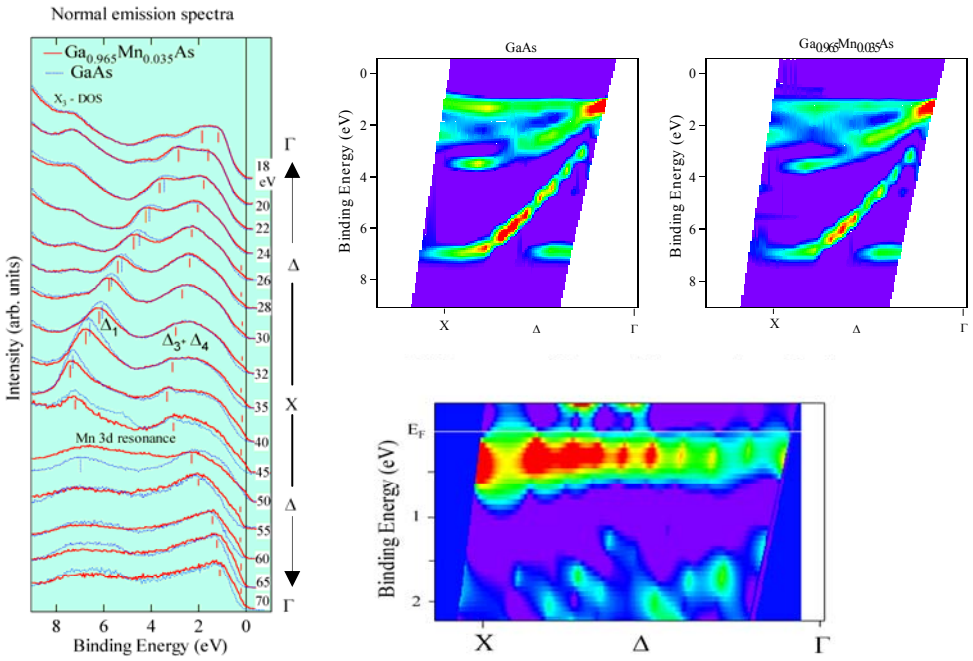

Figure 2.7.5 *Angle resolved photoemission spectra and experimental electronic band structures of pure GaAs and $Ga_{1-x}Mn_xAs$. The impurity band induced by the Mn-doping is determined from their difference. At third generation light sources, the extremely high photon flux will allow the spin resolved photoemission measurements of the impurity band and the determination of the spin-polarization of the charge carrier [9].*

$_xMn_xAs$. As is shown below in the case of manganite materials, spin-resolved photoemission spectroscopy is the most direct measurement technique to determine the spin polarization. Unfortunately, its efficiency falls down by about four orders of magnitude in comparison with the conventional photoemission spectroscopy. Considering the fact that the impurity bands have very small spectral weights in DMS systems, one expects that the measurement will require the extremely high photon flux planned for NSLS-II.

Another class of materials of great interest for magnetism research and applications is strongly correlated materials. In these materials the strong electron correlation in partially filled orbitals causes a whole variety of interrelated phenomena such as metal-insulator transitions, orbital ordering, charge ordering, lattice and magnetic polarons, etc. When these complex systems contain magnetic ions, new phenomena, such as the colossal magneto resistance (CMR) effect, result from the interplay between electronic and magnetic degrees of freedom.

An important example of this kind of interplay is offered by films of $La_{0.7}Sr_{0.3}MnO_3$. This CMR material can carry electric current only when the spins of the itinerant charges are aligned parallel to the spins of the manganese ions fixed in the crystal lattice. This system then constitutes a natural source of ~100% spin-polarized current, i.e., it is a half-metallic material. The existence of half-metallic materials was hypothesized long ago to account for magneto-transport properties of bulk $La_{0.7}Sr_{0.3}MnO_3$. Their existence was recently verified by spin resolved photoemission at NSLS (Figure 2.7.6).

While DMS and highly correlated materials offer great promise in advancing spintronic technologies, these exotic materials must be incorporated into appropriate device architectures. For example, the use of half-metallic materials will be of great benefit in magnetic tunnel junctions (MTJ), which are three-layer devices with two ferromagnetic metallic layers separated by an insulating layer. Currently, there are great challenges in measuring and controlling parameters such as interface quality, tunnel barrier quality, surface/interface roughness, ferromagnetic electrode quality, magnetic domain walls, and, finally, the

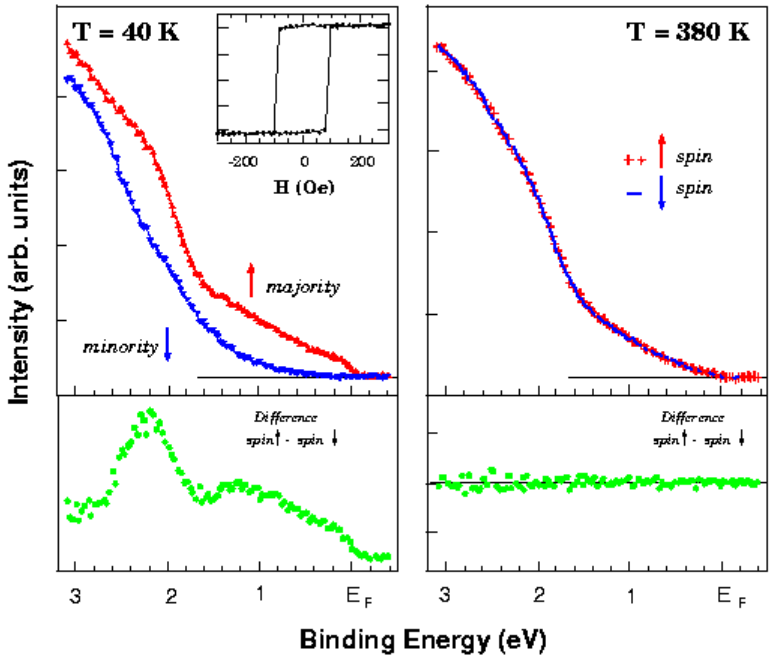

Figure 2.7.6 *Half-Metallic Material: At low temperature (left panel) $La_{0.7}Sr_{0.3}MnO_3$ is conducting. Spin-resolved photoemission spectra from the region close to the Fermi level show that the conduction is totally carried by majority spin electrons (red curve). At high temperature (right panel) this material becomes both paramagnetic (blue and red curves superimposed) and insulating (no intensity at E_f) [10].*

intrinsic behavior of ferromagnetic surfaces/interfaces. Moreover, as miniaturization of components continues, these potential obstacles must be overcome at the sub-micron and even nanometer length scale.

NSLS-II will greatly help in meeting these challenges. For example, its superior flux in the soft X-ray region will provide the perfect opportunity to extend the technique of valence band spin-resolved photoemission to higher kinetic energies. This will enable the investigation of the electronic structure of highly relevant buried interfaces, such as the ones between a ferromagnet and insulator in MTJs. Moreover, synchrotron based X-ray scattering studies, particularly resonant scattering techniques, provide detailed information on issues such as interface quality and spin-orientations at an interface. As these techniques often deal with processes that have an intrinsically low excitation cross section, the increased flux of NSLS-II will be of crucial benefit. Finally, the greatly increased flux of NSLS-II will enable element-specific core-level spectroscopic investigations of materials such as DMS, which often have small amounts of magnetically active components.

2.7.2.3 Magnetic X-ray Microscopy

Current research into magnetic materials focuses on complex, multi-element systems that are often engineered into layered or even more complex geometries. There is a great need to develop analytical tools that can interrogate the magnetic state of a sample with element-specificity as well as nanometer-scale lateral and depth resolution [11]. Real-space imaging techniques based on X-ray microscopies (XRM) such as photoelectron emission microscopy (PEEM) or X-ray transmission microscopy (XTM), combined with an appropriate choice of photon energy and polarization, can provide such a capability on lateral length scales currently around 20 nm, with planned near-term improvements approaching 1 nm [12, 13].

XRM combines a number of features that are found in other forms of magnetic microscopies with capabilities that are unique to synchrotron-based instrumentation. The benefits of XRM for the

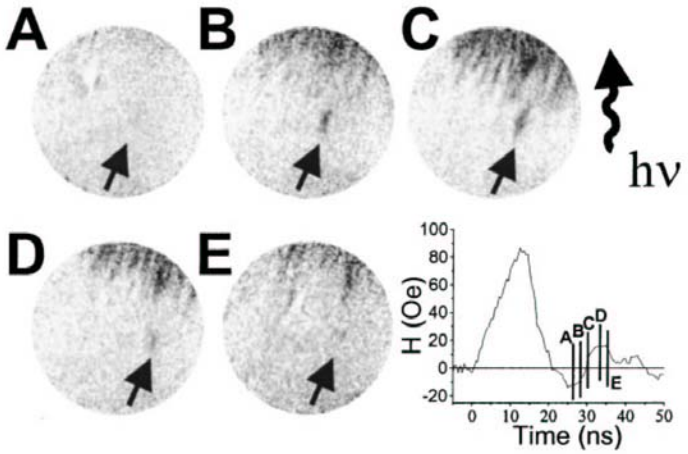

Figure 2.7.7 *Magnetic PEEM domain images of a NiFe layer, taken 13, 15, 17, 20, and 22 ns after the maximum of an 80 Oe field pulse; the field of view is ~120 μm. The arrows indicate a nucleated and subsequently expanding reversed domain. [14]. NSLS-II will enable improvements to both the spatial and temporal resolution.*

investigation of magnetic systems are many and include: element specificity; sensitivity to ferromagnetic & antiferromagnetic order (XMCD & XMLD); measurements in applied fields (photon-in, photon out techniques); quantitative analysis of sample magnetization (spin & orbital moments and identification of magnetization vector); high spatial resolution; and high time-resolution. The last two points in particular will benefit greatly from the improvements in X-ray microscopy that will be attained with the superior capabilities of NSLS-II.

As will be seen in the following section, a thorough understanding of the dynamical processes in magnetic systems is crucial for continued development of advanced magneto-electronic devices. Combining these studies with the high spatial resolution of X-ray microscopy will allow investigators to probe fundamental questions involving issues such as the magnetization reversal processes in advanced magnetic materials and the role of reduced dimensionality on the dynamical response of nano-engineered materials.

As an example, Figure 2.7.7 shows time and element resolved (in this case, the images were acquired at the Fe L_3 edge) PEEM images for a $Ni_{80}Fe_{20}$ (5 nm)/Cu (10 nm)/Co (5 nm) spin-valve like trilayer grown on Si (111) [14]. The PEEM images labeled A through E in the figure show the magnetic domain pattern of the NiFe layer with a spacing of approximately 2 ns between frames after the application of a magnetization reversing field pulse. The images, with a field of view of ~120 μm, clearly show domain nucleation (black arrow) and subsequent growth. NSLS-II will improve these types of studies in two areas. First, the greatly increased brightness of the new source will allow a reduction in the field of view and an improvement of the spatial resolution of the time-resolved images. Also, the shorter bunch length of the upgraded machine, currently planned at 30 psec or shorter, will improve the time resolution of the images.

In addition to the direct, real space imaging techniques outlined above, the availability of coherent X-rays from undulator sources has stimulated the development of magnetic speckle imaging. A growing number of research groups worldwide are developing new full-field magnetic imaging techniques and new techniques for the study of magnetic dynamics. For example, an algorithm based on multi-wavelength anomalous diffraction (MAD) has been developed recently at NSLS for reconstruction of magnetic domain pattern from magnetic speckles [15] and an example of the speckle pattern from microscopic domains in a CoPt thin-film is presented in Figure 2.7.8. This technique can be extended to time-resolved measurements for the study of magnetic dynamic processes.

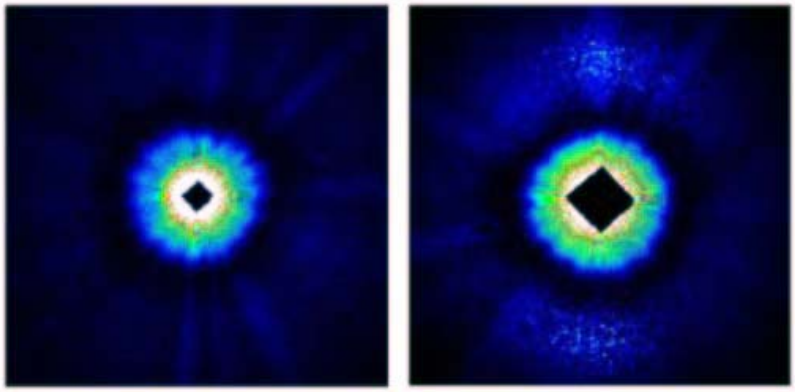

Figure 2.7.8 *Speckle-images measured at the Co L3 edge from a CoPt multilayer (sample from O. Hellwig, IBM Almaden). Left and right panels are the images taken off and on resonance, respectively. On-resonance the magnetic contrast clearly appears as a ring corresponding to the average magnetic domain size (~ 150 nm) [15].*

Magnetic speckle imaging will be of particular importance in examining the interactions within magnetic nanoparticle arrays. Magnetic nanoparticle arrays have been made from monodisperse 3-20 nm particles that self assemble into ordered structures. Just as the exchange and magnetostatic interactions between iron atoms in a crystal lead to the formation of ferromagnetic domains, the magnetic nanoparticle interactions should lead to domain structures. Magnetic speckle techniques using coherent X-rays will enable magnetic domains to be imaged in the nanoparticle arrays. With a smaller interparticle separation or a more conducting matrix between the particles, exchange interactions will become significant [16], and the particle wave function will delocalize over the array, leading to an insulator-to-metal transition [17]. The ability to image magnetic domains while varying the applied field and temperature and while passing spin-polarized currents through the sample would provide a powerful tool for understanding these nanoengineered magnets. Unlike neutrons in SANS or electrons in Lorentz microscopy, the X-ray photons would not be deflected by the external magnetic field. The increased brightness of NSLS-II will greatly improve the signal to noise ratio that is presently a limiting factor in the further development of magnetic speckle imaging.

2.7.2.4 Magneto-Dynamic Phenomena

Dynamic processes, in particular ultra-fast dynamics, are at the forefront of research on magnetic materials [18]. Here the goal is to obtain a detailed description of magnetization reversal processes in magnetic materials subject to external perturbations (magnetic, electric, thermal, or pressure). The detailed understanding of these processes is fundamentally interesting as well as obviously crucial in the development of high-speed recording media as well as other novel magnetic devices (e.g., spin electronics) [19]. Typically, magnetization-reversals in solids (i.e., the transfer of magnetic orientation between atoms) are mediated by spin-lattice relaxations. The relevant time-constants, estimated by considering the emission and lifetime of spin-waves in a crystalline lattice, are in the range of 10^{-12} - 10^{-10} sec [20]. To overcome this limit, several new concepts have been recently suggested such as the possibility of switching the magnetization of metallic nano-particles via injection of spin polarized currents (i.e. via direct exchange scattering) [19]. In this case the relevant time scale would be close to the fundamental dynamics of itinerant ferromagnets (i.e. Stoner excitation ~ 10^{-15} sec) [21]. The development of experimental probes, capable of high magnetic sensitivity and ultra-fast time-resolution, is then needed for these investigations.

Currently ultra-fast magnetic dynamics can be studied by analyzing the magneto-optical Kerr and Faraday rotations induced in ultra-fast pulsed laser sources. These techniques, an example of which is presented in Figure 2.7.9, have already revealed a wealth of extremely useful information but are sensitive

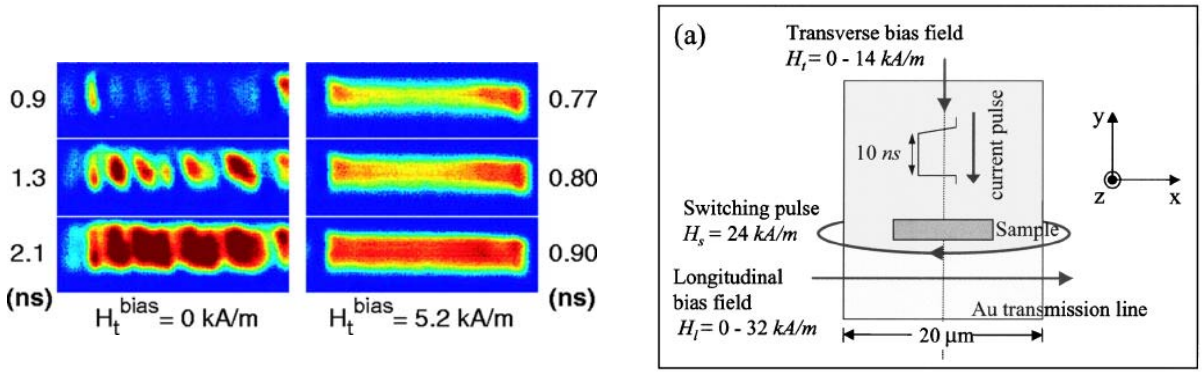

Figure 2.7.9 *a) Schematic configuration of 180 degree magnetization reversal. The magnetization is switched via a current pulse. The presence of bias-fields alters the dynamic mechanisms of the reversal process. MOKE image magnetization reversal in a $Ni_{80}Fe_{20}$ 12x2 μm sample exposed to a fast magnetic switching pulse. Note the change in the domain switching dynamics (both in time and space) obtained applying an external bias field [22].*

only to the average magnetization, and furthermore limited in their ultimate spatial resolution [22]. However the novel materials now being developed for use in magnetic technologies (such as magnetic tunnel-junction random-access memories) are often complex artificially engineered, multi-element and multi-layer structures [19, 23]. Element-specific probes of magnetic interactions on timescales relevant to the physical processes outlined in Table 2.7.1 are therefore required. Ultra-fast, time resolved core-level spectroscopies at NSLS-II will provide the element-specificity required to separate the contributions from the components of new materials. Furthermore, as many of the samples will be based on small devices and structures, the small spot size and increased brightness of the new source will be indispensable.

The availability of photon pulses as short as 11 psec at NSLS-II will greatly aid the development of elementally resolved investigations of dynamic magnetic processes at ultra-fast time scales, providing investigators with an element-specific strobe light at time scales relevant to most of the physical processes highlighted in Table 2.7.1. NSLS researchers recently demonstrated the feasibility of element-resolved magnetic measurements on fast timescales in measurements at the Advanced Photon Source. The

Excitation / Interaction	**Time scale (sec)**
Exchange interaction	10^{-15}
Stoner excitations	10^{-15} - 10^{-14}
Spin Waves	10^{-12} (low q limit)
Precessional rotation and damping	10^{-9}
Domain nucleation	10^{-9}
Domain wall motion	10^{-9}
Spin-lattice relaxation	10^{-9}
Magnetic Viscosity	10^{-6} - 10^{-3}
Spin injection into semiconductors	TBD
Spin diffusion	TBD
Spin coherence time	TBD

Table 2.7.1 *The dynamical processes in magnetic materials span an impressive breadth of timescales. The successful development of ultra-fast magnetic devices (storage memories are now already operating at GHz rates) must take into account the dynamic behavior of materials on extremely short time-scales. Time–resolved, synchrotron-based experiments feasible at NSLS-II will be particularly useful in this research area. A great advantage of NSLS-II over the present NSLS is the dramatically reduced bunch length of 11 ps. This will enable standard pump-probe techniques on time scales relevant to most of the processes outlined above.*

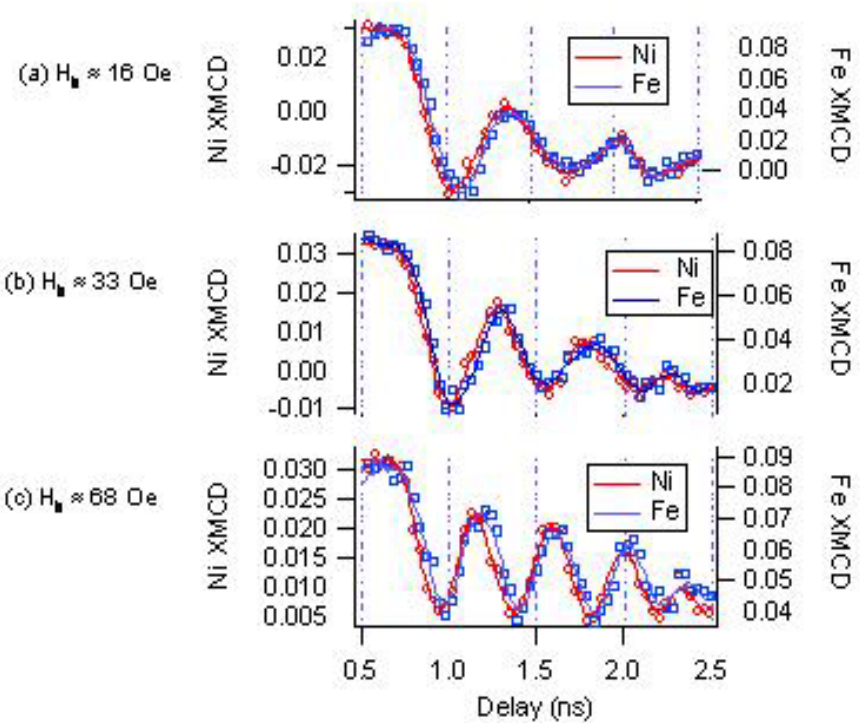

Figure 2.7.10 *Time-resolved X-ray magnetic circular dichroism (XMCD) study in reflection geometry of the relaxation of the magnetization of a 50 nm thick permalloy ($Ni_{80}Fe_{20}$ alloy) film after the application of a fast (~100 psec rise and fall time) magnetization pulse. The measurement was made using standard pump-probe architecture: a variable delay between the magnetization pulse and the photon bunches in the APS storage ring was used to track the horizontal component of the either the Ni (red) or Fe (blue) magnetic moment. After the magnetization pulse, the magnetic moments of the Ni and Fe precess coherently about the bias field (Hb) with decaying amplitude, in agreement with the Landau-Lifschitz-Gilbert theory of magnetization dynamics. The frequency of the precession increases with the bias field, as seen in panels (a), (b) and (c) [24].*

magnetization dynamics of a 50 nm thick permalloy ($Ni_{80}Fe_{20}$ alloy) film was measured with element specificity on a time scale of ~100 psec (Figure 2.2.10) [24]. This proof-of-concept experiment opens up new research areas that will directly address long-standing controversies such as the microscopic origin of ferromagnetic relaxation (e.g. valence exchange, slow relaxer, and fast relaxer models), the interplay between shape anisotropy and demagnetization fields and magnetization reversal mechanisms, and the influence of non-magnetic layers on the dynamical response of ferromagnetic materials. NSLS-II will greatly aid these efforts by providing more intense photon pulses with a time structure almost an order of magnitude shorter than current state-of-the-art storage rings.

Another major advantage of NSLS-II is the dramatic increase in brightness over existing soft X-ray sources. The brightness of the soft X-ray elliptically-polarized undulators will range from 10^{20} (photons/sec/0.1% BW/mm^2/mrad^2) at 200 eV (e.g., C K-edge) to $2x10^{21}$ at 2000 eV (Figure 3.3.3). This represents an increase over the ALS by a factor of 25 at 200 eV to a factor of 3000 at 2000 eV (Figure 3.3.4). This dramatically increased brightness will greatly improve the signal-to-noise ratio of time-resolved experiments. Additionally, it will maximize the data collection efficiency of time-resolved experiments that utilize low-duty cycle pulsers and lasers.

Finally, the soft X-ray insertion devices planned for NSLS-II will have the capability to manipulate the polarization state of the radiation incident on a sample. Switching the polarization between right and left circular polarization forms the basis of many XMCD experiments. Similarly, linearly polarized light will be variable from horizontal to vertical polarization; changes between these polarization states,

combined with appropriate sample geometry, can yield information on anti-ferromagnetic order, or changes in local symmetry due to lattice reconstructions such as the Jahn-Teller distortion in manganites. The soft X-ray range (200-2000 eV) is also particularly well suited to studies of transition metals (L-edges), rare-earths (M-edges) and C, N, O (K-edges). These are the most widely used elements in magnetic systems.

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2.8 Growth and Processing of Advanced Materials

2.8.1 Overview

One of the key scientific challenges in coming decades will be synthesis of advanced materials, ranging from single crystals to thin films and nanoscaled structures. It is clear that in-situ studies will play a central role in understanding synthesis routes and characterizing the samples produced.

Growth of thin films is a non-equilibrium phenomenon governed by a competition between kinetics and thermodynamics. Figure 2.8.1 schematically illustrates common themes that run through all thin film growth processes and methods. The properties of a large fraction of naturally and artificially grown materials depend in detail on the interface between the growing crystal and environment. An important challenge of characterizing growing systems in real time is the wide variation in density in which one finds growing crystal interfaces. It ranges from an ultra-high vacuum environment of less than 10^{-9} Torr through 24 Torr, the vapor pressure of water at room temperature, through to the densest, the liquid/crystal interface. The benefits of photons in the energy range that will be available at NSLS-II for characterizing these interfaces are well understood. The weak electron-photon interaction provides for a deeply penetrating technique that enables the in-situ study of many systems, including the study of many crystal growth systems in real time. The weak photon scattering cross section also results in data that can be interpreted quantitatively.

NSLS-II will take us beyond the study of static surfaces and make the study of dynamically evolving surfaces and interfaces, critical to understanding and optimizing the growth of materials, practical and

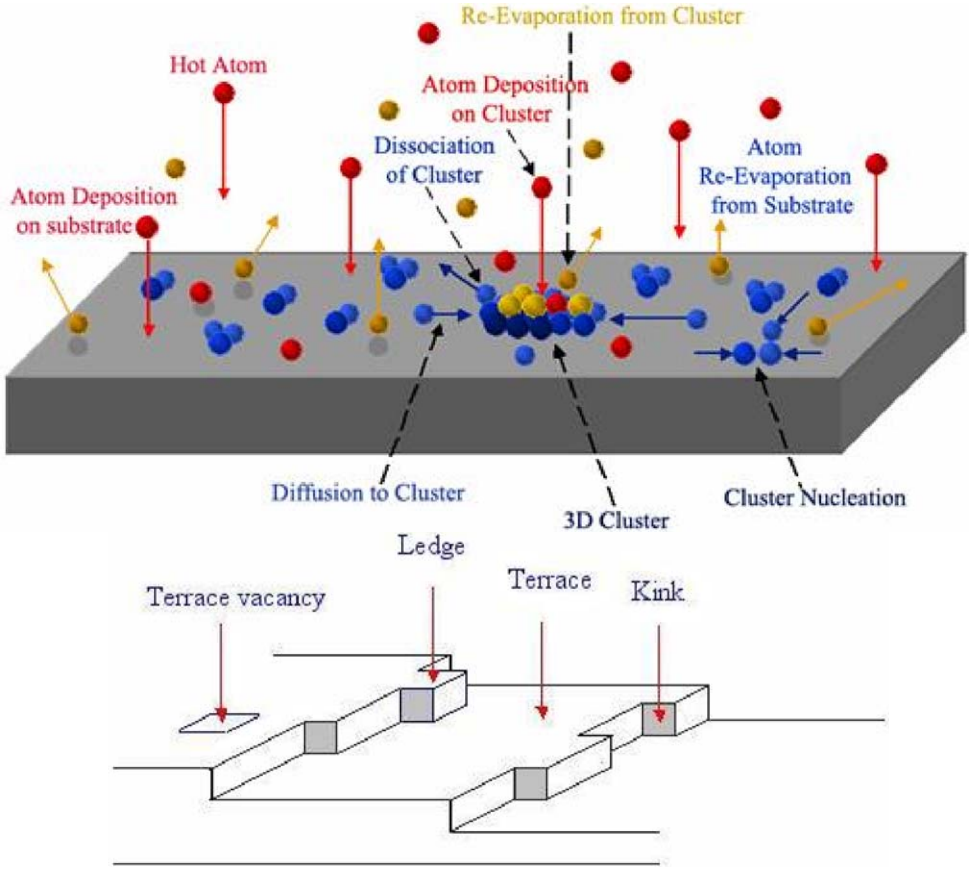

Figure 2.8.1 *In thin film growth, vapor atoms are continuously depositing on the surface. These deposited atoms migrate on the surface and interact with each other, forming 2D and 3D clusters, as well as attaching to the step edges. These interactions determine the morphology of the growing film.*

indeed routine. The challenges and opportunities of key materials growth methods are described in this section together with the significant impact that NSLS-II will have in characterizing, understanding, and ultimately tailoring those methods to produce advanced materials for a host of technological applications. In addition to pointing out the general benefits of NSLS-II, several new instruments that will become feasible with the high brightness of NSLS-II are also outlined.

2.8.2 Scientific Challenges and Opportunities

2.8.2.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a powerful technique for growing thin films from the vapor phase that has increased in importance over the last decade because of its flexibility and advantages for fabricating thin films of complex materials. In PLD, a high power pulsed laser beam is focused onto a target of the material to be grown. As a result, a plume of vaporized material (atoms, ions, molten droplets, and particulates) is emitted and then collected on a substrate to grow the film. Traditional materials systems for PLD are various complex oxides, such as high T_c superconductors and colossal magnetoresistance materials. However, materials of interest include semiconductors and even metallic films, which often require ultra-high vacuum conditions. PLD performed in ultra-high vacuum conditions is referred to as pulsed laser molecular beam epitaxy, or PL-MBE.

One great advantage of PLD is that multi-element materials are deposited with the same composition as the target material, thus greatly simplifying the deposition of thin films of complex materials. Additionally, since PLD is at the ultimate limit of non-equilibrium vapor deposition, metastable materials and nanoscale structures may be formed that are difficult or impossible to fabricate by other means. The laser plume contains energetic particles that may also promote smoothing of surface roughness (interfaces formed by PLD have been reported with < 1 Å RMS roughness in several cases).

Atomic diffusion on surfaces occurs on a picosecond time scale. However, surfaces may evolve on times scales of seconds, or even longer in many cases. PLD presents an interesting opportunity, since film growth is accomplished by bursts of particle flux (composed of atoms, ions and small clusters) that last only a few microseconds. The growth surface then continues to evolve until the next pulse arrives on the order of a second later. The time structure of the growth process thus spans six orders of magnitude.

Figure 2.8.2, shows an example of pulsed growth on a Cu (111) surface. A Kinetic Monte Carlo simulation was performed on a 100 by 100 atom surface at 300K. Instantaneous pulses of 0.1 ML are deposited, each followed by a 100 msec “relaxation”. The figure shows the time evolution after the fourth pulse on an initially flat surface. Upon instantaneous deposition, the surface is covered with many monomers and dimers composed of Cu atoms. Since individual atoms and dimers are highly mobile, they

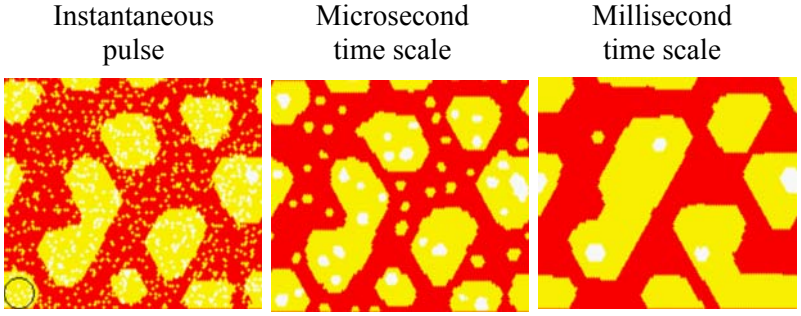

Figure 2.8.2 *Kinetic Monte Carlo simulation of pulsed growth on a Cu(111) surface. The three colors correspond to the initial surface and two incomplete monolayers of deposited copper. The images show that the relaxation of the surface after a deposition pulse spans many orders of magnitude in time. The ability to probe these effects in the time domain with NSLS-II will open up a new window on thin film growth and surface processes.*

rapidly coalesce into metastable 2D islands of 10-20 atoms. With time, the smaller islands are absorbed into larger islands on the surface. This dynamic process is then repeated during subsequent pulses.

Complex materials are thought to follow a pattern similar to the simple case of Cu (111). However, it has been widely speculated that there is an additional "assembly" step in which the elements composing the material aggregate into small units with the correct composition and then diffuse around to join up to step edges or large islands. The assembly process probably occurs only at very early time scales, and has thus far not been observed directly.

NSLS-II will be able to access the full range of time scales relevant to the process, down to sub-microseconds. This will allow access to a rich variety of transient phenomena that will be important for the control of thin film growth and ultimately for the fabrication of state of the art materials. The combination of the high intensity of NSLS-II with an area detector with large dynamic range and millisecond readout times will be crucial for the success of these experiments. The high brightness of NSLS-II will also enable new experiments, such as the study of surface evolution on short time scales with photon correlation spectroscopy.

2.8.2.2 Self-organized Nanoscale Features on Surfaces

Nanoscale features on surfaces can be obtained by sputter etching, strain effects, Stranski Krastanov growth, Volmer-Weber growth, or by phase separation. There is a great deal of interest in using these effects as the basic technology for the formation of "self-organized" structures that have useful properties. Examples include magnetic dots for thin-film recording media and semiconductor quantum dots. Studies of these effects are relevant to conventional in-situ growth studies, however the emphasis in this field is to create and control nanoscale features during growth and processing.

Figure 2.8.3 shows an example of a cobalt surface with 20-50 nm dots formed by ion erosion. The features formed are on a size scale appropriate for high-density magnetic recording media. Additional examples would include semiconductor quantum dots. In such cases, one would like to be able to locally map elemental composition, and strain distributions, either at the surface, or in a buried layer. Similar capabilities would also be required for a range of other materials such as phase separated GaInN layers, diluted magnetic semiconductors, complex oxides, and silicide layers.

NSLS-II will enable X-ray microscopies with 10 nm resolution or better, extending the uses of such techniques into the realm of surfaces and thin films. NSLS-II end station equipment for in-situ growth and processing will included facilities for surface diffraction and grazing angle small angle scattering to take advantage of scattering experiments requiring high flux. To conveniently study nanoscale surface

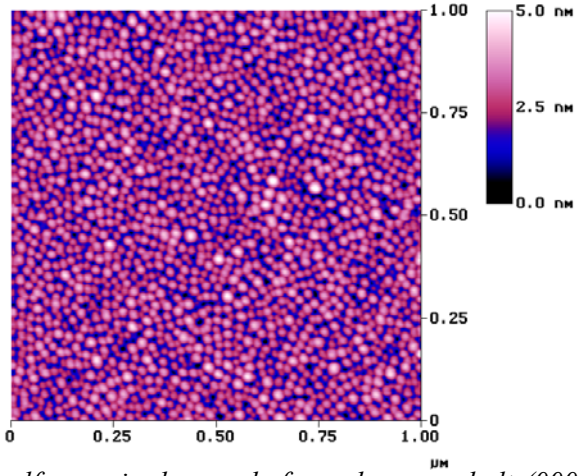

Figure 2.8.3 *AFM image of self-organized mounds formed on a cobalt (0001) surface by 500 eV Ar+ sputter etching. Similar methods can be used to form nanometer scale quantum dots on surfaces.*

features, they will also incorporate complementary microbeam capabilities, facilitating in-situ imaging on length scales of 10 nm or less.

This new capability will address one of the weaknesses of conventional X-ray scattering where fine-scale real space structures are only determined on average, and only in reciprocal space. The very high brightness of NSLS-II will allow the use of local area diffraction or fluorescence mapping, and methods based on back transformation from reciprocal space to obtain nm-scale real-space structural information in non-periodic systems (see Section 2.4.3.2.1). The ability to perform such experiments in-situ will greatly enhance the usefulness of beamline-based growth facilities. Rather than being dependent on the ex-situ analysis of real-space microscopies such as AFM and TEM, the facilities of NSLS-II will approach the ideal of self-contained laboratories for the development of new thin film materials. The high brightness of NSLS-II will enable real-time measurements with many of these techniques and make it possible to study thin film growth, etching, or annealing, as they occur using microbeam-based probes. The natural time scale of these processes is typically ~1 second, except for PLD discussed above.

2.8.2.3 MBE Growth

Molecular beam epitaxy continues to be a powerful growth technique, particularly for compound semiconductors. Because of its importance, the structure of growth surfaces has been investigated with a number of techniques, each with its own strengths and weaknesses, and much has been learned.

Important information on film microstructure and interface structure has come from careful examination of grown films using transmission electron microscopy (TEM). Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) provide vital information about surface morphology and, in the case of STM, atomic reconstruction. While these can be performed in situ, immediately after deposition and without breaking sample vacuum, they typically require that the sample be cooled to room temperature (versus a growth temperature of order 500-800° C) and cannot easily be used in real time, as the material is deposited. Yet it is known that there is often a significant change in surface reconstruction upon cooling. Moreover, contamination, if present, can fundamentally alter the reconstruction once the growth process is stopped. Finally, scanning probe techniques provide only very limited information about the subsurface structure. Disordered layers often exist on surfaces during growth, particularly in the case of growth with Indium. In addition, ordered reconstructions can sometimes have domain boundaries that move around faster than they can be followed by STM. Thus the STM provides only a time-average of the surface structure, not a snapshot. Finally, while careful AFM and STM experiments can provide important information about step motion on larger length and time scales, they don't provide direct information about the dynamics of atoms on the surface during growth on subsecond or second time scales. Typical atom migration times to steps are on this order.

In-situ RHEED is widely used as a real-time diagnostic tool during growth, and it can provide some important quantitative information, in addition to more qualitative information about surface reconstruction symmetry and flatness. However, dynamical scattering effects can limit its quantitative interpretation. It is not generally used to determine the atomic positions in surface reconstructions, relaxations beneath the surface, or quantitative details of surface step morphology.

NSLS-II will enable investigation of the following important issues.

Influence and structure of nucleation: Often a nucleation layer is used to initiate growth, particularly during heteroepitaxy. A detailed understanding of nucleation layer structure and its immediate influence on subsequent growth is often lacking.

Surface morphology and step dynamics during growth: The dynamics of atomic motion on surfaces during growth plays a key role in film growth. Step bunching on the evolving surface can be examined by following transverse lineshapes of X-ray scattering truncation rods. GISAXS measurements can track the evolving lateral correlations of the height, both parallel to and perpendicular to the overall direction of substrate miscut. Important information can come from systematic studies of the time evolution of the X-ray signal at the anti-Bragg position following a sudden stop in the flux of deposited atoms [1-4]. Typically an initial rapid (probably millisecond) change in the diffracted signal appears following the

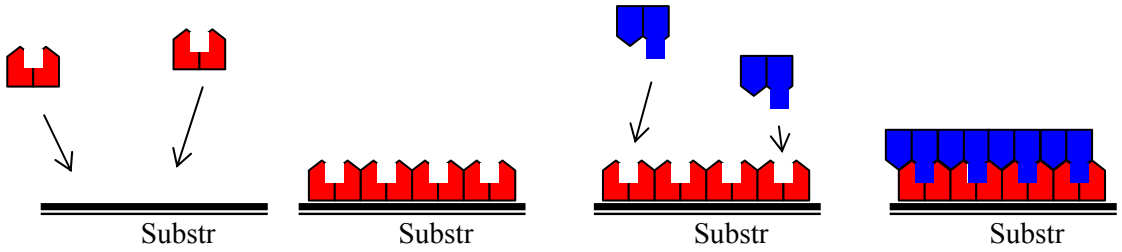

Figure 2.8.4 *Schematic of ALD process. The surface is repeatedly exposed to alternating molecular precursor species (here symbolized by red and blue), typically for approximately 1 sec each. The deposition of each species is self-limiting. A purge and/or carrier gas (not shown) is also typically utilized.*

sudden stop, believed to be due to the initial movement of atoms to lattice positions following deposition. There is a much slower (of order 10 sec) relaxation of atoms onto energetically favorable surface step positions. In layer-by-layer growth, where RHEED and anti-Bragg X-ray oscillations can be observed, the relaxation process varies systematically throughout a single layer deposition process.

Surface reconstruction: STM and RHEED observations cannot directly confirm the vertical structure of the top layers or adlayers. X-ray diffraction scans along the surface diffraction rods are very sensitive to the surface structure since the scattering from the surface layers interferes with the rod scattering coming from the truncated bulk crystal. This technique can be sensitive to the presence of laterally disordered adlayers that do not appear in RHEED patterns. The width of reconstruction peaks can be examined to better understand the evolution of the lateral correlation lengths at the surface.

Strain: Due to the differences in atomic sizes, the strain state of films can play a major role in determining whether the films grow uniformly and with low defect densities. Small strains near the surface will be easily investigated with surface-sensitive X-ray scattering.

Incorporation of Alloy Components: The incorporation kinetics of ternary components into III-V structures can be quite complex, with given elements often acting as a surfactant. X-ray scattering can be used to investigate surface segregation.

Evolution of Surface Structure during Quantum Well Growth: Although quantum wells form an important component of opto-electronic devices, little is known about how the surface morphology and step structure evolve when there is a sudden change in composition. This can be investigated with real-time X-ray scattering.

2.8.2.4 Atomic Layer Deposition

Atomic layer deposition (ALD), a chemically self limiting process, first developed in the 1970's by Suntola [5], is in some aspects similar to chemical vapor deposition (CVD) in that it utilizes chemical reactions between precursor molecules to deposit new material. However, unlike CVD processes, precursor species are introduced individually, in a pulsed mode, as shown schematically in Figure 2.8.4. In conjunction with the proper chemistry limiting the adsorption to a single layer of the reactant molecules, this results in a highly controlled process with inherently atomic-layer resolution.

Typically the beginning of the deposition process, i.e. the nucleation of the film on the substrate, can have rather different kinetics than the subsequent growth. Several layers are often deposited before the film thickness becomes linear in the number of deposition cycles.

Initially, the inherently low growth rates of the technique made it commercially unattractive relative to CVD or physical vapor deposition (PVD) techniques such as sputter, thermal or e-beam deposition. However, with the continued evolution of fabricated structures into the nano-regime, the layer-by-layer growth method characteristic of ALD has come to be seen as a significant advantage. Whereas CVD and PVD rely on precise and uniform control of deposition rate (determined by geometry, temperature and chemical fluxes) and exposure time to determine deposited thickness, ALD is inherently much more forgiving because of its self-limiting nature. Moreover, it can typically operate at significantly lower

temperatures, decreasing unwanted diffusion or thermal degradation of the substrate material. ALD also has excellent conformality in nanostructures with high aspect ratios, much better than PVD or CVD.

Many systems have been grown with ALD, including compound and elemental semiconductors, metals, and ceramics. It is increasingly being used for the creation of nanolaminates on particles [6]. It is also now on the International Technology Roadmap for Semiconductors [7] because of future needs for precise nanoscale deposition of high-k dielectrics, diffusion barriers, and electrodes [8].

In traditional ALD the activation energy for precursor adsorption and reaction comes from the thermal background. To decouple reaction kinetics from substrate temperature, and hence avoid sample damage arising from higher temperatures, plasma-enhanced ALD (PE-ALD) is becoming increasingly important. The use of plasmas to excite molecular hydrogen for the chemical reduction of metal precursors on the sample surface has been particularly promising [9].

Although ALD promises to be important across a spectrum of nanotechnology applications, there are many questions about the detailed processes underlying its success. Chemical species present in the adsorbed molecular film that is a precursor to the adlayer formation have been investigated with infrared spectroscopy. Film thickness has also been monitored in real time using quartz microbalances and optical ellipsometry. The typical pressures of 10^{-3} to 10^{-1} Torr present during the ALD growth process, however, complicate the application of many traditional surface science techniques, particularly those using electrons. In some cases, differential pumping has allowed the use of Auger spectroscopy to examine surface chemical composition. However, none of these techniques offers the ability to examine in real time the detailed atomic and nanometer structure of the growing films, the adsorbed molecular layers or the interface between them.

NSLS-II will enable detailed investigation of the structural evolution of ALD films during both their initial nucleation phase and during their steady state growth phase. Moreover, the millisecond or better time resolution achievable in many of the X-ray techniques will allow examination of the surface evolution as the layer of precursor molecules is adsorbed and/or reacts.

Key issues that will be accessible to such studies at NSLS-II include the following.

Structure of adsorbed gas layer: The ALD process typically begins with the self-limiting adsorption of a monolayer of reactant molecules. To what extent is this layer crystalline or amorphous? In-plane X-ray diffraction can be used to examine this question. With the high brightness of NSLS-II, one can monitor with millisecond time resolution, the structural quality of the adsorbed gas layer changes during the adsorption process itself. Where are the atoms relative to the substrate? During the beginning of the nucleation phase, X-ray standing wave fluorescence can be used to identify the vertical position of medium- and high-Z atoms in the adsorbed layer relative to the substrate surface. SEXAFS can also be used to provide information on the local directional chemical environment around these atoms.

Adsorption and reaction processes: Are these processes spatially homogeneous or heterogeneous on the surface? Do the absorption and reaction processes begin at definite points on the surface (e.g. at step edges) and then propagate laterally along the film surface, or do they happen relatively randomly as gas atoms hit the surface? If the processes are heterogeneous, the resulting variations in atomic structure will lead to electron density variations on the appropriate length scales (probably tens of nanometers) during precursor deposition/reaction. The evolution of the surface inhomogeneity can then be followed in detail with GISAXS or nanoimaging.

Composition of adsorbed gas layer(s): Using X-ray reflectivity, the total electron density profile of the adsorbed layer can be measured. With appropriate modeling, this tells much about the distribution of atoms above the existing film/substrate.

Surface morphology: As mentioned above, ALD often leads to relatively rough surfaces. X-ray reflectivity can be analyzed with well-defined approaches to understand the evolution of root-mean square surface and interface roughness. Examination of crystal truncation rods from the substrate also gives information about the interface width. In addition, the lateral size scale of the developing morphologies can be examined with GISAXS or nanoimaging.

2.8.2.5 MOCVD of AlGaN for Energy Conserving Solid-State Lighting

The metallo-organic chemical vapor deposition (MOCVD) technique has been applied to the growth of quaternary compounds such as AlGaAsP materials. These materials have composition dependent band gaps and lattice parameters that have found many uses in the telecommunications industry as well as other areas. The future challenge for MOCVD growth will be application of these techniques to other wide band gap materials.

Light-emitting-diodes (LEDs) made from aluminum containing epitaxial materials offer tremendous breakthrough potential for 21st century technologies including solid-state lighting and biophotonics. Of the $50 billion annual production of electricity, fully 20% is used for lighting; even modest improvements in efficiency will have great environmental impact. Solid-state lighting has been identified as a national technology priority because of its impact on the nation's energy reserve, economy and environment. The steady improvement in performance of solid-state lighting is shown in Figure 2.8.5.

Specifically, large bandgap aluminum gallium nitride (AlGaN) alloys permit absorption and high intensity emission of light in the deep blue and UV wavelength ranges enabling development and widespread utilization of energy and cost efficient red-green-blue (RGB) solid-state white lighting technologies.

MOCVD growth of gallium nitride (GaN) has been partially successful. It is the introduction of Al to GaN, however, that permits the manufacture of deep blue and UV wavelength LEDs needed for solid-state, white-lighting and biophotonics applications. However, the application of the older AlGa phosphide MOCVD methods appears not to be successful for the higher processing temperatures required for the wider band gap AlGaN materials. MOCVD depends on a complex interaction between the diffusive and convective heat and mass transport and the chemical reactions at the growing interface and in the growth chamber. Depending on the details of the reactor system, heat transport in the solid reactor walls can influence the deposition process significantly. What limits the AlGaN technologies is the inability to predict and control fluid and thermal instabilities associated with AlGaN MOCVD. Such instabilities lead to non-homogeneous residual stress distributions, spiral shaped thickness variations of the thin film and formation of ~10 nm sized Al particles within the gaseous phase. The challenge is to find new techniques

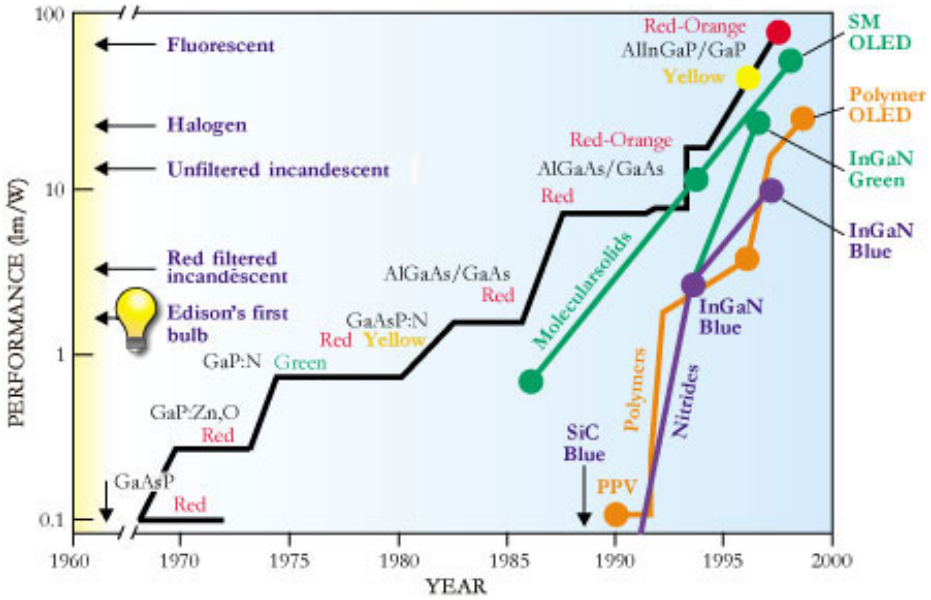

Figure 2.8.5 *Solid state lighting performance has increased dramatically in recent years and has the potential to make an enormous impact in reducing the nation's energy consumption. NSLS-II will contribute to further advances by enabling new techniques for understanding and optimizing methods of growing advanced materials [10].*

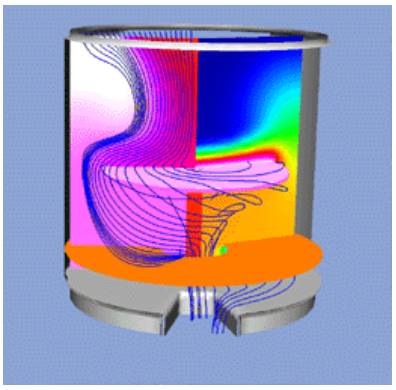

Figure 2.8.6 *Simulation of gas flow in an MOCVD reactor [11].*

that can be applied to the analysis of the gas phase, and in particular assess what is controlling the gas phase nucleation of Al particles. Neither the particulate densities, nor the size distributions have been well characterized in the high-pressure 1000^{o} C processing environment.

Application of the high brightness of NSLS-II in scanning this environment will provide vital information on the thermal/fluid stability issues associated with MOCVD AlGaN wafer production. Figure 2.8.6 shows a simulation of the gas flow in such a reactor. The lines are traces of the reactant flows incident onto a rotating sample disk as in commercially available reactors. Using the high brightness of NSLS-II together with nanometer tracer particles and fluorescence techniques, the simulations can be tested and growth conditions optimized. Using EXAFS techniques in the gas phase one can obtain spatial profile information on the chemical state. This will be in addition to the real time imaging of the growing interface and crystal structure. Clearly, NSLS-II will make substantial contributions to this problem.

2.8.2.6 Thin Film Organic Crystal Growth

The electrical properties of organic field effect transistors depend on many parameters and in particular, on the properties of the organic single crystalline film. High quality single crystal films are required to characterize the transport properties. Organic molecules are bonded by weak Van der Waals interactions and therefore unfortunately can form many polymorphic crystal structures. Understanding what crystal growth parameters favor one polymorph over another would be an important step forward. Furthermore, some of these polymorphs undergo phase transitions, upon cooling from the growth temperature to room temperature, further complicating the situation. The experimental path forward that is most likely to succeed is to observe in situ the structure during crystal growth, during the subsequent cool down, through to fabrication of electronic devices. The issues here are similar to those for MOCVD. Figure 2.8.7 shows on the left a typical growth chamber, and on the right a typical crystal. Such studies will be possible with NSLS-II and will have large impact on technology of organic field effect transistors as well as on the basic understanding of the electrical transport in this class of materials

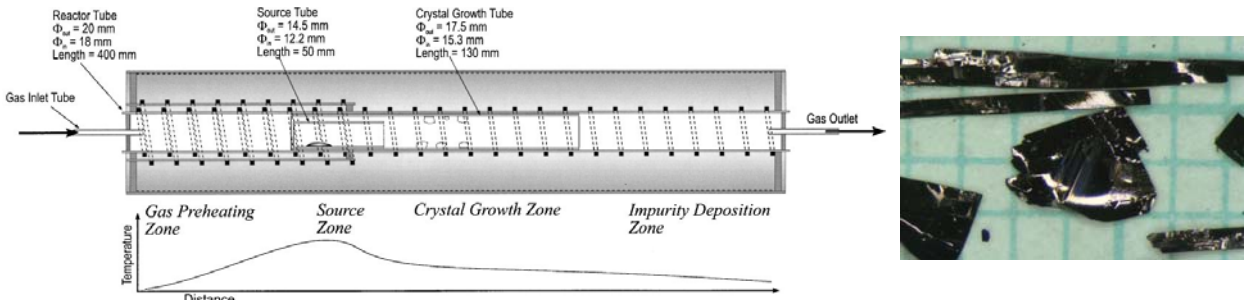

Figure 2.8.7 *Left: Chamber for growing thin film organic crystals. Right: Typical organic crystal [12].*

2.8.2.7 Growth in Fluids

In addition to better time resolution, more intense synchrotron beams will facilitate the study of growth and phase transformations in contact with dense fluids. While scattering studies have already been carried out on samples in aqueous environments, the significant absorption of water at moderate X-ray energies (~ 10 keV) imposes significant limitations on the maximum fluid layer thickness that can be used in an X-ray experiment. In addition to absorption by the fluid itself, in some cases the samples may be contained in pressure cells or other vessels that contribute significantly to the absorption.

Physical systems of interest include heteroepitaxial growth from solution, solidification from the melt, the deposition of polymers from solution, the deposition of metals in supercritical liquids, the electrodeposition of layer structures, and biomineralization. Processes such as these are of great fundamental and technological importance; many are likely to be crucial in the development of novel, low-cost, or environmentally-sound methods. On the whole, given their occurrence in relatively inaccessible (dense, high-pressure, or chemically reactive) fluids, structural studies of such processes have been performed ex situ. With the availability of the high flux, penetrating synchrotron beams of NSLS-II, studies of samples in dense fluids will become as routine as current studies of samples in vacuum or relatively low pressure gas environments.

2.8.3 Impact of NSLS-II

Due to the inadequate spatial resolution and low signal rates, there is essentially no full field imaging of surfaces and interfaces performed at second generation sources with the elastic photon in/photon out channel. Inelastic channel imaging methods, such as the photon in/electron out of PEEM, that take advantage of well developed electron imaging optics, can be performed at second generation sources, but this method does not have the penetrating capability of the 2-30 keV photon in/photon out methods. The high brightness of NSLS-II together with improvements in X-ray optics will enable real time X-ray microscopy studies of growing surfaces.

To study thin film growth, it would be useful to simultaneously and in real time perform imaging and diffraction characterization of a growing surface. Two key quality factors for advanced materials growth are the perfection of the crystalline lattice, and the morphology. Electron microscopy techniques can both image the surface morphology and diffract from the underlying lattice, but these methods are generally incompatible with most interesting growth conditions. A new microscope for the study of thin film growth will be enabled by the high brightness of NSLS-II. This microscope will be integrated with a variety of growth chambers and will run in two modes; a full field reflectance microscope, and a high spatial resolution scanning reflectance microscope.

2.8.3.1 Full Field Reflectance X-ray Microscopy

For the full field mode of the proposed instrument, one can image the morphology of the growing interface in real time, and simultaneously collect the large-angle diffracted beams from the growing crystal. A focused beam is incident onto a growing crystal interface in a crystal growth chamber, with two coexisting downstream detector types, as shown in Figure 2.8.8. The first detector will be a phase preserving, imaging quality optic for hard X-ray photons, configured with a high resolution area detector, to obtain an image with substantial magnification. The second type of detector will be a set of large area detectors to collect the large angle diffracted beams from the lattice. The incident beam focusing optics are at, or near, the 1:1 point to minimize the divergence. The downstream imaging optics and area detectors can coexist because the numerical aperture of the imaging optics is small; even for 10 nm resolution at a wavelength of 0.1 nm the numerical aperture is of order 10^{-2} radians. To enhance sensitivity to the surface, one can orient the incident beam to a fraction of the grazing incidence angle,

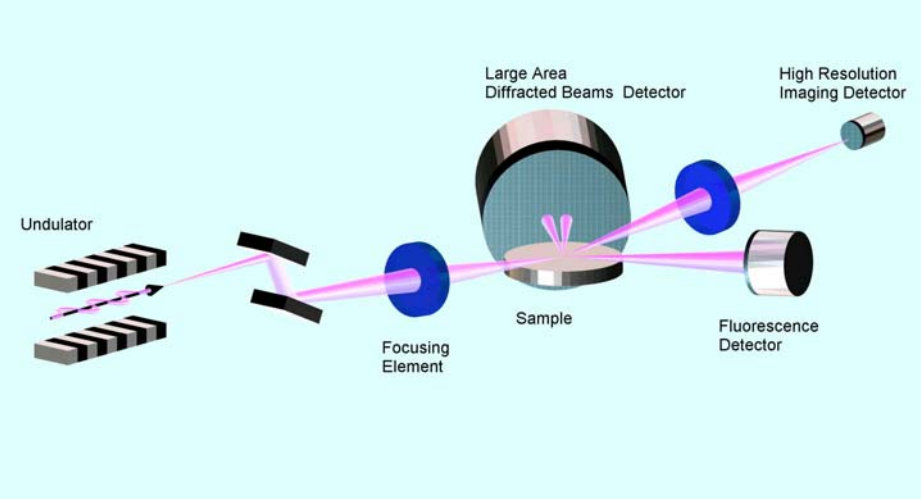

Figure 2.8.8 *Schematic illustration of optics of new microscopy techniques enabled by NSLS-II.*

thus limiting the depth penetrated by the incident flux. Thus, one can simultaneously image the morphology of the growing interface and collect the wider angle diffracted beams that are sensitive to the crystalline lattice, all while under typical growth conditions. This tool can be thought of as analogous to an optical full field microscope, combined with a Reflecting High Energy Electron Diffraction (RHEED) or Grazing Incidence Small Angle X-ray Scattering (GISAXS) for the diffraction pattern.

2.8.3.2 Scanning Reflectance X-ray Microscopy

The scanning reflectance X-ray microscope (SRXM) uses upstream optics to highly demagnify the incident beam and then raster it across the sample while monitoring the diffraction pattern, the fluorescence yield and the reflected intensity. The SXRM is the reflection hard X-ray analog of the transmission type microscopes, for example the electron based STEM, or the soft X-ray based STXM. The small focal spot enables selection of specific features from the heterogeneous features on growing surfaces, such as nano-sized clusters of atoms, growth facets and terraces. For example, for a surface in the step-flow growth mode, one can imagine measuring the time averaged step edge atomic structure, at growth temperature and pressure, to understand how an adatom incorporates into the crystal.

The SRXM requires the high brightness of NSLS-II, and maximizes the sample flux density and hence sensitivity. The ability to convert from a full field view to a scanned spot view of the same area with high spatial resolution will have great practical benefits. The high brightness of NSLS-II will enable it to efficiently achieve spot sizes of 10 nm or less and makes it the ideal source for an SRXM instrument.

2.8.3.3 Oversampling Methods for Surfaces and Interfaces

While there are many existing methods for determining surface crystal structure, a novel and model independent method that is rapidly developing is based on oversampling methods and holds great promise for real time monitoring of growth. A great deal of progress has been made in understanding the nature of molecular adsorption on surfaces by examining highly ordered, reconstructed configurations. These low-energy configurations have then been used to make inferences regarding the typical pathways that occur during departure from equilibrium conditions. For example, CVD growth of an epitaxial layer, which is manifestly a non-equilibrium situation, undoubtedly proceeds by occupation of quasi-equilibrium adsorption sites by diffusing and decomposing surface species. Although knowledge of preferred reaction paths and typical binding sites can aid a great deal in interpreting non-equilibrium structures, the lack of order inherent in such situations greatly compounds the difficulty of measuring their atomic positions. The advent of the scanning tunneling microscope (STM) provided a localized picture of these structures

for a number of favorable cases. However, a STM is a serial instrument, has limited scan rates, cannot operate in all environments, probes only a fraction of the growing surface, and can typically resolve only the outer atoms of the adsorbed molecule. An X-ray based tool is needed that can probe atomic positions within the decomposing molecule as well as determine their locations on surfaces of disordered materials in real time.

The well-known phase problem in crystallography precludes a direct inversion of scattering data. It is necessary to know the phases of the scattered beams to directly determine atomic locations by a simple Fourier transform. However, in favorable cases, scientists have been able to overcome this limitation by oversampling the scattering data (and by using auxiliary information) to assign phases to the scattering data. For the case of surface or interface X-ray diffraction, a continuous intensity distribution is found normal to the surface of a single crystal due to the non-periodicity imposed by the truncation of the crystal (i.e., the crystal truncation rods, or CTR). Recently, it has been shown that by oversampling this distribution, the phase of the scattered intensities can be reliably recovered. This allows a direct inversion showing atomic locations that are occupied in a surface reconstruction.

With present sources, this kind of analysis is limited to well-ordered surfaces. However, surfaces that show limited order, such as molecular precursors and/or reaction products that are adsorbed in preferred sites, could be addressed with the high brightness of NSLS-II. If the adsorbate molecule shows fairly good long-range order, as might be expected for species with an attractive adsorbate-adsorbate interaction, the atomic binding site and internal configuration of the molecular species could be determined. The oversampling would take place along the Bragg CTR rods from the substrate, as has been already demonstrated for the case of well-ordered substrates. However, the signal would be weaker, owing to the imperfect ordering of the adsorbate, necessitating a more intense X-ray source. This powerful application will shed new light on the growth process.

An even more exciting application is the case of fast-decomposing molecular precursors that do not exhibit significant long-range order. This is closer to the situation encountered in actual CVD growth conditions. It is likely that such species occupy a preferred lattice site, but decompose before any adsorbate-adsorbate interactions can foster long-range order. In this case, the lack of long-range order would prevent the use of the methods discussed above, because the overlap of the signal from the adsorbate layer and the Bragg CTR rods would be small. Instead, the diffuse X-ray scattering from the disordered adsorbate layer itself would be exploited, enabling a direct determination of the atomic configuration of adsorbed species. Determination of the structure of metastable species could also be made with suitable growth apparatus. A pulsed beam of precursors could easily be synchronized with the data collection. With an intense X-ray beam, the diffuse signal could be sampled at a particular time after the arrival of the gaseous pulse. If required, statistics could be built up over multiple arriving pulses, but advances in detectors such as those outlined in Section 4.4 could allow a single diffraction pattern to provide a "snapshot" of the surface at a given time.

Finally, we mention the possibility of inverting the data in real time to provide continuous visualization of the species on the growing surface. This advance would require the development of suitable fast area detectors, which is vital to the refinement of many other scattering techniques. Such detectors could record the entire diffuse scattering signal from an overlayer in a single frame. The algorithms currently available can invert a set of CTR data in tens of seconds on a modest workstation or high-end PC. With improved computing power and development of more efficient algorithms, it is reasonable to expect that in ten year's time, such inversions to take less than 100 ms. In concert, it is feasible that diffuse patterns could be recorded and interpreted almost instantaneously, giving the operator of a CVD reactor real-time insight into the growth process.

2.8.3.4 Powder Diffraction

From advanced structural ceramics to catalysts, from semiconductor technology to the frontiers of biology, and from new magnetic materials and devices to framework compounds used to sequester radioactive waste, crystallography plays a crucial role in our understanding of materials. It is apparent that

the ability of crystallographic techniques to handle smaller samples and more complicated structures has been an important driving force in many areas of science and technology. The distinction between single crystal and powder diffraction measurements is blurring, both as it becomes possible to perform single crystal measurements on samples that are the order of the grains in a powder, and as powder techniques evolve to handle problems of great complexity. NSLS-II presents important opportunities to continue this advance.

For non-protein crystals (unit cell dimensions in the range of 10 to 30 Å), the current state of the art to collect a full diffraction dataset with CCD or imaging plate detection and focused synchrotron beams, is a sample volume on the order of 100 μm^3, generally limited by the ability to mount and handle small samples and maintain reasonable signal to background ratios. Even if one can collect diffraction data from a sample of that size, there are issues of interpretation. Several groups are developing the software and techniques to handle diffraction data sets from a sample consisting of a few crystalline grains in the illuminated X-ray beam, on a transparent backing such as a thin silicon nitride film. One could collect quasi-3D diffraction data by tuning the X-ray energy during data collection so that several thick slices of reciprocal space are sampled, without the need to rotate the sample (and thereby avoid parallax effects of grains translating in and out of the beam). With a very bright X-ray beam provided by NSLS-II and sample grains mounted on transparent film, data will be collected to very large momentum transfers, needed for pair distribution analysis of disorder and deviations from the average crystal structure.

There is growing recognition that it is useful to simultaneously measure physical properties and atomic structure, or to measure the structure of a system under some form of external perturbation. For example, in single crystal work done at NSLS beamline X3A, application of a poling electric field to a nonlinear optical material (2-methyl-4-nitroaniline) rotated the molecule by 0.0045(5) degrees and translated it by 0.0019(3) angstrom [13]. Such precisions could never be achieved by comparing, e.g., a poled with an unpoled crystal; instead they depend on the application of an external field during measurement.

NSLS-II will enable implementation of a beamline optimized *both* for physical property measurements *and* for the determination of accurate and precise crystallographic structures, both for single crystal and for polycrystalline samples. Whole new classes of experiments can be envisioned: As batteries discharge what short-range order-disorder results? What are the changes in fuel cell electrolytes and electrodes under real operating conditions (1000° C) as oxygen site occupancies adjust? The construction of cells suitable for *simultaneous* measurement of potential, resistivity, current and scattering are required to address important questions. These cells will give rise to parasitic scattering and so beamline components, including optics, slits etc will need to be optimized for these “real world” experiments.

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2.9 Catalysis and Energy Science

2.9.1 Overview

Catalysis provides a means of changing the rates at which chemical bonds are formed and broken and of controlling the yields of chemical reactions to increase the amounts of desirable products from these reactions and reduce the amounts of undesirable ones. As a result, catalysis is at the heart of the petroleum, chemical, food, and pharmaceutical industries. Today, approximately one third of the U.S. gross national product in materials involves a catalytic process somewhere in the production chain. The proportion of processes using catalysts in the chemical industry is 80% and increasing [1].

Catalysis also plays a crucial role in pollution control and alternative energy technologies. Stabilizing CO_2 emissions is of paramount importance. In the 20^{th} century, power consumption increased 16-fold [2]. The concentration of atmospheric CO_2 increased from 275 to 370 ppm and at the current rate of increase will reach ~550 ppm this century. Climate models and paleoclimate data indicate that this could produce global warming comparable in magnitude but opposite in sign to that of the last Ice Age [3]. Power consumption today is ~12 TW, 85 % of which is based on fossil fuels. To stabilize at 550, 450 or 350 ppm atmospheric CO_2 concentrations requires CO_2 emission-free power by mid-century of 15, 25, or 30 TW [4], respectively. The decarbonization of fuels alone will not be able to mitigate global warming. The combined use of fossil fuels from which carbon has been sequestered, solar and wind power, biomass, and nuclear fusion and fission, in combination with efficiency improvements, hydrogen production, storage and transport, and superconducting electricity grids, is necessary. A broad range of research and development in catalysis and energy science is necessary now to create technological options that permit both climate stabilization and sustained economic development.

Catalysis and energy science represent perhaps the ultimate challenge for characterization, with reactions occurring at specific atomic sites in a complex system, on short time scales, and at high temperatures and pressures. Detailed characterization requires imaging combined with spectroscopic measurements to reveal how atomic and electronic structures change during operation and as a function of reaction conditions. For a working catalyst, the elevated pressure and temperature conditions that are typically necessary are often not readily compatible with the probing and detection schemes.

Synchrotron radiation facilities provide unique and powerful tools for characterizing the temporal and spatial evolution of working catalysts [5]. The structure of catalysts, both crystalline and amorphous, and their microstructure, texture, porosity, domain size distribution, defects, etc., can all be studied by X-ray powder and/or single-crystal diffraction, small-angle X-ray scattering, and X-ray microprobe techniques. Information regarding the valence-band and core-level electronic structure of catalysts and adsorbates can be obtained using X-ray Emission Spectroscopy (XES), Ultra-violet Photoelectron Spectroscopy (UPS), and X-ray Photoelectron Spectroscopy (XPS), and that measured data can be compared with first principles electronic structures calculations. A variety of soft and hard X-ray absorption spectroscopies, including Extended X-ray Absorption Fine Structure (EXAFS), and X-ray Absorption Near Edge Structure (XANES), can be used to study the element-specific and symmetry-projected conduction band electronic and geometric structure of catalysts and adsorbates. Vibrational modes of adsorbate-substrate interactions and rotational tunneling of molecules can be studied by IR absorption spectroscopy.

The high brightness and flux of NSLS-II is essential to enable these tools to be applied with the high spatial, energy, and time resolution necessary to fully characterize these complex systems.

2.9.2 Scientific Challenges and Opportunities

2.9.2.1 Nanocatalysis

The Grand Challenge for catalysis science in the 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity. Through a combination of experiment and theory, a fundamental atomic-scale and nanoscale understanding of catalysis must be developed. The ability to control and manipulate atoms using nanotechnology portends major breakthroughs in catalysis. Since catalytic processes are largely controlled by local phenomena, changes in local electronic and physical structure brought about by tunable 'nanostructuring' can alter the physical and chemical properties of catalytic systems and powerfully impact their heterogeneous chemistry. The ability to synthesize, and structurally and kinetically characterize, unique and well-defined nanostructured materials presents an opportunity for theoretical and experimental catalysis investigators to progress towards the compelling goal of tunable catalyst design from first principles.

The essence of nanocatalysis can be highlighted by gold's size-dependent reactivity. Although gold is the least reactive of all metals, it nevertheless becomes a catalyst for the oxidation of CO to CO_2 when deposited as nanoparticles on certain surfaces, such as TiO_2 (Figure 2.9.1). Competing theoretical models suggest that either the substrate-nanoparticle interaction provides highly reactive oxygen atoms or that the inherent "step edges" of nanoparticles provide more reactive sites. Measurements of the static and dynamic physical and electron structure, as can be provided by real space imaging methods, are necessary to resolve these questions.

As another example, nanostructured oxides introduce tunable properties—multiple valences, structural variations, phase diagrams, electronic structure, acid-base and redox functionalities—that, in principle, can be controlled and manipulated through catalyst design. There is also diversity at the surfaces of these materials—ionic to covalent behavior, acidic to basic nature, defect structures, and

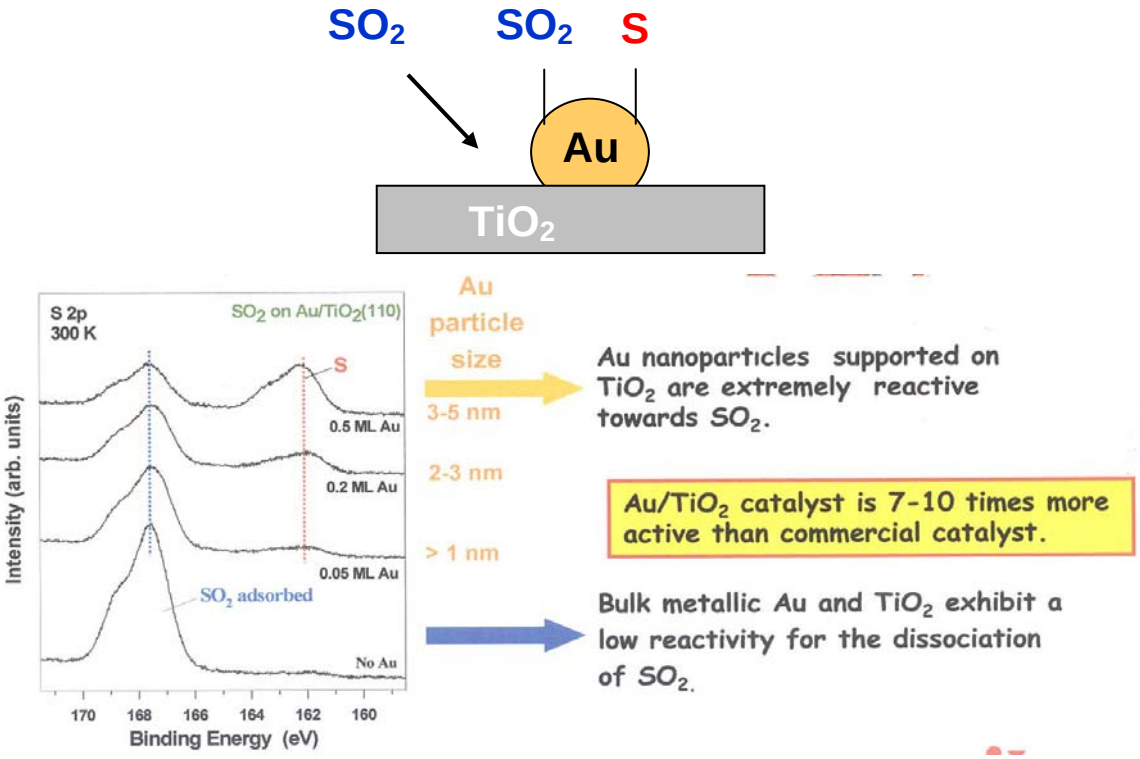

Figure 2.9.1 *Nanocatalytic effect of Au particles supported on TiO_2 as evidenced by the reduction of SO_2 to S as a function of particle size.*

oxidative to reductive chemistry.

Understanding of interaction of oxygen, carbon and sulfur with single-crystal surfaces on the nanoscale with sub-second temporal resolution will fill in existing gaps in our understanding of surface chemical transformations. The opportunity to follow simultaneously the evolution of the surface structure, the rate of its growth, the rate of its transformation in presence of reactants, and its thermal and temporal stability will be enormously important for the description and understanding of the kinetics and dynamics of processes occurring on the catalyst surface.

Combining nano and molecular science, synthetic chemists working with catalysis and materials scientists will develop new nanocatalysts based on many different strategies, with the ultimate goal being engineered nanostructured assemblies. One can envision using self-assembly to produce functional microstructures in bound, ready-to-use, form incorporating selective barriers, with engineered porosity and distribution of active sites.

2.9.2.2 Hydrogen Storage

The search for materials with high hydrogen storage per unit volume and weight is a very active research area being pursued worldwide. In his January 2003 State of the Union Address, President Bush announced the Hydrogen Fuel Initiative "so that America can lead the world in developing clean, hydrogen-powered automobiles." Hydrogen storage technology is the bottleneck to carry enough hydrogen on-board a vehicle to provide a 300-mile range. The Department of Energy has issued a Grand Challenge to the scientific community to develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications. The goals are to develop and verify on-board hydrogen storage systems achieving 4.5, 6, and 9 wt% hydrogen storage by 2005, 2010, and 2015, respectively. These technical targets were established through the FreedomCAR partnership between DOE and the U.S. Council for Automotive Research. No existing technology meets these challenging performance criteria to make hydrogen-powered vehicles competitive with traditional vehicles (Figure 2.9.2).

Presently there are three basic routes for the storage of hydrogen in materials: adsorption in metal hydrides, adsorption in carbon-based and microporous materials, and chemical reaction using complex metal and chemical hydrides. Sorptive processes require highly porous materials to maximize the surface area and allow for easy uptake and release of hydrogen. Therefore, basic research is needed on the size effects of adsorptive processes, in particular at the nanoscale.

The use of nanomaterials in energy generation and storage may not only allow for higher storage capacities and higher charge and discharge rates but also for better control over the chemical processes

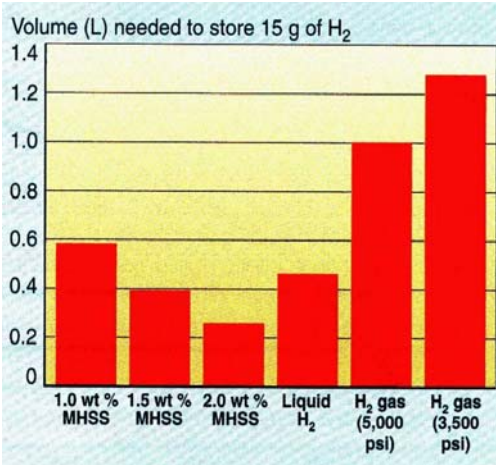

Figure 2.9.2 *Comparison of volume needed to store 15 g of hydrogen. Metal hydride storage systems (MHSS) which can store more than 1.5wt % hydrogen contain more hydrogen than liquid hydrogen.DOE's Grand Challenge calls for 4.5 wt % by 2005.*

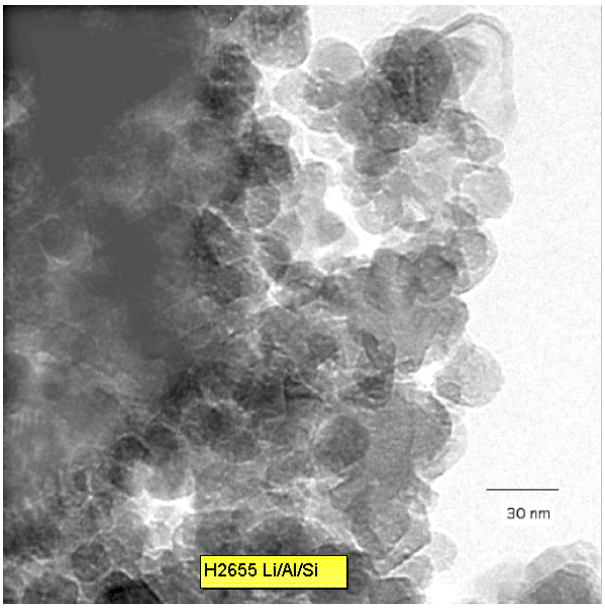

Figure 2.9.3 TEM of LiAlSi nanocomposite made by a hydrogen-driven metallurgical reaction.

involved (i.e. adsorption, charge transfer). As an example, magnesium and its alloys can store about 7.7 wt % hydrogen, but their adsorption and desorption kinetics are very slow. One approach to remedy this is to increase the surface area by making nanocomposites of Mg and $MgNi_2$ by ball milling. The addition of $MgNi_2$ catalyzes the H_2 dissociation and thereby increases the rate of hydrogen adsorption.

An alternative way of making such nanocomposites is to use hydrogen driven, solid state, metallurgical reactions (HDMR) [6]. When a hydrogen storage alloy is subjected to cyclic hydriding-dehyriding (HD) reactions it may undergo large cyclic volume changes that lead to reversible disproportionation into a stable binary metal hydride and other metal components, with the hydride and other components recombining upon removal of the hydrogen. This is a very flexible process that promises to provide novel materials with not only high hydrogen storage capacity, but also other unique properties, such as nanocatalysts, electrodes, and nanomagnets.

X-ray powder diffraction is crucial for the in-situ monitoring of the reaction products and their grain sizes. Figure 2.9.3 shows a TEM of a LiAlSi composite made using a HDMR [7]. The inherent inhomogeneity of nanocomposites requires small X-ray beams to probe specific areas. The high brightness of NSLS-II will significantly enhance the ability to characterize such heterogeneous nanocomposites.

A major breakthrough was achieved when it was observed that in the well-known reaction sequence, $NaAlH_4 \rightarrow \frac{1}{2}\ Na_3AlH_6 + 2/3\ Al + H_2 \leftrightarrow NaH + Al + 1.5\ H_2$, the dehydrogenation is rapid and reversible under unprecedented moderate conditions when adding a few mole % of selected dopants such as $Ti(OBu)_4$ [8]. $NaAlH_4$ has a theoretical reversible H_2 storage capacity of 5.6 wt %. Other potentially viable systems such as $LiAlH_4$ (7.9 wt %), $MgAlH_4$ (7.0 wt %), $Ca(BH_4)_2$ (8.6 wt %) or $Fe(BH_4)_2$ (9.4 wt %) have not yet been made to store hydrogen reversibly. Therefore fundamental studies of the Ti:$NaAlH_4$ model system must continue in order to provide an understanding of the role of the dopant. Once again, in situ powder diffraction is the ideal tool to follow the reaction kinetics of this and other systems.

Another class of hydrogen storage materials under intensive investigation is nanoporous carbon fibers and nanotubes. Microporous hollow carbon fibers have shown high permeability and selectivity as hydrogen membranes and are currently being scaled up to commercial levels [9-11]. Adsorption of a hydrogen gas monolayer onto a graphite surface occurs at low temperatures and yields an uptake of 4.1 wt % hydrogen. Nanotubes are seen as more useful hydrogen storage materials since they can retain hydrogen at room temperature, and because the nanotube wall curvature increases the binding energy of

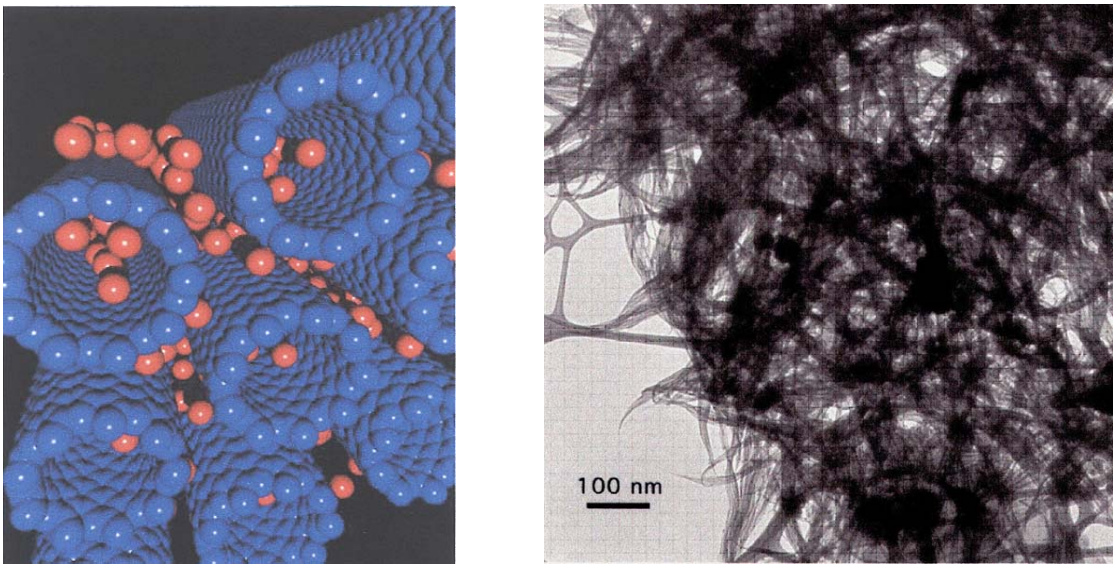

Figure 2.9.4 *TEM image of ropes of single wall nanotubes (SWNT) (left), which allow hydrogen (in red on the right) to be adsorbed into the interstitial spaces.*

the H_2 molecules compared to that on a flat graphite surface. When single-wall carbon nanotubes (SWNT) are synthesized, they form "ropes" that are triangular, close-packed parallel cylinders (Figure 2.9.4). This stacking provides a total hydrogen storage capacity of 4 wt % [12]. New strategies are being devised to increase the hydrogen-to-carbon ratio and achieve even higher hydrogen storage density and faster adsorption/desorption kinetics [13].

Yet another class of novel hydrogen storage materials is "nanocubes" of metal-organic frameworks (MOF). These are very porous materials (~3000 m^2/g) that can be synthesized from low-cost starting materials such as zinc oxide and terephthalate, which is a component of plastic (PET) soda bottles (Figure 2.9.5) [14]. With a density of only 0.59 g/cm^3, this MOF is one of the most porous materials known. By comparison, carbon nanotubes have a density of 1.3 g/cm^3. Furthermore, with 3000 m^2/g specific surface area, these materials exceed the corresponding figures for commercially activated carbons (800 to 2000 m^2/g), zeolites (700 m^2/g), and carbon nanotubes (200 m^2/g). Recharge capacities of close to 2 wt % have already been achieved.

Due to their large surface area these materials are polycrystalline powders and their structural characterization relies on high-resolution synchrotron powder diffraction. The high brightness and flux of NSLS-II will allow their adsorption properties to be monitored in real time using fast time-resolved in-situ powder diffraction.

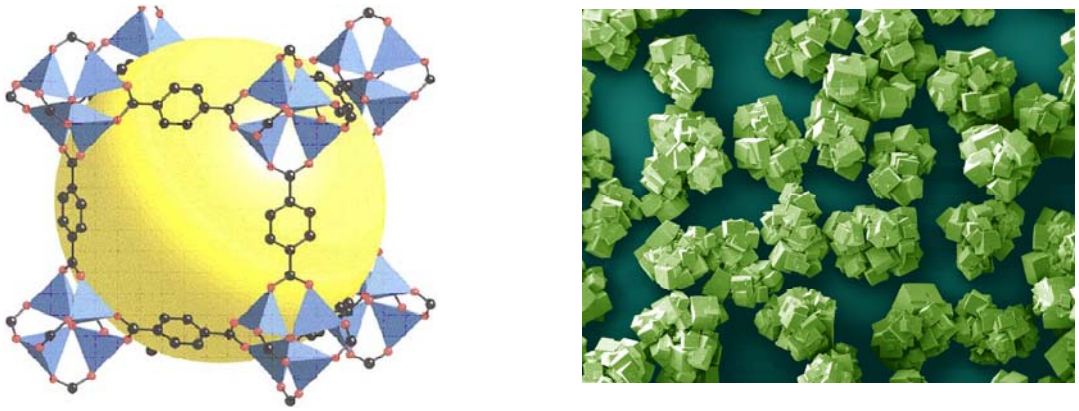

Figure 2.9.5 *An example of a metal-organic framework structure (above) and its microstructure. Over 90 % of the crystal volume is open space (orange ball) which can be used for gas storage (H_2,CH_4,N_2).*

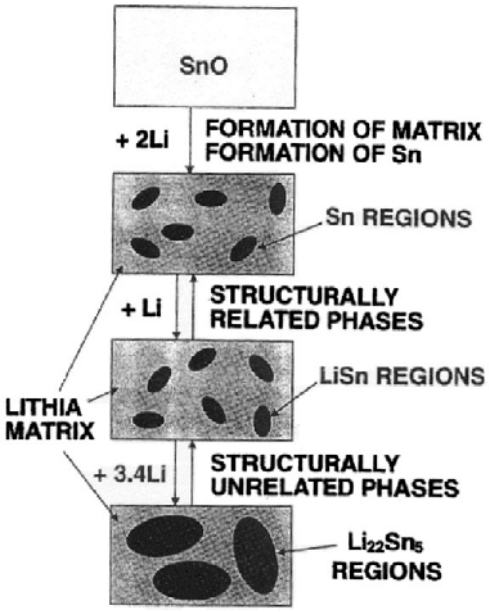

Figure 2.9.6 *Fuji-type glass for Li battery: 4SnO : 1B_2O_3 : 1:P_2O*

2.9.2.3 Battery Materials

Rechargeable batteries with high energy and power density and that are also light weight and environmentally friendly are in great demand as energy sources for numerous uses, such as space applications, notebook computers, portable telecommunication devices, and hybrid electric vehicles. The main challenges facing researchers in the field are (1) development of new cathode and anode materials, with high intrinsic discharge voltage, large charge storage capacity, good charge/discharge reversibility, and high rate of charging/discharging; (2) development of new classes of electrolytes that are environmentally friendly and cost effective to replace the toxic salts currently used; (3) understanding the complex material responses under realistic operation conditions.

For example, the current commercial lithium ion battery is based on $LiCoO_2$ cathode. Due to the high cost of Co, there is great interest in developing cathodes based on V, Mn or Ni. Because of the large structure changes in these layered Li-intercalated oxides during lithiation and delithiation, it is essential to be able to characterize the structural and electronic changes of these new cathode materials during electrochemical cycling. In recent years, synchrotron x-ray diffraction and spectroscopy have played important roles in elucidating the average long-range and local structure changes that accompany the charge/discharge cycle. However, the electronic structure changes associated with the charge compensation mechanism are still not clear. In addition, completely new materials, many of which are based on nano-composites (Figure 2.9.6) due to their increased lithium adsorption capacity and faster kinetics, are also being actively pursued.

With the high brightness and flux of NSLS-II, in-situ x-ray diffraction and spectroscopy studies of individual grains of the cathode materials will be possible. Novel x-ray techniques, such as resonant and non-resonant x-ray Raman scattering, will also be applied to determine the electronic structure by providing shallow core-level absorption spectroscopy information, particularly the K-edge of oxygen and the L edges of 3d transition metals, using hard x-rays.

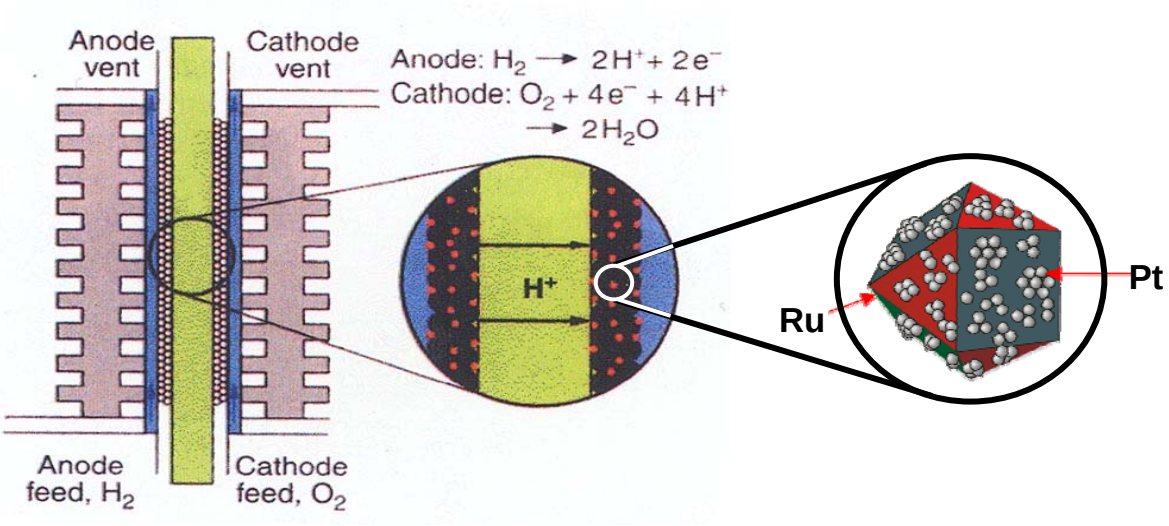

Figure 2.9.7 *H_2/O_2 fuel cell and the chemical reactions occurring at the anode and cathode.*

2.9.2.4 Electrocatalysis and Fuel Cells

Fuel cells represent one of the greatest opportunities for clean and efficient power generation, including electric power for transportation. Continuous progress has been made in electrocatalysis over the last two decades, in particular in areas related to fuel cell research. Fuel cells are soon expected to become one of the major sources of clean energy. Considerable environmental benefits and some preservation of fossil fuels will follow if this direct energy-conversion electrochemical power source becomes an economically viable alternative.

Much research has been devoted to developing electrocatalysts, since the success of fuel cells largely depends on improving their performance. However, despite considerable progress technical challenges must be overcome before fuel cells can be widely used in electromotive and residential applications, including low loading of noble metals, enhanced catalytic activity, and long-term stability [15-17]

To meet these requirements, the development of new electrocatalysts with increased activity and reduced noble metal content is necessary. This challenging task will only be accomplished with atomic level design of electrocatalysts, which requires a new level of characterization of the structural, electronic, and dynamic properties of supported nanoparticle electrocatalysts.

One approach to synthesis of the next generation of electrocatalysts that has been demonstrated consists of a submonolayer-to-monolayer deposition of Pt on carbon-supported metal nanoparticles [18-19]. In this synthesis, all the Pt atoms are placed on the surface of carbon-supported metal nanoparticles, i.e., exactly where they are needed for the reaction. Thus, an ultimate reduction of Pt loading can be achieved since there are no 'bulk' Pt atoms present, as there are in standard electrocatalysts.

An electrocatalyst for a fuel cell anode with 1/8 monolayer of Pt on Ru nanoparticles deposited on carbon (1/10 of Pt loading in standard electrocatalysts) has been shown to have an excellent activity for H_2 oxidation, good tolerance to CO impurities in H_2 and excellent long-term performance stability. Figure 2.9.7 shows the schematic of a H_2O/O_2 fuel cell and a model of the recently developed Pt/Ru electrocatalyst nanoparticles.

The characterization of electrocatalysts requires the high brightness of NSLS-II in combination with high-speed detectors for time-resolved studies of the kinetics of electrocatalytic processes and surface atom mobility. An important feature of the monolayer-level electrocatalysts is that all of the Pt atoms are active. Hence, the observed electronic and structural properties can be unambiguously correlated with their catalytic activity. However, the signal from such samples is weak and high-intensity sources can greatly improve these studies. Again, NSLS-II is needed for these measurements.

Surface segregation is a key to a long-term structural stability of alloy catalysts. To characterize subtle changes in structure and to understand dynamic aspects of these processes requires the power of NSLS-II, which will be especially critical for characterization of metal monolayer electrocatalysts on tailored alloy nanoparticles prepared by the above method, and for catalysts prepared by combinatorial methods for large scale screening of novel materials.

2.9.3 Impact of NSLS-II

Modern catalysts acquire a considerable amount of their multifunctionality from their complex multielemental composition. As an example of such a complex chemical "factory", consider a modern automotive catalytic converter that is typically made up of a porous alumina oxide honeycomb impregnated with nanoparticles of Pt, Rh, ceria, zirconia, lanthana and baria: Pt oxidizes hydrocarbons and CO, Rh reduces NO_x, ceria and zirconia work as oxygen storage components enabling the oxidation of hydrocarbons and CO while the engine is running fuel-rich, lanthana stabilizes the alumina surfaces, and baria traps the catalyst poison SO_3. Modern synchrotron-based tools therefore must provide time-resolved elemental information to investigate *in-situ* the complex chemical reactions involved.

The unprecedented brightness and flux of NSLS-II, in combination with high-speed detectors, will extend the existing techniques to include time-resolved studies of the kinetics of catalytic processes on msec timescales or faster and enable the use of combinatorial methods for large scale screening of novel materials. It will also enable the application of new experimental techniques, such as high-resolution X-ray emission spectroscopy and X-ray Raman scattering, to provide new spectroscopic information; allow spectromicroscopy characterization of model systems with better than 10 nm spatial resolution to characterize novel nanometer sized catalytic materials, as well as the active sites and adsorbate-substrate interactions in model systems; and enable high-pressure studies of model systems to help bridge the pressure gap. The impact of these new developments is illustrated below.

2.9.3.1 Quick EXAFS and Dispersive EXAFS

Catalysis is a dynamic phenomenon, with the active phase often only formed in the presence of the reactants and/or products. Gaining detailed knowledge about the electronic and geometric structure of the active phase is paramount to developing a deeper understanding of the active sites necessary for a particular catalytic reaction. With this knowledge, it should be possible to predict the structures necessary for other reactions. While some catalytic structures can be determined under steady-state conditions, there are many cases where it is advantageous to obtain the information about the active structures by perturbing the conditions in some manner, such as by applying a temperature or pressure pulse, or by pulsing the reactants as opposed to continuous flow. This is especially true in partial oxidation reactions, or in catalysts comprised of several different elements, all of which could undergo redox chemistry.

Dispersive EXAFS [20] and quick scanning EXAFS [21], coupled with a reactor supplied by an automated manifold capable of both continuous gas flow and fast switching valves for pulse flow, can be used to follow transformations on the millisecond time scale. With a quick scanning monochromator, full EXAFS scans can be collected in the few second time scale. In this manner, redox changes can be followed using XANES, and once an interesting regime of pressure and temperature is identified, the quick scanning monochromator can be used to obtain detailed local structure information. Figure 2.9.8 shows the time-resolved EXAFS (QEXAFS) data for a heteropolymolybdate catalyst where the evolution of the active phase is clearly identified.

Another important application of a QEXAFS beamline on NSLS-II will be to follow structural transformations in supported bimetallic and trimetallic catalysts. For example, a more rigorous structure determination is obtained if the EXAFS of both edges in a bimetallic catalyst are refined simultaneously. Currently, this data is obtained by collecting the EXAFS data twice, once from one element and then by repeating the entire EXAFS data collection from the second element. Using a quick scanning

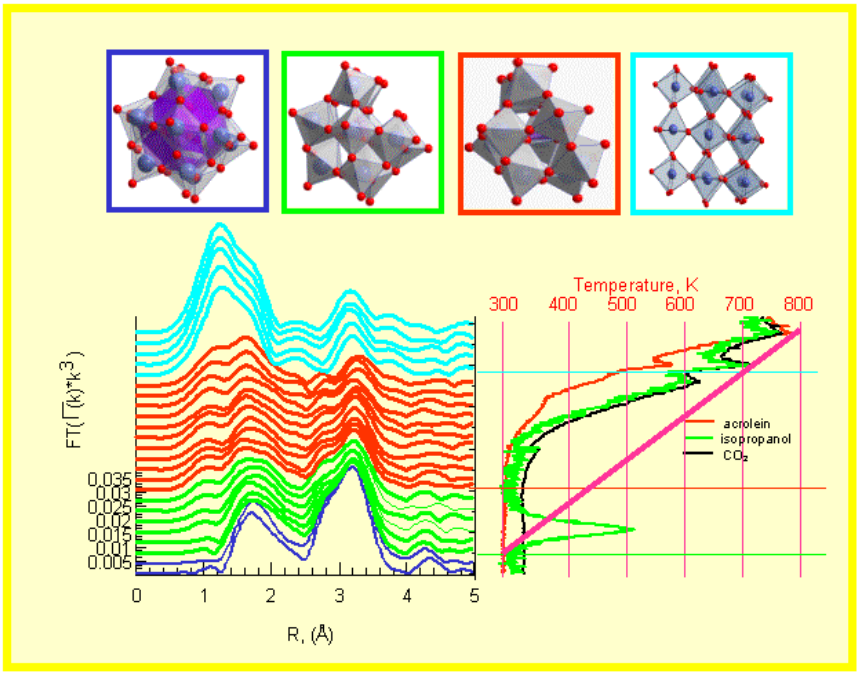

Figure 2.9.8 *FT-EXAFS and in-situ catalysis data of propene oxidation over a $H_4PVMo_{11}O_{40}$ HPA catalyst. Multiple structure-activity relations for acid catalysed (green) action, for selective oxidation (red) and for deactivation (blue) were found [22].*

monochromator, the data can be obtained in a pseudo-simultaneous manner by slewing quickly from one edge to the next. This would then ensure that the data are collected under essentially identical conditions and thereby lead to more reliable data analysis. A typical example application would be measurements of methanol or reformate fuel cell anode catalysts, where it has been demonstrated that the most active catalysts are bimetallic/trimetallic catalysts [23]. This is an area of very active research in which devices are sought that will be economically viable.

With the high brightness of NSLS-II, it will be possible to apply these techniques to reactions on msec time scales, well beyond what would otherwise be possible.

2.9.3.2 High Resolution Powder Diffraction Studies

The best of all catalysts for the production of acrylonitrile are mixed metal-oxide molybdenum systems. The first one, patented by Mitsubishi Chem. Ind., is a MoVNbTe-oxides that was claimed to have 59% yield with 63% selectivity. It was found that the active catalyst forms only under mildly reducing conditions and is made up of two prominent phases, denoted M1 and M2. Recently, the structure of the orthorhombic M1 phase was determined by using a combination of TEM, high-resolution synchrotron and neutron powder diffraction [24].

The atomic structure of this catalyst component (Figure 2.9.9) reveals that the sites partially occupied by V^{5+} (red) , V^{4+} (green), and Te^{4+} (light blue) cations are isolated and provide sites for the propane amooxidation catalysis to occur on terminal [001] planes. In particular, the ionicity of the metal-oxygen bonds in corner-sharing octahedra with V^{5+} and V^{4+}/Mo^{4+} centers provides particularly nucleophilic bridging oxygen, which is critical to propane activation. The Mo^{6+} sites have been shown to act as propane adsorption and nitrogen insertion sites in bismuth molybdates, which are also used for propane ammoxidation. This demonstrates how the multifunctionality of complex oxide catalysts is based on their multielemental distribution. High-resolution synchrotron powder diffraction provides unique information about the phase composition of such multicomponent catalysts.

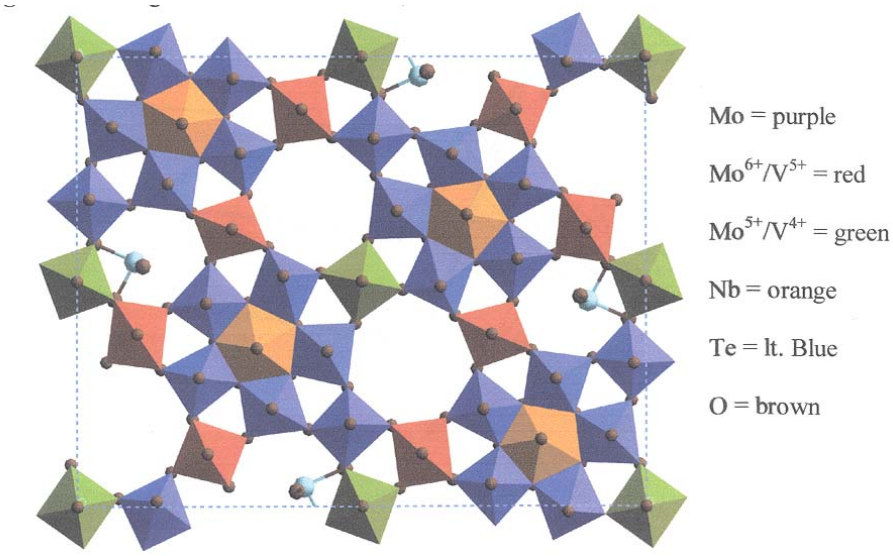

Figure 2.9.9 The average structure of $Mo_{7.5}V_{1.5}NbTeO_{29}$.

By providing even higher flux and smaller beams, NSLS-II will make it possible to isolate diffraction contributions from different phases originating from different grains and thereby unravel the complex structure of individual grains as well as the strain and texture effects that might be beneficial for catalytic processes. In-situ and time-resolved powder diffraction of 'real' catalytic processes will provide an unprecedented wealth of understanding that will lead to new approaches to the design of novel multifunctional catalysts. The high brightness of NSLS-II combined with fast position sensitive X-ray detectors will provide a unique opportunity to study industrial catalytic processes at atomic resolution in real time and under real working conditions of pressure and temperature.

2.9.3.3 High Resolution X-ray Emission Spectroscopy

The electronic structure of a catalyst is often the overriding factor in determining its activity. Up to now, a common method used by many researchers in catalysis, is to record the XANES "white line" as an indicator of the density of unoccupied states, particularly for the Pt group metals, which are extremely important catalytic elements. In a recent breakthrough, deGroot, et al., [25] using high resolution X-ray emission spectroscopy, showed for bulk Pt metal that the normally accepted model for Pt, that the Pt $5d_{3/2}$ level is filled, is not true. This has profound impact for our understanding of the chemistry of supported Pt-based catalysts, where it has been taken de facto that this level is filled. de Groot states, "the present spectra are limited by experimental resolution. With the prospect of an improved experimental resolution for X-ray excitation and decay, the Pt edge absorption spectra could be obtained with even better resolution, thus providing a high-resolution hard X-ray probe of the empty density of states with important advantages for *in-situ* and high-pressure studies". Data collected in this manner, when coupled with reliable user-friendly ab initio XANES codes, e.g. FEFF8, will provide dramatic and powerful insight into the electronic structure of supported metal catalysts.

Currently, a multi-element high-resolution crystal analyzer funded by NSF is being developed at the NSLS. NSLS-II will provide the high brightness and flux necessary to extend this technique to higher energy resolution and to real-time *in-situ* studies. A high-resolution X-ray emission spectrometer can also be used in resonant inelastic X-ray scattering (RIXS) measurements, where the rich soft X-ray spectroscopic information could be obtained using hard X-rays. The feasibility of this technique has been demonstrated in a recent 1s2p RIXS study of α-Fe_2O_3, where the incident energy is tuned to the Fe K edge and Fe Kα emission lines are analyzed with high-resolution spectrometer [26]. Figure 2.9.10 shows the applications of Fe 1s2p RIXS to an important industrial catalyst, Fe-ZSM_5 [27].

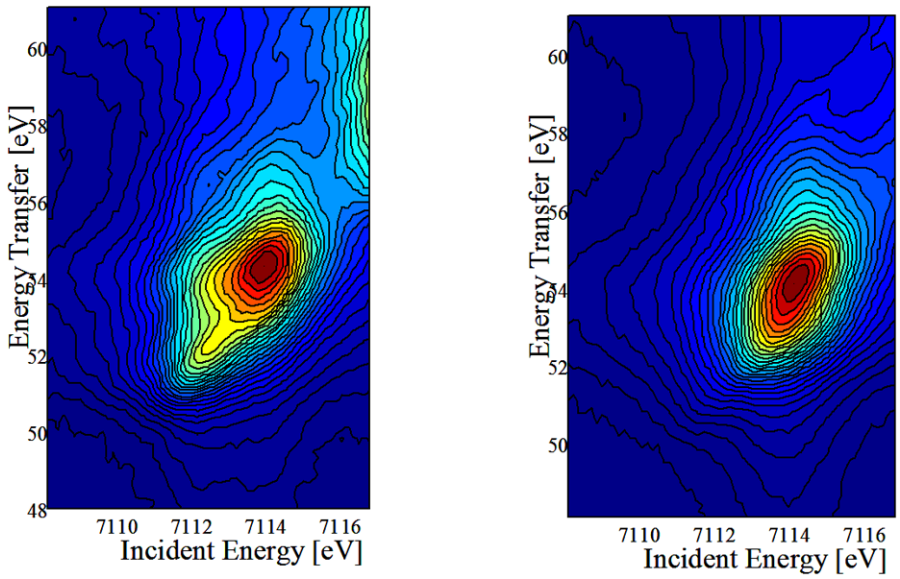

Figure 2.9.10 *1s2p RIXS spectra of Fe in a ZSM-5 catalyst: The left-hand figure shows the catalyst at partially reduced state and the right-hand figure shows the fully oxidized state.*

2.9.3.4 Anomalous Small Angle X-ray Scattering & Diffraction Anomalous Near Edge Structure

One of the most fundamental characteristics of a heterogeneous catalyst is the size distribution of the metal particles, which is traditionally determined using transmission electron microscopy (TEM). However, there are difficulties with TEM characterization of heterogeneous catalysts: the smallest particles, which are of the greatest importance for catalytic chemistry, are difficult to identify; the conclusions are based upon the analysis of extremely small samples; and the technique is very labor intensive and not readily performed *in-situ*.

A technique that removes these shortcomings and complements TEM is anomalous small angle X-ray scattering (ASAXS). Like TEM, small angle X-ray scattering (SAXS) is sensitive to objects with sizes below 10 nm. Because its contrast mechanism originates from electron density differences, SAXS cannot normally directly link features in a scattering profile to specific components in a composite system. For a catalyst this means, for example, that pore structure scattering cannot be separated from scattering from metal particles. However, by taking SAXS data above and below the absorption edge of an element of interest, so called ASAXS, scattering from it can be isolated. Being a photon-in/photon-out technique, ASAXS measurements can be made on catalysts in reactive environments. Thus, one could use ASAXS to understand the resistance of a heterogeneous catalyst to sintering, and hence activity loss, under working conditions, such as temperature and environment.

Diffraction anomalous fine structure (DAFS) is an important development in X-ray absorption spectroscopy [28]. It provides a probe of site-selective local structure for systems with chemically identical atoms. To apply this technique to catalysis problems requires the capability to perform DAFS on dilute powder samples, which is an extremely demanding experiment. The feasibility of performing diffraction anomalous near-edge structure (DANES) was recently demonstrated [29] on a ZSM-5 zeolite catalyst with 3 wt % platinum loading.

With the increased brightness of NSLS-II, DAFS from catalysts with relevant weight loading of metal will be possible and it will be possible to conduct these studies *in-situ*.

2.9.3.5 Inelastic X-ray Scattering

Significant progress has been made in understanding the relationship between structure and functionality for heterogeneous catalysts. Because of its ability to provide chemical and physical state information about a catalyst in a reactive environment, hard X-ray absorption spectroscopy has been a crucial tool for obtaining such information. Studies on working catalysts have been complemented with studies on model systems, both single crystal and powders, using VUV radiation. With VUV radiation it is possible to study the first row elements, in particular the carbon K-edge, and the 3d-transition metal L-edges. However, VUV studies of powder catalysts suffer because they are usually limited to pre-natal/post-mortem characterization in vacuum or, at best, in the presence of a few milli-Torr of gas. In principle, inelastic X-ray scattering (X-ray Raman scattering) can provide the same information as VUV and soft X-ray spectroscopy under "real" reaction conditions. The feasibility of using X-ray Raman scattering for this kind of application has been demonstrated recently [30].

The increased brightness and flux of NSLS-II in combination with the development of higher energy and larger area crystal analyzers will increase the sensitivity of this technique by several orders of magnitude and revolutionize our understanding of working catalysts.

2.9.3.6 Photoemission and Surface Microscopies

The high brightness and flux of NSLS-II will allow the acquisition of photoelectron spectra down to msec time scale. With current capabilities, these spectra are acquired in a time interval of 5-120 seconds. The improved time-resolution will allow the monitoring of the evolution of surface reactions as a function of time under changing temperature and/or reactant conditions. Another important aspect is the gain in sensitivity that will result from the use of a high brightness X-ray source. Currently, it is extremely difficult to detect low concentration species on a catalytic surface because the data acquisition time is too long to prevent contamination of the sample surface. The increased brightness of NSLS-II will allow the detection of adsorbate concentrations on the order of 0.05 % on the surface of a catalyst.

The increased brightness of NSLS-II will be particularly important for imaging techniques. Given the complex nature of even the simplest catalytic systems, detailed understanding of the relationships between structure and reactivity is difficult to achieve. Genuine comprehension of catalytic processes requires multi-dimensional imaging techniques. For example, serious limitations have come to light by virtue of the discovery of dynamic patterns on catalyst surfaces under reaction conditions. The presence of patterns on crystal facets in supported catalysts is also confirmed. With the further development of photoemission electron microscopy (PEEM), it will be possible to image these intricate patterns *in-situ* with chemical sensitivity and sub-10 nm spatial resolution.

In operation, heterogeneous catalysis at gas-solid interfaces occurs at pressures much higher than those typical of electron-based spectroscopies. New electron energy analyzer designs compatible with 'high pressure' sample environments, based on differential pumping and tailored electron optics, are being developed to lower the pressure gap by allowing the surface chemistry to occur at elevated pressures (100 mbar) while tracking the surface electronic structure and composition using X-ray photoelectrons. This is a very exciting development and will allow, for the first time, detailed information on the oxidation states of the elements in the catalyst combined with detailed knowledge of the electronic structure of weakly adsorbed intermediates on the catalyst surface.

2.9.3.7 Carbon K-edge Fluorescence Yield Near Edge X-ray Absorption Fine Structure

In heterogeneous catalysis involving carbon-containing species, distinguishing among the electronic states of the carbon atoms is critical to understanding reaction intermediates. While this is not typically revealed in XPS, NEXAFS can make this distinction because it samples the local valence electron density

as excitations from core levels to unoccupied molecular orbitals relax, emitting photons or emitting Auger electrons. On planar model catalysts, the molecular orientation of surface intermediates can be determined under reaction conditions using polarized X-rays. Even though the photon yields are low (~0.0012), this technique provides a photon-in photon-out spectroscopy that can track the concentrations of various forms of carbon under working catalyst conditions. Mixed-element technical catalysts often suffer from background scattering. Rather than increasing the incident X-ray intensity, a process that often damages the sample, it is better to improve the signal-to-noise ratio. In a recent breakthrough, a near-normal-incidence focusing multilayer mirror detection system tuned for carbon-based signals has shown the ability to reject non-carbon background and makes possible the analysis of carbon in technical materials [31]. This detector potentially enables a whole new class of *in-situ* photon-in photon-out soft X-ray absorption measurements.

The high brightness of NSLS-II, together with these advances, will make millisecond time resolution for kinetic analysis a key future direction.

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2.10 Earth and Planetary Science

2.10.1 Overview

The evolution of the Earth and other planets is a vast process lasting billions of years, involving huge amounts of materials (crystalline and molten silicates, metals, and volatile constituents), at temperatures from near absolute zero to several thousand degrees, and pressures from a fraction to millions of atmospheres. The present state of the Earth, as well as its evolution through time, is governed by the properties of these materials. Their properties at the relevant conditions of pressure, temperature, and stress dictate the red and blue regions of a seismic tomographic image (Figure 2.10.1), or control the depth and time history of earthquakes (Figure 2.10.2). These materials also define the frequencies of the oscillations of the Earth and the rate that plates slide over the surface.

With the symbiotic development of synchrotron radiation and high-pressure techniques, experimental studies of earth materials are experiencing an unprecedented surge of breakthroughs that were deemed inconceivable a decade ago. Synchrotron sources have fundamentally altered the nature of high-pressure experimentation, from reconnaissance study with limited capabilities to high-precision study with comprehensive material characterization over a wide range of pressures and temperatures. In particular, rheological properties, phonon related properties, and dynamics of chemical reactions can now be investigated at very high pressures and temperatures. By studying the materials of which the Earth is made, high-pressure research using synchrotron high-energy X-ray and infrared radiation has contributed significantly to understanding of the phenomena, processes, and state of the Earth. This information allows addressing issues that range from the chemical heterogeneity of the Earth's interior to the processes responsible for deep focus earthquakes.

2.10.2 Scientific Challenges and Opportunities

2.10.2.1 Elastic Properties at Pressure and Temperature

Elasticity measurements on minerals are the bridge between the observed seismic velocity structure of the Earth and properties at depth, such as chemical composition and temperature. The sound velocity

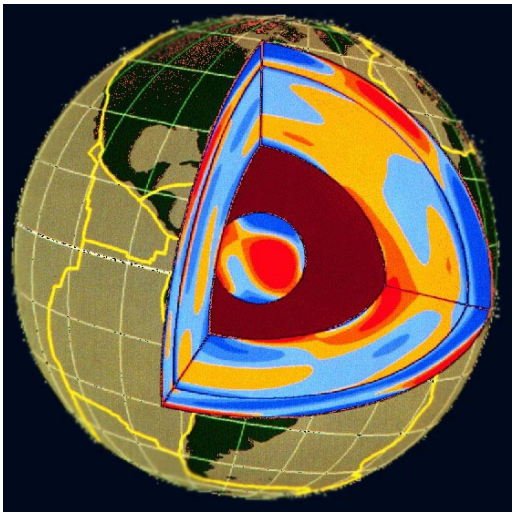

Figure 2.10.1 *A seismologist's view of the Earth. Red regions indicate slow sound wave velocities, blue are fast. This structure may represent the flow patterns of hot (slow) material rising with sinking cold (slow) regions. Actual association of fast with either thermal or chemical variations requires high pressure laboratory data.*

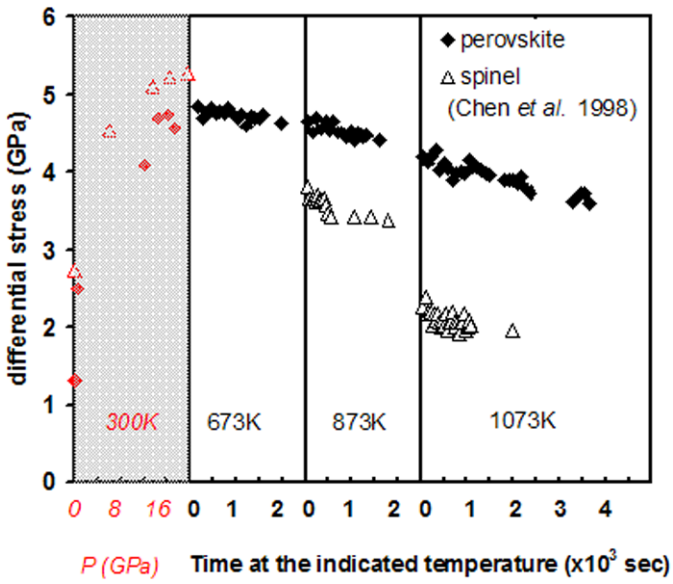

Figure 2.10.2 *Data acquired on the large-volume press at NSLS X17B1. Time-resolved EDXRD shows that perovskite is stronger than other minerals at high P-T. Data explains why no earthquakes start in earth's lower mantle [1].*

structure of the Earth is known from the surface to the center of the core, through seismological studies. Tomographic studies of 3-D velocity structure are providing detailed images of fast and slow regions that relate not only to our notions of the current compositional state of the mantle, but to convective flow and mixing over time [2]. Observations now reveal the penetration of some slabs into the lower mantle, the stagnation of other slabs in the transition zone, and broad differences in velocity structure beneath continents and oceans. In other studies of reflected and converted seismic phases, subtle undulations in the depths of seismic discontinuities are being mapped and being related to the properties of phase transformations that likely causes them. Elastic anisotropy, reflecting the single crystal elastic properties coupled with large deformations, traces out the stress-strain history of the planet. At the core-mantle boundary, astonishing degrees of heterogeneity and complex velocity structure are observed that may be related to chemical reactions between the mantle and core, and/or the recycling of subducted material in a slab graveyard.

Synchrotron X-rays are a vital part of acoustic velocity measurements in multi-anvil apparatus at high pressure and temperature. The travel times for elastic waves traveling through a sample are measured, from which wave speeds and elastic moduli are calculated. This technique provides relatively high precision data, it can be used with transparent or opaque samples, and it yields the bulk elastic properties without the need for single crystals. The direct measurement of sample length by X-ray imaging greatly reduces errors in velocities and elastic moduli. In the future, capabilities will be expanded from measurements at pressures of 14 GPa and temperatures of 1300^{o} C to pressures greater than 20 GPa and temperatures of more than 2000^{o} C using the state-of-the-art high pressure systems.

Measurement of velocities and elastic properties allow the raw information provided by seismology to be interpreted in terms of physically meaningful quantities such as chemistry, temperature, dynamics and stress history. Without accurate information on the variation of mineral acoustic velocities with temperature, pressure, and composition, it is not possible to form a realistic picture of Earth's interior.

The ambitious challenge facing the mineral physics community is to develop the ability to measure sound velocities on any Earth material throughout the entire range of pressure-temperature (P-T) conditions in Earth's interior and to recover both aggregate elastic properties and single crystal properties.

The dynamics and processes associated with texture development in the inner core represent a major problem in geophysics. Seismic anisotropy reflects oriented texture in elastically anisotropic minerals. To address this question, the technique of radial X-ray diffraction was pioneered at the NSLS [3, 4]. In these

measurements, strain anisotropy was observed that corresponded to variations in diffraction intensities and suggest the presence of preferred crystallographic orientations. These deformation experiments at inner core pressures provide information about flow processes within the Earth and are relevant to the possible development of anisotropy during outer core convection. It is now essential to extend these studies to alloys and compounds of iron with hydrogen, carbon, oxygen, silicon, sulfur, and nickel. Studies at high temporal, spatial, and wavelength resolution require a dedicated facility that is capable of quantitative texture analysis. Empirical modeling techniques have been developed to extract elasticity information from such X-ray diffraction studies on textured polycrystals.

With NSLS-II, a new generation of direct in situ investigations of the rheology and texture of materials at extreme pressures will be carried out in entirely new domains of pressures and temperature. In situ structure, equation of state, and phase equilibria studies of light element alloys will be possible at extreme conditions. Inelastic scattering of X-rays promises to provide a new leap in elasticity data. The facility will provide an important means to extend inelastic X-ray scattering measurements for high pressure phonon studies. Phonon scattering contains crucial information about not only the acoustic velocity of the polycrystal, but also information about the single-crystal elastic moduli. Recovery of this information will provide new insights into the deep Earth by allowing interpretation of seismically defined elastic anisotropy. Phonon density of states reflects thermal properties of the material. Measurements of this property with pressure and temperature will give better interpretations of the thermal state within the Earth. This is currently one of the poorest, yet important physical parameters for the deep Earth.

NSLS-II will provide the flux and energy range that is needed for these experiments in both multi-anvil cells and diamond anvil cells. Through these studies, the entire region of the Earth‘s interior can be explored.

2.10.2.2 Rheology Challenges

It is no more than a decade since synchrotron radiation has been applied to the understanding of rheology of polycrystals at high pressure and temperature. With the rapid development of high pressure facilities and techniques, progress in probing the rheological properties of deep Earth materials has enhanced understanding of the dynamics of the Earth and other terrestrial planets. For example, two new types of high-pressure apparatus, a modified cubic apparatus (D-DIA) (Figure 2.10.3) capable of providing quantitative rheological information and a rotational Drickamer apparatus (RDA) able to produce very large plastic strains, are now becoming available to users. With synchrotron radiation, these tools can be used for quantitative measurements of stress (± .01 GPa) and strain (± 10^{-4}) at high pressure and high temperature (15~25 GPa, 2000 K). Results have been as fundamental as giving us an improved

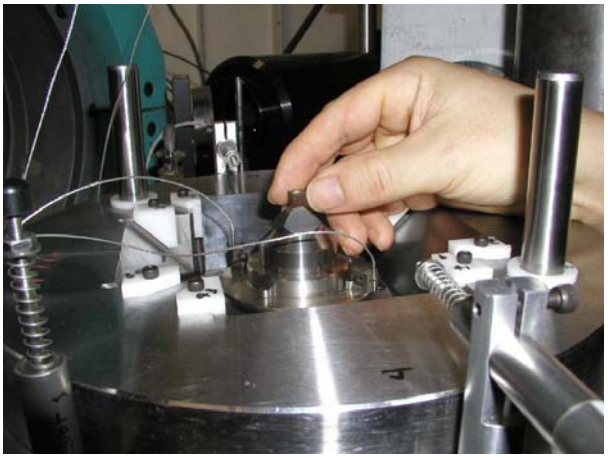

Figure 2.10.3 *Sample being loaded into the D-DIA high-pressure deformation device.*

understanding of mantle convection and dynamic processes such as deep earthquakes.

The remaining frontier that needs exploration in connecting seismic studies with laboratory experiments is the time scale. Seismic studies use millihertz acoustic waves to probe the Earth, while laboratory studies use megahertz acoustic waves. Differences in these time scales are expressed in the attenuation, or the Q (quality factor), of the stress-strain relationship. With the newly developed synchrotron tools, unprecedented flexibility in controlling the stress and strain during the deformation process at mantle pressure and temperature is feasible. Knowledge gained will bring important constraints on the thermal, velocity, and density structure of the Earth.

To measure Q, we need to measure stress relaxation times and strain retardation times as a function of frequency. In particular, to describe seismic wave attenuation and related transient creep, we need to resolve strain with a precision of 10^{-6} [5]. Current techniques in NSLS beamline X-17B2 allow a precision of 10^{-4}, good for plasticity studies, yet two orders of magnitude lower than what is need for anelasticity study. Improvements on both X-ray source and detection instrumentation are essential to reach the strain precision of 10^{-6}. NSLS-II will be able to offer an intensive high energy X-ray beam with source size two orders of magnitude smaller than current beam size. This makes the increase in strain precision possible. Instrumentation improvements include use of asymmetrical cut single crystal analyzer, phase contrast imaging, and the development of a hard X-ray microscope.

NSLS-II, together with the new high resolution strain instrumentation, will enable measurement for earth materials of Q at high pressure and temperature and measurement of quantitative flow laws using multi-anvil cell to 20 GPa and 2000K and using diamond anvil cell to 100 GPa and 1200K.

2.10.2.3 Study of Melt Property and Liquid-liquid Phase Transition at High Pressures

Liquid silicates have shaped the surface of the planet that we live on. It has been the most significant chemical filter in the history of the planet and it still plays a role in dictating its future. The earth's core is predominantly liquid and creates the magnetic field. Whether liquids sink or float is determined by the local structure of the melt and the chemical partitioning between the melt and residual solid. Liquids have long been ignored because adequate tools have not been available for providing insight.

While pressure-induced phase transformations in crystalline solids are common and have been extensively studied, phase transitions in liquids or melts have caught scientists' attentions only very recently. As almost all solids transform to a denser phase when pressure is applied, it is very reasonable to expect that local structure changes also occur when a liquid is subject to high pressures. The lack of understanding of melt phase transitions is mainly due to experimental difficulty. Crystalline phase transitions can be very well characterized using in situ X-ray diffraction. X-ray scattering by noncrystalline materials, however, is much less straight forward. In addition, in-situ measurements while the specimen is maintained simultaneously at high pressure and high temperature make the study even more technically difficult. Nevertheless, study of liquid-liquid phase transitions has gained rapidly growing interest. Materials that reportedly show a liquid-liquid phase transition so far include C, Si, P, Ge, I, Bi, Se, Te, H_2O, SiO_2, GeO_2 and $S_{l2}O_3$-Y_2O_3 melt [6-16]. Experimental techniques used in these studies include X-ray scattering, X-ray absorption spectroscopy and melt density measurement through X-ray absorptions.

The pressure-induced local structure transition is a new class of phase transformations. It is undoubtedly important in terms of pure physics. In addition, understanding melt behavior and structure under high pressures has been a dream of the scientists in national defense programs as well as Earth and planetary sciences. Melt properties are essential information for simulations of a nuclear explosion, and for understanding volcanism and the role of partial melting in the Earth mantle. More significantly, the liquid outer core portion of Earth's interior (Figure 2.10.4) is still mysterious. It likely gives rise to the Earth's magnetic field, but is least understood by scientists. It consists of mostly liquid iron but little is known about its local structure and phase transitions. Studies of liquid local structure and phase transitions at elevated pressures (<100 GPa) are likely to become one of the hottest topics in condensed

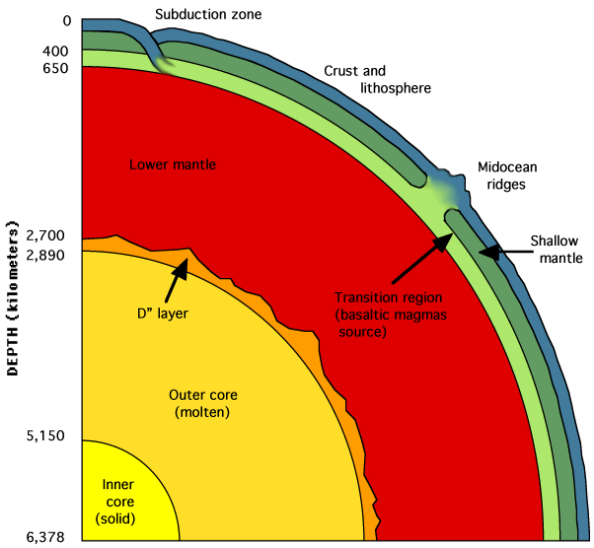

Figure 2.10.4 *Illustration of the Earth's interior (Courtesy of Windows to the Universe, http://www.windows.ucar.edu). The molten outer core is the least known portion of the Earth's interior.*

matter physics, and understanding the melt structure of the Earth's outer core at pressures > 135 GPa will be a great challenge for the next decade and beyond.

At the NSLS superconductor wiggler beamline X17B, experiments have been carried out to study liquid properties (density and viscosity) at high pressures in a multi anvil press using high energy X-rays. An X-ray radiograph imaging technique has been developed to measure density of melts [17]. Figure 2.10.5 demonstrates a melting volume measurement of a very important Earth core material, FeS. Studies of radial distribution function of melts are also on the way. Although X-ray absorption spectroscopy is a very powerful tool to study the local structure of melts, energies of the absorption edges of the most important elements to Earth science (e.g. Si and Al) are too low. Photons with those low energies are completely absorbed by the high pressure cell, even through Be gaskets. Study of local structure around these light atoms at high pressures is currently impossible.

The above challenging scientific issues require an improved brilliant high-energy X-ray source, and integrated X-ray optics and measurement techniques. NSLS-II will offer these capabilities, and enable the following scientific challenges to be met with great impact on physics and Earth science: X-ray scattering at extremely high pressures (>100 GPa) for deriving radial distribution function of melts; expanding all current phase diagrams of elements and compounds into the field of melts; mapping local structures around light atoms in melts using X-ray Raman spectroscopy; and understanding property and structure of the melts existing in the Earth outer core.

2.10.2.4 Phase Transformations at High Pressures

Studies of mineral phase transformations at high pressures are the key for understanding the Earth and planetary interiors. For example, the Earth's mantle is marked by two prominent seismic discontinuities at 410 and 660 km depth, where abrupt jumps in seismic velocities have been detected through the analysis of seismic waves created by earthquakes. It is now widely believed that both discontinuities are related to the phase transformations in olivine, the most abundant mineral in the Earth's upper mantle. With the detailed phase relations in olivine mapped out in the laboratory, the seismic determinations of the discontinuities can be translated into chemical composition and temperature for the mantle. Because of their importance to our quest of knowledge about the Earth's interior, phase relations in relevant silicate systems have been the subjects of the most extensive investigation in high-pressure research in the past half-century.

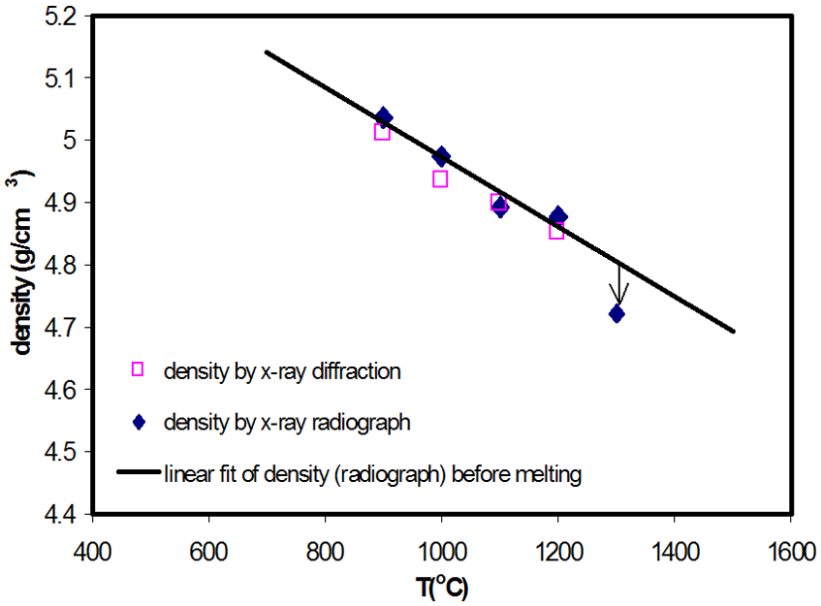

Figure 2.10.5 *Measured densities of FeS as function of temperature at 4 GPa. Melting causes a significant density drop.*

In situ synchrotron X-ray measurements have been used to study mineral phase transformations at high pressures. Compared to the conventional quench/recovery method, synchrotron-based techniques provide much better environmental control. For example, precision in pressure measurements is about ten times higher than in quench experiments. Furthermore, important variables related to phase transitions, such as pressure and deviatoric stress, can be monitored throughout each experiment. This has led to much needed improvement in the determination of phase boundaries, which is critical to deciphering the detailed structures of seismic discontinuities, hence the Earth models, and to the determination of thermodynamic properties of minerals. Synchrotron-based techniques also provide the only reliable method for studying phase transitions that involve unquenchable phases, such as Ca-silicate perovskite.

Synchrotron X-rays allow time-resolved studies of phase transformation processes at high pressures, a fundamental problem in solid-state physics. Kinetics and mechanisms of phase transitions in the silicate system are also important for understanding the Earth's dynamic interior. Much like metamorphism that occurs in the Earth's crust over geological time, similar processes also occur in the Earth's mantle owing to the mantle convection. That is, materials in the mantle are subjected to constant changes in pressure and temperature, and hence the physical and chemical states of the mantle are not only depth-dependent, but also time-dependent. Phase transition kinetics could play an important role in defining the properties of convective currents in the mantle.

There are several shortcomings for present measurements that will be solved using the higher brightness of NSLS-II. One is that it is difficult to introduce various metal capsules and pressure-transmitting materials to control fugacities of oxygen and other volatile components within the sample charge. Thus the effects of these volatiles on the phase transitions can not be investigated quantitatively. The second is that it is not possible to investigate the local structure change during phase transitions using techniques such as EXAFS and XANES. The current X-ray acquisition time necessary for identification and characterization of the phases under high pressure and temperature also needs to be reduced in order to capture kinetics of fast phase transformations and transition characteristics near phase boundaries.

2.10.2.5 Oxidation and Spin States

The application of pressure often dramatically affects magnetic properties. While measurements of the magnetic susceptibility provide the magnetic moment, diffraction can provide the three dimensional

structure in magnetically ordered materials. Theoretically predicted pressure-induced magnetic collapse [18] is important for transition-element ions that, with their variable valence and magnetic states, control major geochemical and geophysical processes, such as oxidation and reduction, chemical differentiation, elasticity, geomagnetism, conductivity, and radiative heat transfer.

Depending on temperature and pressure the deceptively simple composition FeS crystallizes in at least five modifications with structures related to the NiAs-type. The spin state of iron in FeS can be determined from the Fe K_β spectrum by X-ray emission spectroscopy (XES) [19]. In the 2+ oxidation state of iron, the low-spin state is characterized by a total magnetic moment equal to zero. This collapse of the 3d magnetic moment has a distinct signature, since the exchange interaction vanishes and the resulting spectrum consists of a single narrow line. Measurements on troilite (FeS) show a high-spin to low-spin transition at 7 GPa coinciding with the FeS II-III structural transition [19]. Such studies have also been applied to FeO, indicating that there must be a maximum T_N above 300 K and 40-60 GPa with re-entrant behavior back to the paramagnetic phase above 80 GPa [20]. Likewise, a high-spin to low-spin transition occurs in hematite at 50 GPa [20].

The above mentioned transformations occur over a broad range of conditions up to >100 GPa. Hence direct study of these transitions and the high pressure phases by in situ X-ray diffraction, spectroscopy, and inelastic scattering will require the integrated capabilities of NSLS-II. The new generation of high-pressure devices based on large single crystal CVD diamond [21] will facilitate these studies.

2.10.2.6 Amorphous Materials and Nanomaterials

Pressure-induced amorphization transformations and pressure induced amorphous-amorphous transitions have been observed in a growing number of materials. Porous Si is one technologically relevant example and a number of other amorphous materials, including high-silica glasses, can be irreversibly compacted by pressure. A densified form can be retrieved on quenching to ambient conditions. This provides materials with a range of optical properties, densities, and chemical properties, which can be continuously tuned by changing synthesis conditions. Apart from the compaction of liquids and glasses, pressure can also induce certain classes of crystalline material to amorphize if compressed to pressures well outside their stability fields.

In situ diffraction studies of these materials and transitions are critical for understanding these processes. Some samples can be quenched in metastable states at atmospheric pressures and these recovered samples have been studied with standard diffraction techniques. The first high-pressure diffraction experiments with full radial distribution function analysis of amorphous materials were carried out at the NSLS on SiO_2 glass to 28 GPa [22]. This study demonstrated the importance of in situ measurements because the high-pressure structures were not quenchable. The primary barrier to in situ high pressure investigations has been the typically small sample sizes and limited incident beam flux, combined with the complicated data normalization procedure necessary when using high pressure cells.

Intermediate range structural order in permanently densified GeO_2 and SiO_2 glasses has been a subject of debate in recent years. The question as to whether a discontinuous transition takes place over a certain range of pressures and temperatures still appears to be open. Measurements on permanently densified GeO_2 show that although changes in the short range order are small, the intermediate range order is altered substantially. High energy X-ray diffraction measurements performed on normal and permanently densified GeO_2 glass (10 GPa) have revealed in detail the changes in local structure under pressure. The main conclusion from this study is that densification produces a change in the intermediate range order that subsequently causes a change in the short range order in the GeO_2 glass.

Similarly, recent studies on the archetypal glass $GeSe_2$ have shown that there is a breakdown of intermediate range ordering in liquid $GeSe_2$ at high pressure that may lead to a liquid-liquid phase transition [23], as seen in glassy GeO_2. Whereas only corner sharing units are known to exist in GeO_2, both edge and corner sharing units exist in the network forming $GeSe_2$ glass, so the situation becomes more complex. In-situ studies of the structure of GeO_2 and $GeSe_2$ glasses at 6-10 GPa and high

temperatures (1000^{o} C) using diffraction would give critical insight into the structural nature of amorphous-amorphous and liquid-liquid transitions. In addition, isotopic substitution measurements of both the Ge and Se atoms would allow unprecedented structural information to be obtained.

Understanding the structure of magnesium silicate liquids and glasses is important for interpreting the behavior of refractory liquids produced by melting processes of the Earth and Lunar mantles. Although magnesium-rich silicate minerals are primary constituents of the Earth's mantle there is little information available on either the structure of the magmas produced when they melt or the associated thermodynamic properties. This paucity of information is due to the refractory nature of these phases, which makes in situ study of the liquids at high P-T conditions difficult and also because the liquids do not form glasses very easily, which limits the study of quenched phases. There are also important implications for the early history of the earth and moon since low-silica magnesium-rich liquids are considered to have played an important part in development of magma oceans and komatiite volcanism. More fundamentally, the change in liquid behavior could relate to the underlying changes in liquid structure that may be expected to occur as the liquids are compressed at deep Earth conditions.

High-pressure also provides a powerful means for tuning the properties of nanomaterials. A variety of studies of pressure-induced transitions in fullerenes and nanotubes have been reported, including transformations to novel superhard phases [24]. Studies of nanocrystalline chromium [25] indicate that antiferromagnetic order in the body-centered-cubic phase of powder and consolidated ultrafine-grain-size chromium samples can be suppressed to well below the Neel temperature of coarse-grained and single-crystal chromium.

With advances in pressure cells coupled with bright high energy X-ray beams, radial distribution function from in situ pressure amorphized solids will be possible. These investigations can be coupled with detailed vibrational spectroscopic studies carried out with synchrotron infrared spectroscopy over a wide pressure range. Detailed X-ray and infrared investigations of novel properties of nanomaterials will be carried out over a wide P-T range. This includes extensions of recent studies of pressure-induced transitions in nanotubes. It will be possible to examine previously reported but poorly understood transitions in fullerenes at higher pressure. The effects of intercalation of other components to form novel high pressure phases, including potential hydrogen storage and superhard and electronic materials can be explored with the diversity of techniques available.

2.10.2.7 Hydrous Minerals and the Deep Earth

High P-T experiments offer the only practical means to examine directly the chemistry and physical properties of materials that comprise the deep interior of the Earth and other planets [26]. This information is crucial for understanding the Earth's water cycle and the connections between dewatering of the interior, formation of the oceans and recycling of water in subduction zones. Most water held within the crystal structures of minerals is released during subduction of the oceanic slab and then recycled back into the overlying mantle wedge where it can trigger melting or enter into reactions with other minerals. However, some of this water may be transported from the subducted slab into the mantle via dense hydrous magnesium silicates. For example, recent experimental studies [27] have shown that dehydration-rehydration reactions involving OH-clinohumite [$Mg_9(SiO_4)4(OH)_2$] could be an important mechanism for transporting water into the transition zone (400 km).

Hydrous minerals play a major role in low temperature geochemistry and are increasingly implicated in deep earth processes such as mantle convection and deep focus earthquakes. For example, layered hydrous phyllosilicates such as the clays, amongst the most common minerals at the earth's surface, are thought to be involved in the dehydration of the down going slab in subduction zones. Nominally anhydrous [28] as well as novel high pressure magnesium silicates have been suggested as phases for water storage in the mantle [29, 30]. Finally, the strength and rheological properties of the polymorphs of Mg_2SiO_4 suggest they might provide mechanisms for storage of stress in the mantle and that dewatering processes in these and other hydrous phases my lead to the reactivation of faults in the lithosphere. The properties of these minerals then impacts a variety of surface and deep earth processes. A comprehensive

understanding of the phase relations, structures, elasticity, strength and rheological properties is a useful first step to bounding the mineralogical controls on these processes.

The transformations that clay minerals undergo when exposed to high temperatures and pressures are of great interest for both fundamental and applied science. Clays occur in nature in a variety of environments, and hydrothermal influences on their structures and properties are important for understanding their genesis and geological transformations, including geohazards such as earthquakes. From a fundamental perspective, the response of clay minerals to changes in pressure can shed new insight into understanding of the balance between different interlayer cohesive forces. However, detailed information of such transformations involving interlayer hydrogen bonds requires accurate determination of hydrogen atom positions by single-crystal diffraction. More generally, the presence of hydrogen bonding in solids can determine stability and properties of other materials [31, 32] and pressure provides a particularly “clean" variable for this study.

Dense hydrous phases are a key to efforts to understand the Earth’s deep interior. As demonstrated by recent work at the NSLS, the combination of synchrotron X-ray diffraction and infrared spectroscopy has proven essential for investigating these important deep Earth materials [33]. Higher P-T studies using the full complement of integrated synchrotron techniques are essential for understanding these systems. Provided single crystals are available, many of the techniques now used routinely for high pressure single crystal X-ray diffraction will be transferred and implemented with large gem anvil cells.

2.10.2.8 Oxides and Silicates of Earth’s Interior

The high P-T behavior of silicates and oxides are particularly important for understanding the nature of the Earth’s deep interior [26]. These materials exhibit numerous intriguing equilibrium and metastable transformations under pressure. For example, $(Mg,Fe,Al)SiO_3$ silicate perovskite is likely to be the most abundant mineral in the planet. The oxygen deficiency and cation-site distribution of silicate perovskite control its physical and chemical properties, including density, bulk modulus, defect mobility, ionic transport, flow behavior, oxidation states, hydration, and minor-element solubility. These properties of perovskite, in turn control the geophysical and geochemical processes of the Earth.

The basic crystallographic characteristics of the silicate perovskite were previously determined by conventional X-ray diffraction techniques [34]. The defect crystallography of silicate perovskite, however, requires a new generation of diffraction, inelastic scattering, and spectroscopic techniques. A new generation of in-situ crystallographic studies of complex silicate perovskites over the entire P-T range of the Earth’s lower mantle are required to shed light on long-standing puzzles of the unusual effects on compressibility, the strong P-T-X dependence of iron-magnesium partitioning between the perovskite and magnesiowüstite, the effects of the high-spin/low-spin transition in ferrous and ferric iron, and the controversy surrounding electrical and mass transport properties of perovskite in the lower mantle. Coupled with new large volume megabar devices, accurate measurements will become possible on multicomponent systems to the P-T conditions of the core-mantle boundary.

2.10.3 Impact of NSLS-II

Understanding the behavior of Earth and planetary materials at high pressures and temperatures requires an integrated experimental approach that utilizes a combination of complementary measurements. It is often essential to study the same sample at the same pressure and temperature with a broad range of techniques, including spectroscopy and diffraction. NSLS-II will be unique by virtue of its range of X-ray through infrared capabilities and the proven success of the NSLS in high-pressure geo-science during the past decade.

High-brilliance, high-energy synchrotron radiation provides the non-destructive probe to penetrate through the gaskets or anvils of multi-anvil presses or diamond cells. Newly developed X-ray focusing optics (described in Section 4.1.1.5), detectors and analytical techniques together with NSLS-II, will

enable a myriad of crystallographic and spectroscopic measurements with resolutions rivaling studies at ambient conditions.

With NSLS-II, major advances will be made in understanding the Earth from its surface to its center.

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2.11 Environmental Science

2.11.1 Overview

Identification of the chemical form and the chemical, physical and biological processes that control the distribution of contaminants in our environment is a core mission of the Department of Energy (DOE), one of the leading sponsors of cutting-edge research in the environmental sciences. Such research is focused on developing a better understanding of how contaminants are distributed, bound and react in the environment. Whether they are heavy metal toxins such as mercury or lead, radioactive contaminants such as uranium, plutonium or radon, or greenhouse gases such as sulfur dioxide; DOE's commitment to the clean-up of impacted sites and long-term stewardship of the environment is reflected in its funding of environmental research at DOE facilities.

Without a detailed knowledge of contaminant behavior, remediation of highly impacted sites will likely be less effective and far more costly than needed. The major questions involving environmental contaminants concern their speciation, distribution, reactivity, transformations, mobility, biogeochemical cycling, and bioavailability. These issues ultimately depend on molecular-scale structure and properties, best determined using spatially-resolved spectroscopic techniques. Basic understanding at this scale is essential for development of clean-up strategies and risk assessments for both local and global scale pollution problems. Such basic spectroscopic studies will lead to new techniques to remediate contaminated soils, natural waters, and the atmosphere and novel approaches to safely isolate from the biosphere hazardous wastes from past U.S. weapons production, agricultural activity, energy production, manufacturing, and mining.

One of the major challenges to understanding fundamental biogeochemical processes in earth's near-surface environment is the characteristically heterogeneous nature of the impacted materials. Soil, sediment, and rock samples commonly contain multiple solid phases, as well as liquids, air, and complex biomaterials. Relevant particle size distributions extend into the sub-micron range, which hinders characterization by conventional bulk methods. The low concentrations that are typical for many contaminants make their detection difficult without high sensitivity analytical techniques. The high brightness of synchrotron radiation sources allow small, intense X-ray beams to be produced. Synchrotron-based methods have allowed a new level of characterization by offering element and chemical state specificity, high spatial and energy resolution, excellent detection sensitivity at ppb levels, and the ability to work in-situ, for example with wet samples safely sequestered within environmental cells. These types of studies have led to unique information on many of the chemical processes that affect contaminant elements, particularly those occurring at solid-water interfaces.

The high brightness and flux of NSLS-II will provide much enhanced capabilities in environmental science research and enable continued advances in this critical area of research.

2.11.2 Scientific Challenges and Opportunities

The wide range of scientific challenges in environmental science is reflected in the inter-disciplinary nature of this field of study, which draws scientists from soil and agricultural sciences, geochemistry, chemistry, physics, biology, microbiology, hydrology, ocean sciences, climatology and atmospheric sciences. The following broadly defined scientific challenges and opportunities in environmental science demonstrate how the new capabilities made available by NSLS-II will play a critical role in shaping the future of environmental science research and its contributions to society.

2.11.2.1 Speciation of Contaminants in Complex Natural Systems

The speciation of toxic elements is a critical factor in controlling their mobility, bioavailability, and toxicity in aqueous and terrestrial environments. Speciation refers to the chemical and physical form of an

element in a geochemical setting and includes the following components: the identity of the contaminant of concern or interest, the oxidation state of the contaminant, the associations and complexes to solids and dissolved species (surface complexes, metal-ligand bonds, surface precipitates), and molecular geometry and coordination environment of an element. The more of these parameters that can be identified, the better one can predict the potential risk of contaminants to humans and make sound decisions about remediation. Natural materials such as soils and sediments are very complex and heterogeneous, being composed of an array of primary and secondary minerals, phyllosilicates, hydrous metal oxides, and humic substances. The processes and reactions that occur at the interfaces between minerals, water, organic matter, and microbes dictate the speciation and species transformations over a wide range of spatial and temporal scales.

Traditionally, bulk elemental analysis, sequential chemical extraction, and analytical techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microprobe analysis (EMPA), and scanning electron microscopy (SEM) have been employed to glean information about speciation, mineralogy, elemental chemical state and spatial distributions, including elemental associations. These approaches, however, do not directly give information about the speciation of elements and can have other drawbacks including poor detection sensitivity and spectral artifacts due to ex-situ analysis. The use of micro-focused X-ray absorption and fluorescence spectroscopies, micro-diffraction, micro-tomography, and multielement spectromicroscopy can provide the means to determine such parameters in-situ, which is critical in such heterogeneous natural systems. These techniques allow us to evaluate the speciation of toxic elements over a range of environmentally relevant spatial and temporal scales.

An example of the type of nanoscale heterogeneity commonly observed is shown in Figure 2.11.1. In this example, a scanning transmission X-ray microscope (STXM) was used to acquire a series of images over the oxygen K edge (giving a spectrum at each pixel) in order to study lutetium (a homologue for the actinide americium) incorporation into iron oxide phases as amorphous ferrihydrite crystallizes into hematite. Such measurements contain considerable information but it can be difficult to recognize the key themes due to complexity. By using cluster analysis methods, one can simplify this information into an image shown in the top left panel. The red areas correspond to lutetium enrichment and indicate that the crystallization process excludes lutetium from the hematite structure. These results suggest that lutetium-substituted hematite might not be thermodynamically stable, and therefore, the abundance of iron oxides in soils and sediments may not protect against long-term actinide mobility.

The increased brightness of NSLS-II is required for this type of research to take advantage of advances in beam focusing optics and detectors that will enable spectroscopy studies at lower detection limits with nanoscale spatial resolution.

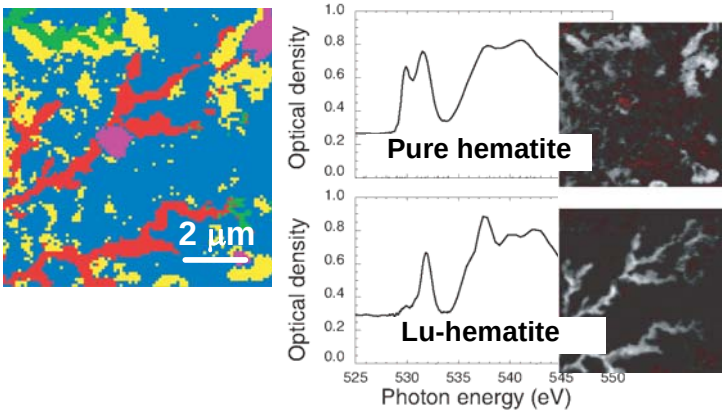

Figure 2.11.1 *STXM images and oxygen K-edge μ-NEXAFS spectra showing regions of lutetium enrichment in hematite. Work conducted at the NSLS beamline X1A2.*

2.11.2.2 Contaminant fate, Wasteforms, Remediation, and Long-term Stewardship

The cradle-to-grave strategy for management and disposal of environmental wastes from point sources such as nuclear fuel production and spent fuel disposal, industrial and agricultural wastes and from non-point sources such as suburban pollution poses a tremendous burden to regulators, scientists, engineers and the public. Developing remediation strategies is complicated because of the incredibly diverse forms such wastes represent, the differences in approaches to short- and long-term waste storage and treatment, the inherent heterogeneity of contaminated environmental media (e.g., soil, biota, rock) and the laws that strictly govern the classification and disposition of such waste. Long-term environmental stewardship and waste management activities require a thorough knowledge of the contaminants and their interactions (i.e., fate) with their environment.

Synchrotron-based techniques are uniquely suited to providing the detailed knowledge required to support the decision-making process for selecting remediation strategies, optimizing waste treatment processes and evaluating nuclear waste form stability in geologic repositories. A prominent example is that of high-level waste (HLW) residing in aging subsurface tanks at DOE sites. HLW is a high volume (several tens of millions of gallons) waste form that is highly radioactive, exists in multiple forms (e.g., sludge, salt cake and solution) and contains fissionable actinide elements such as plutonium. Its management and treatment alone is estimated to be in the hundreds of billions of dollars. When vitrified, this material is ultimately intended for long-term geologic storage in a repository such as Yucca Mountain, NV.

To ensure the isolation of long-lived radionuclides within the repository, scientists need to understand how the repository's geologic material will interact with the waste. X-ray micro-Fluorescence (micro-XRF) images shown in Figure 2.11.2 reveal that Pu sorption on heterogeneous tuff rock occurs preferentially on manganese oxide rich areas and not on iron oxide rich areas. In addition, Pu L-edge micro X-ray Absorption Near Edge Structure (micro-XANES) spectra (data not shown) indicate that localized regions of Pu enrichment are comprised of a mixture of Pu(V) and Pu(VI) oxidation states. [1] The oxidation state and mineral phase associations observed here would not have been possible without synchrotron-based micro-analytical techniques. The improved spatial resolution and lower detection limits achievable at NSLS-II will significantly improve the quality of information derived from this type of study. Furthermore, the higher beam brightness will significantly reduce data collection time and thereby allow greater sample thru-put that is critical to improving the statistical significance of physicochemical parameters used to predict contaminant behavior in highly variable field-scale settings.

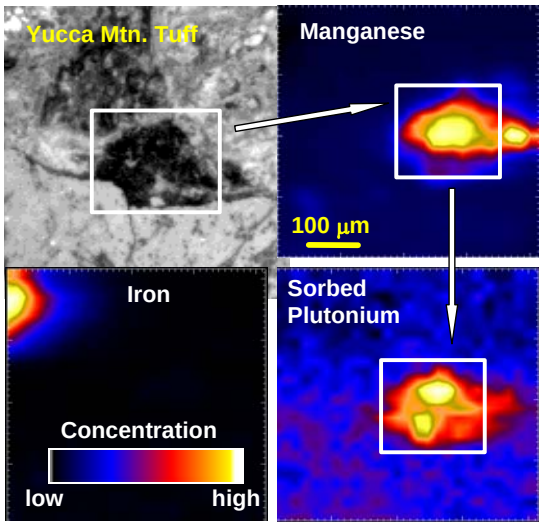

Figure 2.11.2 *Micro-XRF image map of Mn, Fe and Pu distribution in Yucca Mountain Tuff. Images collected at the NSLS X26A.*

2.11.2.3 Biogeochemical Processes, Rates, and Element Cycling

Among the most important biogeochemical processes are dissolution and precipitation, reduction and oxidation, sorption, and the complex reactions associated with the metabolism of micro-organisms. Ultimately, understanding these biogeochemical processes requires that we identify the rates and mechanisms of the most important reactions that occur between each component in the system. While this level of understanding seems fundamental, it is lacking for most environmental systems. The greatest barrier to understanding such processes is the inherent complexity and heterogeneity of natural systems. While synchrotron-based studies of complex real-world samples have proven invaluable in providing a great deal of information about the distribution and speciation of contaminants, environmental scientists have long-since recognized the need to study model systems of varying degrees of complexity to explore fundamental aspects of important biogeochemical processes. Results from these model system studies have proved to be essential for interpreting studies of contaminant behavior in complex environmental systems.

Synchrotron-based model system studies have provided fundamental information about aqueous solute complexes, poorly crystalline materials, solid-liquid interfaces, mineral-aqueous solution interactions, microbial biofilm-heavy metal interactions, heavy metal-plant interactions, complex material microstructures, and nanomaterials, all of which are important components or processes in the environment. [2] These studies range from standard bulk X-ray absorption fine structure (XAFS) spectroscopy measurements of contaminants in suspensions of model oxide colloids to X-ray and VUV investigations of contaminants on atomically flat single crystal oxide surfaces.

One topic of significant interest concerns the role of micro-organisms in biogeochemical processes. Figure 2.11.3 shows a STXM and μ-NEXAFS study of how OSY3 bacteria (isolated from sediment at a DOE site) reduce aqueous Cr(VI) to the less toxic and sparingly soluble Cr(III) species. The Cr L-edge μ-NEXAFS spectra collected at intervals across a single bacterium (transect a-b in lower STXM image) reveal that the reduction process is localized at the bacteria-water interface. The ability to explore microbe-driven processes is essential for designing and implementing microbial remediation strategies. Studies of metabolic processes require high brightness in the energy range from 100 eV to 5 keV to probe

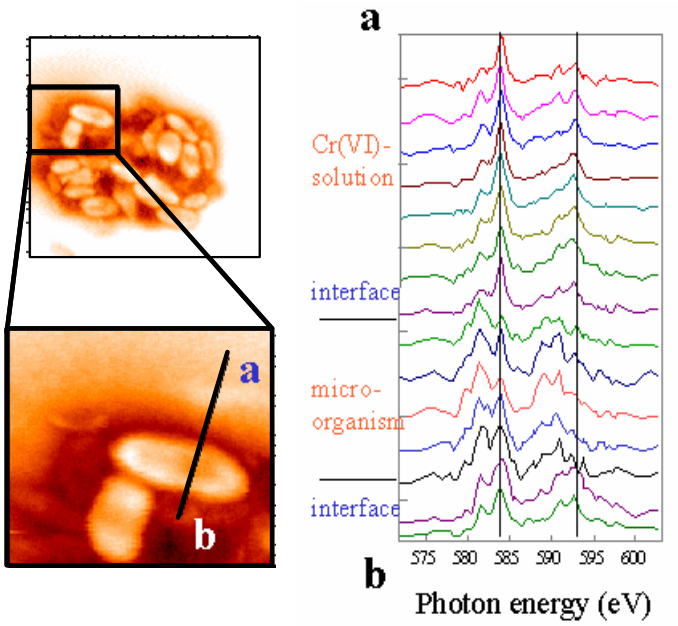

Figure 2.11.3 *STXM images and Cr L-edge μ-NEXAFS spectra collected at intervals along the transect a-b drawn in the lower left panel show Cr(VI) reduction on the bacteria surface. From ALS beamline 11.0.2.*

both contaminant L-edges and biologically relevant elements such as C, N, P, S, Cl, and Ca.

The high brightness of NSLS-II will significantly enhance the tools used to explore biogeochemical processes in model systems. For example, studies of contaminant speciation and transformations in solution will finally extend to environmentally-relevant micro- and nano-molar concentrations. Moreover, the increased brightness will greatly advance our ability to explore biogeochemical processes in increasingly complex systems that more closely resemble real-world conditions by adding thick water layers, biofilms and competing chemical species. Finally, NSLS-II will enable time-resolved spectroscopic studies on time-scales relevant to important biogeochemical processes. Understanding the kinetics of biogeochemical processes is essential for predicting contaminant behavior.

2.11.2.4 Structure and Chemical Properties of Environmental Nanoparticles

Nano- and micron-sized particulates generated by weathering of geological materials, biological processes, and the emissions of industries and automobiles are ubiquitous in the environment. The role of environmental nanoparticles (Figure 2.11.4) in the solubility, transport and bioavailability of aqueous contaminants is well established, but the composition and structure of these particles and their influence on the aforesaid processes are poorly understood. The mineralogical and associated organic molecule composition of such particles in the atmosphere influence light scattering, and water adsorption, condensation and particle growth, which in turn modify global temperatures and climates. Composition and reactivity of these particulates also influence the chemistry of rainwater. At present, attempts to model climate fluctuations are limited by the lack of specific mineralogical and chemical characteristics of these particles. Several atmospheric particulates, such as asbestos and other mineral dust, have deleterious effects on human health, and a correlation between health effects and particulate composition is yet to be established.

Properties that dictate the behavior of nanoparticles in the environment are their composition, morphology, and bulk and surface structure. A majority of environmental nanoparticles possess complex composition and consist of inorganic constituents, such as iron oxides (e.g. magnetite produced by bacteria) and oxyhydroxides (e.g. ferritins common in several organisms), aluminum oxyhydroxides (e.g. acid soils and waters), metal sulfides (e.g. all reducing sediments and soils), and organic molecules of

Figure 2.11.4 *Iron oxyhydroxides precipitated from acid waters through biotic and abiotic processes play a central role in controlling the solubility of several toxic elements, such as As, Cu, Cd. Such acid environments are common around abandoned and active coal and sulfide mines all over the world. The picture on the left shows the precipitation of iron oxide nanoparticles in a stream in Eastern Pennsylvania. Electron microscopy studies of sediments collected from a sulfide mine (picture on the right) shows the existence of ZnS nanoparticles (green) in the biofilm matrix (blue). [3]*

different sizes and functional groups (e.g. humic substances). Their small size and sensitivity to the surrounding chemical environment make them very reactive and structurally labile. Thus sample drying and characterization with vacuum methods, such as electron microscopes, are not suitable for examining a majority of environmental nanoparticles because of changes such as the loss of volatile constituents from samples. Consequently, the ability to do experiments in environmental cells at synchrotron facilities provides a powerful approach to study nanoparticles under environmentally realistic conditions.

Information on the compositional and structural heterogeneity of nanoparticles is central to predicting their reactivity, stability, and structural lability in the environment. Element-specific methods (e.g. X-ray absorption spectroscopy) are ideal for examining the chemistry of environmental nanoparticles in their pristine state. At present, the composition and structural characterization of particles below ~500 nm cannot be examined at any facility in the world. Availability of spatially resolved chemical and structural information on these nanoparticles could contribute significantly to the understanding of the chemistry of nanoparticles in the environment.

Spectromicroscopy facilities with a broad energy range, from a few eV to several keV to allow simultaneous probing of organic molecule functional groups and metal ions, and with facilities for structural characterization are essential if significant progress is to be made in this important research area. While radiation damage will provide the ultimate limit on studies of organic molecules, NSLS-II will provide sufficient brightness for studies of 10 nm colloidal particles where optics and sample damage considerations allow.

2.11.2.5 Environmental Genomics and Toxicology

To fully model the interaction of toxins with the environment, it is important to not only determine the physicochemical processes that control their mobility, but also understand their bioavailability to micro-organisms, plants, animals, and even humans. But fully assessing a toxin's bioavailability requires a detailed understanding of the complex interrelationship between factors such as toxin speciation, its metabolic pathways in organisms, and how gene expression influences biological interactions with not only the toxin but also nutrients, soil and water. For the environmental scientist, this defines a challenging new discipline that has been referred to as Environmental Genomics [4], the study of the inter-relationship between environmental changes and the gene expression of organisms. With synchrotron-based techniques it may be possible, in real time, to explore how toxin speciation varies with changes in gene expression in plants and micro-organisms, with the eventual goal of engineering gene expression to promote toxin sequestration from contaminated environments. Although in its infancy, there is a strong appreciation both among the environmental sciences community and the U.S. government of the potential importance of studies in environmental genomics. For example, in July 2002 DOE announced that funding would be made available from the Genomes to Life program to "support post-genomic research in new technologies for generating energy from biological sources, sequestering carbon, and cleaning up the environment." The EPA has similarly expanded its investment in genomics research.

The unique capabilities provided by synchrotron radiation, and especially the greatly enhanced capabilities enabled by NSLS-II, will play a critical role in shaping and advancing the emerging field of environmental genomics. For example, researchers at the NSLS are involved in several phytoremediation studies to determine how contaminant uptake and speciation in selected plant species respond to changes in soil and atmospheric chemistry. Contaminant and micronutrient element uptake by plants is controlled by complex formation with organic molecules that are in part produced in the root exudates of plants. Figure 2.11.5 reveals how complexing organic molecules can dramatically alter contaminant uptake and translocation in plants. The micro-XRF images in the upper and lower right panels show high lead concentrations in the tobacco plant stem only when EDTA, an organic molecule that readily complexes cations, is added to the contaminated soil. Synchrotron investigations probing changes in speciation as metal ions or radionuclides are sorbed by roots, translocated through the plant, and then returned to the soil as the plant dies are possible but the quality of the spectroscopic information is currently limited by beam brightness and flux. The development of transgenic plants to remediate certain metals in soils and to

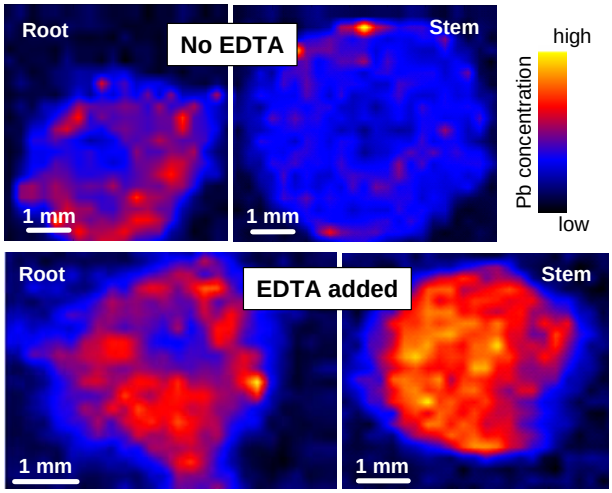

Figure 2.11.5 *Micro-XRF images of lead distribution in tobacco roots and stems with and without EDTA added to a contaminated soil. Images collected at NSLS beamline X26A.*

better use mineral nutrients is becoming a possibility but confirming the expected effects of genetic manipulation on element chemistry is critical. This can be done in part at synchrotron facilities, and such studies should reveal the relationships between certain genes (perhaps through "knock out experiments") and metal speciation.

Although studies in this area of environmental science have been remarkably successful, this research requires improvements in beam brightness, flux, and spatial resolution. In many of these biological systems the elemental abundances are low, ppm to sub-ppm levels, requiring higher brightness to provide improved detection sensitivity. NSLS-II will allow for detection levels to be improved by at least an order of magnitude. Concurrently, better detection sensitivity and higher count-rates at NSLS-II will also provide order of magnitude improvements in data acquisition time and quality for X-ray absorption spectroscopic studies. As we endeavor to understand contaminant interactions at bacterial and cellular levels, improvements in spatial resolutions are also required and will be provided by NSLS-II.

2.11.3 Impact of NSLS-II

As we have seen from the above examples, the goals in environmental science research are to obtain information on the speciation of contaminants in the natural environment, and to use this understanding to obtain improved and lower cost methods of environmental cleanup. It is increasingly apparent that this information must be obtained on sub-micrometer length scales, because at larger size scales one may obtain misleading interpretations based on an average over distinctly different structures in a specimen.

Most methods in synchrotron-based environmental science research involve not just simple imaging, but collection of signals from a microprobe beam on the sample. It is therefore of prime importance to have as many photons as possible in as small a spot as can be achieved. As was first pointed out at Brookhaven Lab a quarter of a century ago, [5] this is intrinsically linked to the brightness of a synchrotron source. Therefore, the improvement in brightness of NSLS-II by 10,000 times over the present brightest beamline at NSLS should lead to the ability to understand contaminants in the environment at size scales 100 times smaller than can be studied at the present NSLS. This can lead to fundamental improvements in the understanding of environmental science problems, because it should make it possible to distinguish (for example) between surface and bulk interactions of environmental nanoparticles.

To understand the impact of NSLS-II for these types of environmental analyses, consider the X26A hard X-ray microprobe beamline at the NSLS, a beamline historically dedicated to environmental science research and one of the most heavily over-subscribed beamlines at the NSLS. Given the anticipated

source characteristics of NSLS-II, the same endstation optics (Kirkpatrick Baez microfocusing mirrors) will achieve *minimally* an order of magnitude improvement in detection sensitivity and at least 10X improvement in spatial resolution. Thus, techniques such as XRF, XANES, and EXAFS will have sensitivities in the range of 100 ppb, 1-10 ppm, and 100-1000 ppm, respectively, or better.

Focusing mirrors that are commercially available today typically have about 1 μrad slope errors. It should be noted that recent studies of mirrors manufactured using numerically controlled plasma chemical vaporization techniques reportedly achieve line focusing widths of 0.12 and 0.2 μm FWHM at 15 keV. [6] Zone plates also show great promise for focusing hard X-ray beams to sub-micron resolution. They have been demonstrated to focus 8 keV X-rays to 150 nm FWHM focal spot size in the first-order focus and to 90 nm in the third-order focus. Their effective use at X26A is hampered by the significant loss of flux density relative to the Kirkpatrick-Baez. But with the significantly higher brightness of NSLS-II, such optics become an attractive and viable choice for hard X-ray microspectroscopy.

Such highly focused, high intensity beams will allow environmental scientists to apply micro-spectroscopic analysis in-situ at much higher spatial resolution than previously available, directly probing the interface of contaminant species with grain surfaces or biological organisms. For example, using the hard X-ray microprobe, scientists from the University of Wisconsin-Madison have found compelling evidence that micro-organisms play a central role in the formation of certain mineral deposits (see Figure 2.11.6). These results shed light on the basic question of biology's function in the formation of some metal ores, and hold out the promise for applications in mining-site remediation. Improved spatial resolution allows for not only analysis of aggregate biofilms, but of individual precipitate minerals on cell walls. NSLS-II will provide much higher flux density in much smaller spot sizes and enable understanding contaminant speciation in nanoparticles using X-ray absorption spectroscopy.

The high flux of NSLS-II will significantly enhance almost every technique critical to environmental research. Reflectivity or bulk EXAFS experiments, for example, would be able to be done in 1/10th the time with potentially order of magnitude improvements in detection sensitivity. These experiments would also be able to make better use of new technologies that allow for "on-the-fly" scanning for kinetics studies that currently are not feasible.

Environmental scientists and geoscientists have made extensive use of NSLS beamlines ever since NSLS began operations in 1982 and estimates indicate that this research currently comprises 10-15% of the total user base at the NSLS. As the user base has evolved to one more dominated by scientists interested in the application of developed techniques, the subscription of beamlines whose core mission is in environmental sciences has risen dramatically. Typically these beamlines are strongly oversubscribed. User statistics show that in the last 10 years earth and environmental sciences research at the NSLS has almost tripled. Such statistical trends are mirrored at the other DOE synchrotron facilities [2] and in the scientific literature. For example, in *Geochimica et Cosmochimica Acta*, a leading international journal focusing on the geochemical sciences, articles referencing synchrotron-based X-ray absorption data increased from 25 in 2000, to 32 in 2001 and 54 in 2002. Similar trends can be seen in the journal

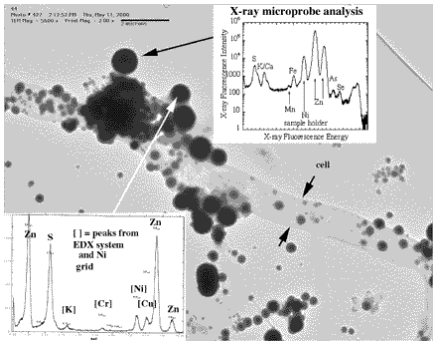

Figure 2.11.6 *Results of EDX (bottom left) and X-ray microprobe fluorescence (top right) analysis of specific biomineralized zinc sulfide precipitates. Scale bar is 2 μm. From APS beamline 2-ID-D [3].*

Environmental Science and Technology, with 11 articles in 2000, 16 in 2001, and 39 in 2002. An important driver for this continuing growth is the generation of new environmental science users from a diverse range of scientific and engineering communities such as soil science, plant biology, microbiology and environmental engineering.

Environmental Sciences research at the NSLS plays a major role in advancing our understanding of contaminant speciation and fundamental biogeochemical processes in nature. This information is an essential contribution to DOE's environmental management decision-making process. NSLS-II is critically needed if the environmental science community is to meet the ever increasing challenges for spectromicroscopy analyses with high spatial resolution of complex environmental samples necessary to meaningfully support regulators and engineers responsible for environmental assessment, remediation and management.

NSLS-II will greatly advance the quality and utility of environmental science research in a number of ways including:

- Ability to explore chemical, biological and mineralogical heterogeneity in complex environmental samples at the nanoscale with soft and hard X-ray probes
- Ability to probe biologically-important elements such as C, N, P, S, Cl, and Ca in fully-hydrated samples
- Ability to probe aqueous contaminant speciation at micro- and nano-molar solution concentrations
- Ability to perform time-resolved spectroscopic studies on times scales relevant to important biogeochemical processes
- Significantly reduce data collection time and thereby enable greater sample throughput

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