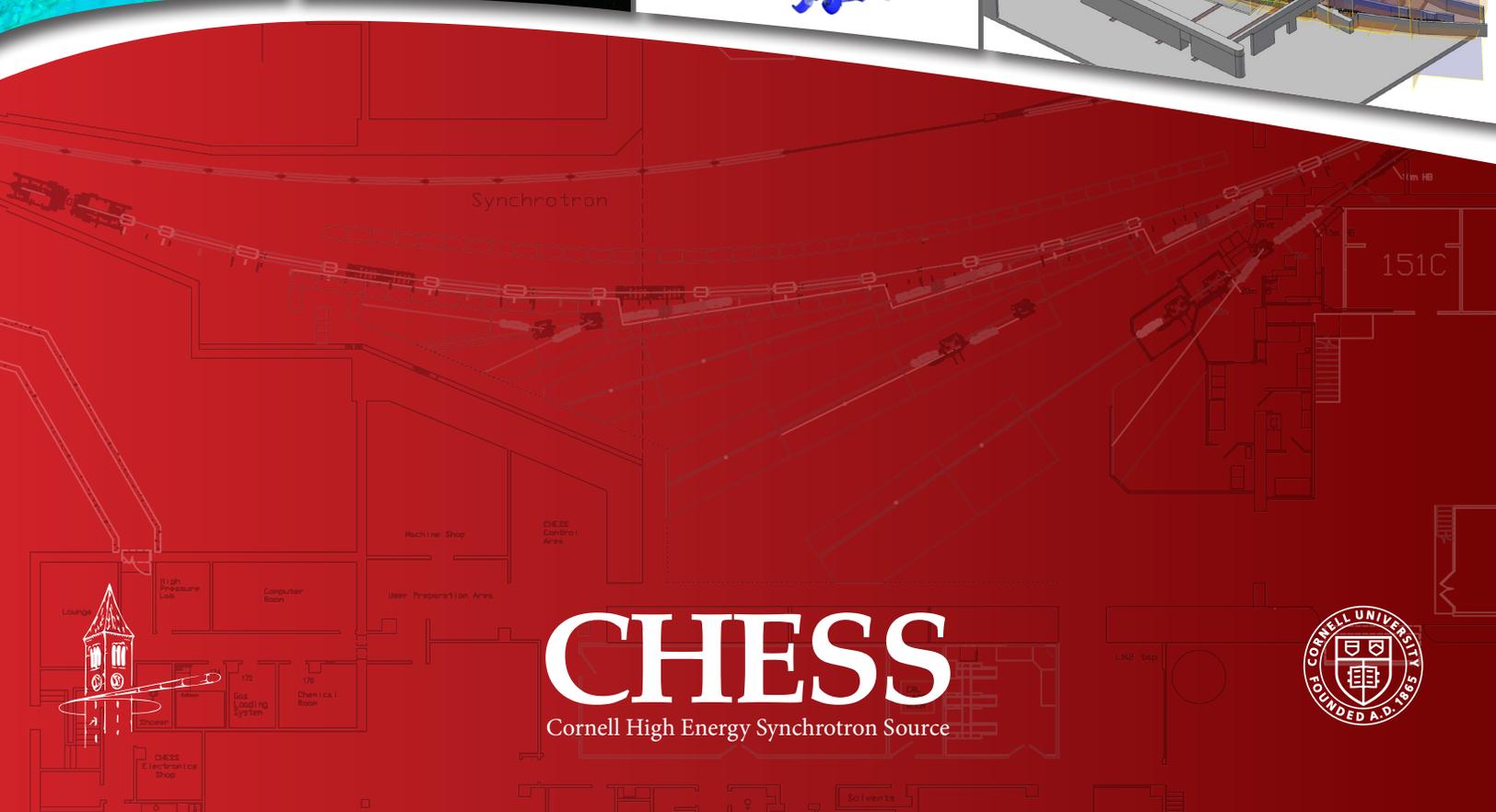
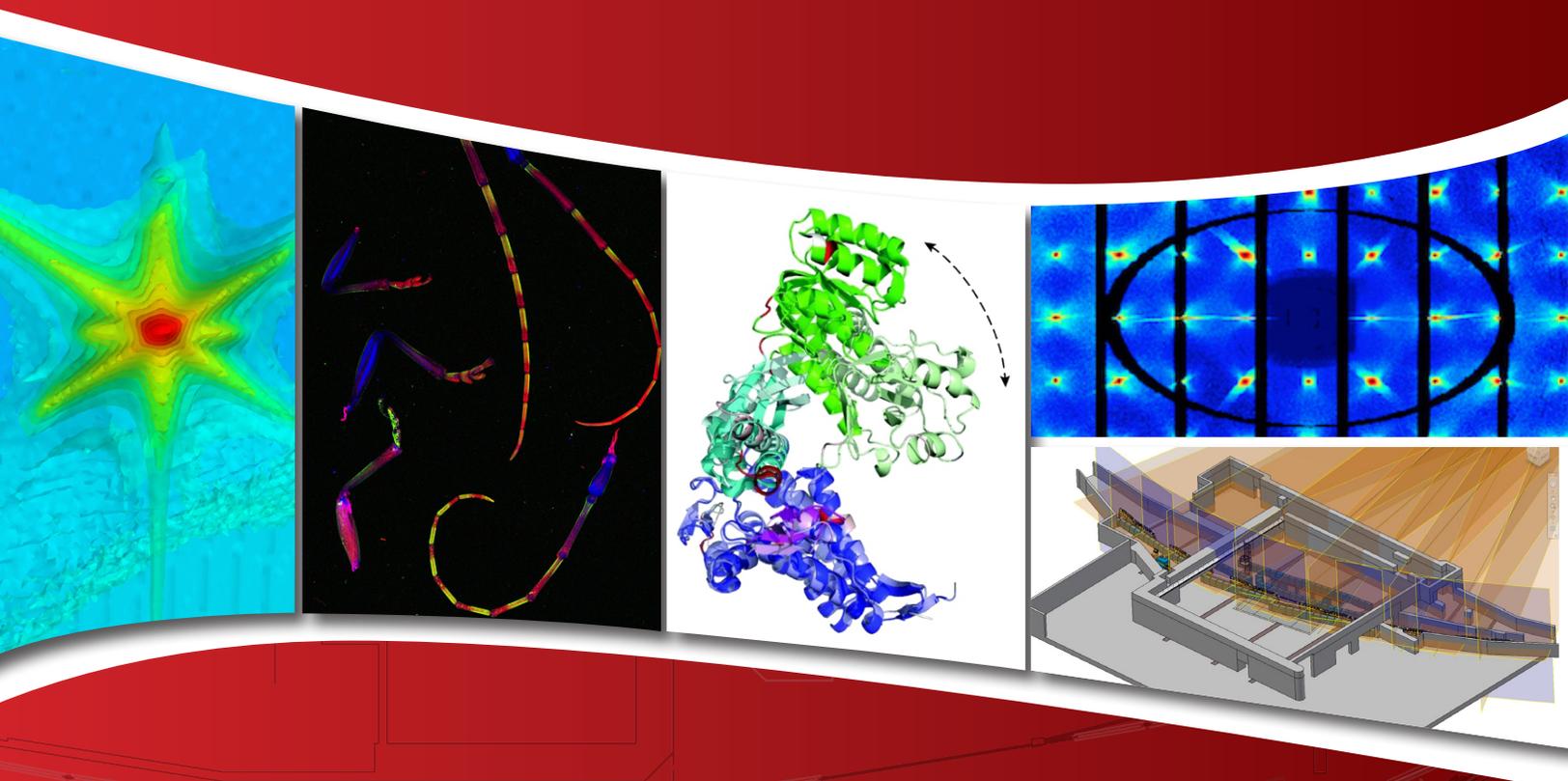


NEW SCIENCE MADE POSSIBLE BY CHESS-U

September 15, 2016



CHESS

Cornell High Energy Synchrotron Source



I. Preface

CHESS-U will generate high-flux, hard (10 keV) and high-energy (>25 keV) 3rd generation synchrotron X-ray beams, as well as high single-shot flux. This document highlights a subset of the compelling opportunities that these exquisite X-ray beams will enable scientists to pursue. It links these opportunities to CHESS-U's capabilities and explains potential impacts on science, technology, and society. The research community identified these and other opportunities at a series of six international workshops held in June 2016.

This document does not describe important ongoing research that will continue to exploit CHESS's existing capabilities. It does not capture CHESS's important roles in developing new synchrotron x-ray technologies and techniques and in training synchrotron users and professionals. It does not provide a detailed plan for designing instruments. It will, however help to establish a scientific foundation that will inform CHESS's strategic planning and investments over the next several years. During the ongoing CHESS planning process, we will balance the scientific opportunities and impact with instrumentation needs, available resources, and infrastructure.

Preparation of this Science Case

In collaboration with its External Advisory Committee (EAC) and Users' Executive Committee (UEC), CHESS organized six workshops on specific scientific topics. Teams of local and external organizers developed speaker lists. In total, the workshops involved 21 organizers, 60 speakers, and 351 participants (in person or virtually). Each workshop generated one or more white papers. The workshop organizers, CHESS scientists, EAC, and UEC identified seven themes from the white papers: structural materials, high-precision plant phenotyping, nanocrystal superlattices, *in-situ* processing of organic semiconductors, atomically thin films and interfaces, catalysts, and disordered materials. The remainder of this document describes each scientific theme. In each theme, CHESS-U plays an indispensable and powerful role in enabling scientific progress.

Table of Contents

I.	Preface	i
II.	Contributor List	2
III.	Executive Summary and Overview.....	3
IV.	Structural Materials.....	9
V.	High-Precision Plant Phenotyping.....	18
VI.	Nanocrystal Superlattices	27
VII.	<i>In-situ</i> Processing of Organic Semiconductors.....	36
VIII.	Atomically Thin Films and Interfaces	45
IX.	Catalysts, Man-Made and Biological	51
X.	Disordered Materials	57
XI.	Technical Overview of the CHESS-U Project	66
XII.	Conclusion	75
XIII.	Appendices.....	78
XV.	References.....	80

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III. Executive Summary and Overview

Over the past 30 years, the intense, highly collimated X-ray beams created by synchrotron X-ray sources have revolutionized X-ray spectroscopy, scattering, diffraction, and imaging. In particular, the hard (10-keV) and high-energy (25- to 150-keV) X-rays delivered by large, high-energy (>5 GeV) synchrotrons have transformed the study of bulk materials. High-energy X-ray beams penetrate deeply into matter, up to many centimeters in organic materials and several millimeters in the transition metals. They enable *in situ* or *operando* studies because they can penetrate complex, bulky sample environments such as tensile mechanical stress testing rigs, high-pressure diamond anvil cells, low-temperature cryostats, and high-temperature furnaces. Perhaps counterintuitively, life scientists who study biological materials also need high-energy X-ray beams to minimize radiation damage to their specimens, which occurs primarily as a result of the photoelectric effect. High-flux X-ray beams enable researchers to study weakly scattering or dilute systems or to conduct time-resolved studies by taking a series of snapshots at short exposure times.

The Cornell High Energy Synchrotron Source (CHESS) is a NSF funded National User Facility located on the Cornell University campus in Ithaca, New York. With 11 experimental stations serving over 1,300 user visits a year, CHESS provides hard and high-energy synchrotron X-ray facilities for academic and industrial researchers from the physical, biological, engineering, and life sciences, as well as cultural specialists such as anthropologists and art historians.

For most of its history, CHESS ran as a parasitic lightsource while the High Energy Physics research program operated the Cornell Electron Storage Ring (CESR) to perform electron-positron colliding beam experiments. The conclusion of the colliding beam experiments in 2008 enabled CHESS to begin in earnest a program to optimize CESR for X-ray production.

The CHESS-U project is the first major effort to upgrade, in concert, both the CESR source and CHESS X-ray beamlines. The project will convert CESR into a single-beam machine with multibend achromat magnet technology and will install undulators as lightsources on all CHESS beamlines. These advances will optimize CHESS instruments to deliver high-flux, high-energy X-ray beams to all researchers. A typical experimental station will focus 10^{13} photons/second/eV into an X-ray spot size measuring 25 μm x 300 μm . Stations with wide-energy-bandpass X-ray optics will deliver hundreds of times more photon flux. Straightforward secondary focusing optics will produce beam sizes from 0.1 to 10 μm .

At the scheduled completion of CHESS-U in December 2018, CHESS will operate 10 independent undulator X-ray beamlines with high-energy capability. Even then, researchers worldwide will have access to high-energy X-ray beam lines only at an elite group of five large synchrotron facilities: CHESS, the Advanced Photon Source (APS) at Argonne National Laboratory, the European Synchrotron Radiation Facility (ESRF) in Grenoble, the Positron-Electron Tandem Ring Accelerator (PETRA-III) in Hamburg, and the Super Photon ring – 8 GeV (SPring-8) in Japan. All these sources have planned upgrades. In the United States, the planned APS-U project complements the CHESS-U project. APS-U is optimizing beamlines and instruments to deliver high-coherence X-ray beams. CHESS-U is optimizing beamlines and instruments to deliver the highest possible X-ray flux from a 6 GeV storage ring.

The remainder of this document describes seven of the many science opportunities that CHESS-U will enable, followed by a brief overview of the technical aspects of the CHESS-U project.

Structural Materials

Engineers who design buildings, airplanes, automobiles, and bridges must overdesign them because the research community lacks an understanding of how structural materials fail. Our understanding of the fatigue behavior of structural materials remains incomplete. We need to learn how fatigue cracks initiate and propagate in structural materials. We need a qualitative understanding of the connections among properties, processing, external loads, and microstructure.

CHESS researchers and our colleagues have developed two new characterization techniques that have opened new windows into the processes by which structural materials deform. *High-energy X-ray diffraction microscopy* enables us to measure non-destructively the microstructure and the micromechanical state of a polycrystalline solid *in situ* as we deform it mechanically. For the first time, we can observe the key characteristics and phenomena associated with polycrystalline structural materials dynamically and in real time as we subject the material to loading conditions that mimic processing or in-service conditions. Synchrotron-based *energy dispersive X-ray diffraction* enables us to measure the strain field as a function of position near locations where fatigue cracks may initiate and grow. The high flux of our high-energy X-ray beam will enable CHESS-U researchers to map residual stress in thick steel components up to 4 cm thick.

Research into structural materials at CHESS-U will enable the scientific community to gain a long-sought quantitative understanding of the interrelationships among properties, processing, external loads, and microstructure. It will enable engineers to design safe structures with optimal microstructure and minimal macro-scale overdesign.

High-Precision Plant Phenotyping

Part of any strategy to produce enough food for 9.6 billion people by 2050 must be to accelerate the breeding of novel climate-resilient food crops with higher nutritional content. The scientific community has sequenced the genomes of 41 food crops. However, we don't yet understand the phenotypes of crop plants well enough to know what anatomical or physiological features we must alter in order to improve nutritional yield and robustness, much less which genes influence which traits.

CHESS-U will optimize a beamline to the study of plant phenotypes by X-ray fluorescence microscopy, fluorescence tomography, X-ray absorption spectroscopy, and phase contrast imaging. This beamline will greatly expand the research community's access to synchrotron X-ray techniques for plant phenotyping. It will enable the research community to image plant structure, elemental distributions, and plant dynamics systematically and routinely.

CHESS-U will support a high-energy end station with phase-contrast imaging and a large field of view. High-energy X-rays penetrate more deeply into materials and thereby allow researchers to study large plants (up to several centimeters thick). They enable researchers to image roots within soils. High-energy X-rays damage biological samples less severely than low-energy X-rays. Furthermore, researchers need a large field of view to image macroscopic regions of plant anatomy. Among U.S. synchrotrons, only CHESS-U is co-located with one of the world's top institutions for plant science.

CHESS-U will enable researchers to quantify phenotypes and match the phenotypic traits to the associated genes and gene variants. Their overarching goal will be to learn how instructions from a single gene or the whole genome, combined with environmental factors, translate into the full set of an organism's phenotypic traits. They will provide plant breeders with new genetic targets in their efforts to strengthen traits such as yield or stress resistance.

Nanocrystal Superlattices

Nanocrystals in colloidal solutions can self-assemble into *nanocrystal superlattices* with long-range order. Nanocrystal superlattices consist of 3D ordered arrays of metallic, semiconducting, magnetic, or insulating nanocrystals. Researchers often refer to these materials as “artificial solids” in which nanocrystals take the place of atoms. Nanocrystal superlattices exhibit not only the size- and shape-dependent properties of their nanocrystal building blocks but also new collective properties that emerge from the optical and electronic interactions among them. Nanocrystal superlattices will expand by orders of magnitude the range of materials that engineers can select to solve any given problem.

A team of CHESS researchers recently developed an innovative technique known as *super-crystallography*, which makes it possible to determine the atomic scale, nanoscale, and mesoscale structures of nanocrystal superlattices with unprecedented spatial resolution. This technique reveals the nucleation, growth, and transformation of nanocrystals within superlattices. CHESS-U researchers will apply this technique and others to address questions such as these: How do nanocrystal superlattices assemble? How does the electronic and optical coupling of nanocrystal superlattices change as a function of nanocrystal size, shape, pressure, and temperature? What symmetries manifest in nanocrystal superlattices with various chemical compositions? How can we controllably increase the size of nanocrystal superlattices to mesoscale and then to macroscale?

To advance the state of knowledge in this field, a research team needs the synthetic expertise to fabricate large nanocrystal superlattices, a source of high-energy synchrotron X-rays, the experimental capability to collect high-energy SAXS and WAXS data simultaneously from the same volume as a superlattice rotates along an axis, and the theoretical expertise and software to analyze the collected data sets. CHESS can provide all those capabilities. Going forward, the high-energy, high-intensity X-ray beam at CHESS-U will enable researchers to analyze small (< 100 μm) crystals of nanocrystal superlattices, nanocrystal superlattices with light elements that scatter X-rays weakly, nanocrystals within processing chambers or reaction vessels, and nanocrystal superlattices that change rapidly as we vary the experimental conditions. We will also take advantage of fast (nanosecond to millisecond), high-dynamic-range detectors developed by Cornell faculty and staff members.

***In-situ* Processing of Organic Semiconductors**

Market research firms and scientific organizations have predicted that the market for organic, flexible, and printed electronics may exceed \$300 billion per year by 2030. To realize this potential, we must acquire a thorough understanding of the processes by which organic semiconductors self-assemble. It will be impossible to design and process high-performance organic semiconductor devices rationally until we elucidate the relationships among processing, microstructure, and electronic properties.

X-ray diffraction with a high-energy, high-flux synchrotron beam is the most effective technique for studying the microstructure of organic semiconductors *in situ* in real time. CHESS-U will optimize a beam line for this application. We will develop a *grain mapping* tool, an instrument that can determine the size, shape, location, and orientation of grains and grain boundaries in organic semiconductors. CHESS-U will support time-resolved studies to reveal the kinetics of structure formation. Researchers will elucidate the self-assembly process and learn to control the ways in which domains nucleate and grow. Researchers will investigate the microstructural impacts of all materials processing techniques in order to acquire a detailed and holistic fundamental understanding. Their overarching goals are to understand and eventually to eliminate all factors that compromise the performance of organic electronic devices.

Atomically Thin Films and Interfaces

Ultra-thin complex oxide films, graphene, and two-dimensional dichalcogenides have demonstrated extraordinary properties. For example, scientists have observed metallic behavior, superconductivity, and ferromagnetism at the boundaries between insulating oxides. Graphene is an excellent electrical and thermal conductor with high carrier mobility and surprising molecular barrier capabilities. Single-layer transition metal dichalcogenides offer interesting and potentially useful electronic, optical, mechanical, and magnetic properties.

These properties depend on the atomic structure of the materials. They also depend on the interplay among strain, temperature, crystallographic phase, and the properties of the substrate. However, it is difficult to characterize these aspects of materials that may be only one or two atomic layers thick. As a result, it is difficult to understand and control the properties of interest.

CHESS-U will accelerate the fundamental studies and the commercial applications of two-dimensional materials. Our advantage in the total intensity of X-ray energy on the sample will enable time-resolved experiments with the shortest possible time intervals. We can achieve this high intensity because of the electron beam characteristics, our multi-layer monochromator technology, and an undulator source.

CHESS-U will enable researchers to measure film thickness, crystalline phase, and strain by X-ray scattering and to measure the atomic composition of films by X-ray fluorescence, all *in situ* and in real time. We will exploit an existing experimental platform that makes it possible to monitor film growth by MBE and by plasma-assisted atomic layer epitaxy. Researchers will identify the growth conditions that optimize the desired structure and the desired properties. We will also collaborate with industry to realize the commercial potential of 2D materials.

Catalysts, Man-Made and Biological

Catalysts facilitate important chemical transformation processes in the chemical, pharmaceutical, petroleum, and power generation industries. However, the research community lacks a mechanistic understanding of how man-made catalysts and biological catalysts operate. We lack the knowledge base that would enable chemists to design highly efficient, highly selective catalysts rationally for any application.

CHESS-U will optimize synchrotron X-ray processes to study catalytic reactions *in situ* under relevant conditions. High-energy, high-flux beams will enable our users to follow study catalysts in different phases (solid and solution) and under a range of relevant operating conditions (e.g., at high pressure, at high temperature, in flowing solutions, and during electrochemistry). High

flux will make it possible to investigate the structural changes of catalysts as they undergo fast reactions. Researchers will determine how their composition and their structure affect their performance. Researchers plan to identify the cycle of intermediate reactions, the bond-breaking and bond-forming steps by which catalysts accelerate various chemical transformations. Researchers will gain an atomic-level understanding of how nature's enzyme catalysts carry out their efficient reactions, then develop design rules for engineering artificial catalysts that approach the activity, selectivity, and efficiency of enzyme catalysts.

Disordered Materials

Correlated microstructural disorder creates the useful properties of many materials, including catalysts, alloys, liquid crystals, oxide superconductors, and relaxor ferroelectrics. We need a robust typology to describe the symmetries and rules of local disordered structures. CHESS-U researchers will address a grand challenge in materials science: to develop a quantitative, robust, and intuitive understanding of the fundamental building blocks of *disordered states of matter*.

To this end, we will optimize a beamline for *diffuse X-ray scattering* studies of disordered materials. Diffuse X-ray scattering generates a broad, slowly-modulated background of scattering that reflects short-range correlations on a spatial scale from several Ångstroms to hundreds of nanometers. In general, researchers have not relied strongly on diffuse scattering experiments for two reasons: first, the diversity of disorder observed in nature has made it difficult to devise universal analysis techniques; second, the research only recently gained access to the required tools, such as computers that can analyze the enormous data sets and detectors that can detect the weak features without being saturated by the strong Bragg scattering.

The beam at CHESS-U will overcome these obstacles. Its high flux will enable us to resolve weak scattering signals. Its high-energy beam will penetrate through bulk crystals and alleviate self-absorption problems, enabling us to collect data over full 360° rotations rather than narrow regions of reflection from the sample surface. As a result, we will be able to standardize the measurement procedure from sample to sample and thereby simplify every aspect of the experiment. Furthermore, CHESS provides a 6-megapixel high-dynamic-range pixel array detector (Pilatus6M) for use on high-energy (> 40 keV) beamlines, as well as an advanced computing infrastructure. This combination of assets is ideal to support diffuse scattering experiments.

Researchers will learn to probe correlated disorder in its various manifestations: structural, magnetic, orbital, spin, electronic, etc. They will learn to measure these properties on microsecond, nanosecond, and even picosecond time scales in order to understand the dynamics of local states. They will learn to control correlated disorder in order to engineer materials with novel functionalities.

Technical Overview of the CHESS-U Project

The goal of the CHESS-U is to upgrade both CESR and the X-ray beamlines. CHESS-U will reconfigure CESR to operate with only a single type of particle, raise the beam energy, increase the beam current, and, within those restrictions, minimize the beam emittance and upgrade or rebuild the X-ray beamlines.

Accelerator Upgrade: The CHESS-U upgrade will improve the quality of the particle beam. It will increase the energy from 5.3 to 6.0 GeV, increase the current from 100 to 200 milliamps,

and reduce CESR's particle beam emittance from the present 100 nm-rad at 5.3 GeV to around 30 nm-rad at 6.0 GeV. We will engineer the lattice to minimize coupling between the vertical emittance and the horizontal emittance. By keeping the coupling below 1%, we will maintain the vertical emittance of the beam below 300 pm-rad. CHESS-U will provide space for up to 10 independently tunable insertion devices that will deliver X-rays to as many as 12 experimental stations.

Beamline Upgrade: The single CHESS-U particle beam will enable us to operate state-of-the-art undulators (X-ray sources). Each beamline will optimize its undulator design for specific types of experiments by taking advantage of either conventional undulators, cryo-cooled superconducting undulators, or the customizable and cost-effective Cornell Compact Undulator (CCU). CHESS-U X-ray optics will generate beams with diameters ranging from 0.1 microns to several millimeters at the sample position.

IV. Structural Materials

Abstract

Synchrotron-based High Energy X-ray Diffraction (HEXD) is changing the way scientists and engineers characterize structural materials. Rather than generating 2D images of microstructure, HEXD experiments produce 3D datasets that describe not only the microstructure but also the mechanical response to loading of every crystal within the diffraction volume. These unique micromechanical data will shed new light on failure mechanisms such as the initiation of fatigue cracks, thus enabling engineers to avoid overdesigning buildings and vehicles. Materials engineers will apply the same understanding to design new lightweight, high-strength materials. The high energy/high flux beams of X-rays at CHESS are perfect for HEXD. The CHESS research community has established a leadership position in developing and applying HEXD methods over the past decade. We have exported our methods and instrumentation to other light sources around the world. The *InSitu* center at CHESS focuses on structural materials and supports a broad range of HEXD experiments and associated micromechanical material models. CHESS-U will enhance the structural materials characterization capabilities at CHESS by providing smaller beams, even greater flux, enhanced material loading capabilities, and larger experimental stations to interrogate both material samples and engineering components. The understanding gained by the HEXD experiments at CHESS will enable engineers to apply known materials more skillfully and materials scientists to develop new materials rationally, rather than by expensive and time-consuming traditional processes of trial and error.

The term “structural materials” refers to metallic alloys, ceramics, composites, and other materials that have to support mechanical loads. Engineers select structural materials to design buildings, airplanes, automobiles, bridges, etc. In some contexts, structural materials must support their loads under demanding conditions: high temperatures, low temperatures, impact forces, corrosive environments such as sea water, etc.

The most important characteristics of structural materials are their mechanical properties: stiffness and strength (yield strength, fracture strength, fatigue strength etc.). To understand the concept of *stiffness* from an engineer’s perspective, think of a spring: the more we load it, the more it stretches. If we plot load vs. displacement, the slope of the plot is the stiffness. *Strength* is the load or stress at which the material fails. A design engineer must determine what loads a structure will experience, and then choose the right materials in the right geometry to assure that it won’t fail under those conditions. Mechanical and structural engineers have been designing structures in this way for centuries.

The problem is that properties originate due to processes that operate on multiple size scales, from the component scale to the atomic scale. Until now, quantitative information regarding mechanical properties such as strength have been available only at the macroscale; hence, neither the industrial engineering community nor the academic research community understands strength with the confidence needed to make sound, physically-based predictions of performance. Instead, we rely on empirical understanding gained by performing mechanical tests on specimens that contain different *microstructures*. For example, we don’t know how a fatigue crack initiates within an individual crystal across the broad range of loading and service environments encountered in service. However, we have quantified fatigue life associated with a particular “picture” of the material microstructure, and we can often estimate the uncertainty of that life. As a result, current analyses associated with mechanical design endeavor to *manage* failure, not to conquer it. We employ an empirical, brute force approach based on *factors of safety*. If a structural engineer determines that a structure is likely to experience a maximum load of X, she

may, limited by the material properties available to her, design that structure to withstand a load of 2X. She designs an object that is twice as large, twice as heavy, and perhaps twice as expensive as it needs to be. She thereby establishes a factor of safety equal to 2. A more complete “multiscale” understanding of the intrinsic response of the material to mechanical loads would enable her to design equally safe structures with less material.

It is essential to develop new high-strength, lightweight structural materials. Engineers have been developing structural materials for centuries via trial and error. In the modern era, the trial-and-error method has become sophisticated; metallurgists study microstructure by imaging techniques based on visible light, electrons, and X-rays. Even so, it is extremely time consuming and expensive to develop and certify a new alloy for an existing component, or even to tune the properties of a known alloy for a new application. It takes longer to develop and qualify a new material than it does to develop a new product. As a result, engineers tend to design new products with materials they know and trust. The Materials Genome Initiative explains the problem in this way:¹

As today’s scientists and engineers explore a new generation of advanced materials to solve the grand challenges of the 21st century, reducing the time required to bring these discoveries to market will be a key driving force behind a more competitive domestic manufacturing sector and economic growth. The lengthy time frame for materials to move from discovery to market is due in part to the continued reliance of materials research and development programs on scientific intuition and trial and error experimentation. Much of the design and testing of materials is currently performed through time-consuming and repetitive experiment and characterization loops.

We find a similar statement in a report from the National Materials Advisory Board’s Division of Engineering and Physical Science:²

Materials are a strategic aspect of engineered products in many different industries, including aerospace, automotive, electronics, and energy generation. Over the years, the development of advanced materials and their incorporation in new products has enabled the United States to maintain a significant competitive advantage in the global economy. Therefore it is a matter of great concern that the materials discipline has not kept pace with the product design and development cycle and that insertion of new materials has become more infrequent. While the materials engineer is a member of the integrated product development team, materials selection and materials design now happen outside the computationally driven design optimization loop. As a result, materials are increasingly becoming a design constraint rather than a design enabler. This shortcoming reduces the potential design space, is a drag on innovation, increases manufacturing risk, and gives customers suboptimal end products.

Driven by such challenges, a *Three Dimensional Materials Science* (3DMS) community has emerged over the past decade. International conferences focused on 3DMS have emerged and have grown sharply in popularity.³ Three dimensional “images” of material microstructure – obtained by either serial sectioning methods combined with electron imaging^{4,5,6} or by HEXD methods – are rapidly becoming the standard for polycrystalline metallic alloy research. CHESS users have elevated HEXD into a prominent position in the field of 3D characterization.

The CHESS-U research community will continue to improve our understanding of failure in structural materials so that engineers can *a)* integrate known materials into structures that are equally safe but much lighter and *b)* develop new lightweight, high-strength structural materials – and in both cases, complete their designs rationally rather than by time-consuming and expensive processes of trial and error. Our work provides the critical data needed to validate models and to establish the links among processing-structure-properties-performance (PSPP). It will facilitate structural design engineers in their drive to reduce certification/qualification times, manufacturing costs, life cycle costs, space requirements, fuel requirements, and environmental burdens. The implications of our work extend to the new industrial process of additive manufacturing, where establishing the connection between manufacturing process variables and product performance is the *sine qua non* of practical implementation.

Summary of the State of Knowledge

The properties of structural materials depend on their elemental constituents and on their microstructures. The *microstructure* consists of all the internal structural entities that affect the macroscopic material properties. For example, the microstructural building blocks of a metallic alloy consist of millions or billions of tiny crystals. The sizes of these crystals can range from 1 μm x 1 μm to 1 mm x 1 mm. Figure 1 shows the microstructure of steel (type ASTM A36).⁷ It contains 20- to 30-micron crystals of ferrite (white) and pearlite (dark).¹ Engineers specify ASTM A36 steel for bridges, buildings, and oil rigs. In turn, the microstructures of the materials depend on the ways in which we process them (e.g, by rolling, forging, welding, additive manufacturing, etc.).⁸

The research community has learned to image microstructures and measure the sizes and shapes of crystals in structural materials via a spectrum of techniques, including three-dimensional methods. We have learned to measure the distributions of the crystals' orientation in space, a necessary task because the crystals are anisotropic (i.e., their stiffness and strength vary with orientation of the atomic planes). We can measure the spatial distribution of the constituent elements, the types and densities of defects, the properties of grain boundaries, and the locations of phase boundaries. We have gained a qualitative understanding of the connections among properties, processing, external loads, and microstructure.

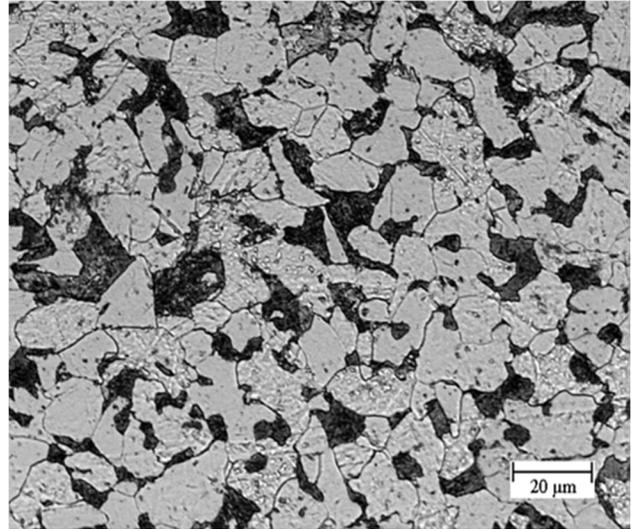


Figure 1: Microstructure of ASTM A36 Steel

¹ Ferrite is a solid solution of iron containing less than 2% of carbon, all in a body-centered cubic crystal structure. Pearlite is a two-phased structure with alternating layers of ferrite (88% by weight) and cementite (FeC_3 with an orthorhombic crystal structure, 12% by weight).

Knowledge Gaps

Materials scientists and engineers have traditionally characterized metallic alloys via 2D image-based experiments pre-loading or post-mortem. For example, Figure 2 shows a fatigue crack through a Ti-6Al-4V (titanium) sample imaged by a scanning electron microscope (SEM).⁹ This beautiful image tells us nothing about the fatigue process that produced the crack. Typically, a researcher would create a “story” about a static image such as Figure 2 to explain how the crack initiated and grew. To understand fatigue crack initiation and growth, we need quantitative, dynamic data that describe the real material response during mechanical loading, not after failure. Over 90% of metallic engineering structures ultimately fail due to fatigue,^{10,11} but we truly do not know how a crack initiates nor how it grows in a material such Ti-6Al-4V.

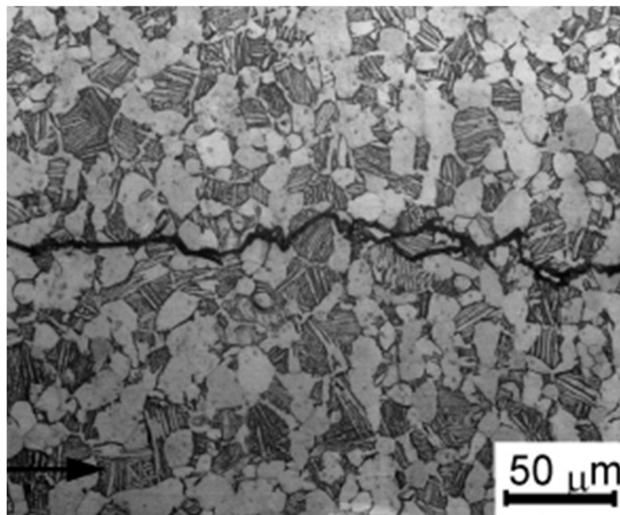


Figure 2: Microstructure of Ti-6Al-4V Alloy with a Fatigue Crack

Residual stress (the stress that remains within structural materials after processing and before loading) is another important quantity to understand for mechanical design. Models of structural materials require accurate estimates of residual stress as their inputs in order to predict accurately the lifetimes and failure mechanisms of bridges, buildings, and other structures. Without a confident estimate of the residual stress, rendered by a physically-based model that is validated by experiment, the design engineer relies on the conservative assumption that residual stress may approach the intrinsic strength of the material. This assumption leads him to increase the factor of safety, add more weight, and compromise efficiency. Researchers have approximated residual stress via diffraction methods for decades, but never with the level of fidelity necessary for design. We have recently developed the tools that make it possible to measure residual stress within structural materials with good enough spatial resolution and fidelity to be useful to structural designers.¹² High-energy x-ray synchrotron radiation enables us to map residual stress in a practical engineering component.

The next step in the progression of our knowledge will be to gain a quantitative understanding of the connections among mechanical properties, processing, external loads, and microstructure so that scientists and engineers will be able to predict the properties of a material with a given elemental makeup and microstructure, or to design and process a material that can operate safely under specific loading conditions. To understand how materials deform, the research community will develop and apply models. To validate the models, we need data. Researchers will rely on CHESS-U’s capabilities for advanced X-ray characterization of structural materials.

New X-ray Techniques With Which the CHESS-U Research Community Will Characterize Structural Materials

CHESS-U researchers will accelerate progress in the science of structural materials via two emerging HEXD characterization techniques, one using X-rays at a single wavelength

(*Monochromatic High-Energy X-Ray Diffraction*), the other applying polychromatic or white X-rays (*Energy-Dispersive X-Ray Diffraction*). These two techniques place us at the dawn of a new age of discovery science in terms of our ability to understand metals and alloys and to blend experimental data with sophisticated models of behavior.

Monochromatic High-Energy X-Ray Diffraction Microscopy

Recent developments in experimental HEXD techniques and allied analysis procedures have led to a revolutionary new technique known as Monochromatic High-Energy X-ray Diffraction.¹³ MHEXD opens an unprecedented real-time window into the *in situ* processes on a grain-size length scale by which structural materials deform.¹⁴ In an MHEXD experiment (Figure 3), a small (hundreds or thousands of microns square) monochromatic X-ray beam passes through a polycrystalline sample and diffracts from suitably oriented lattice planes. The apparatus rotates the sample with the aid of a precision diffractometer in order to probe the entire diffraction volume.¹⁵ A near-field detector placed millimeters from the sample collects data that enable us to map the *grain morphology* and the *intra-granular crystallographic orientations*. A far-field detector placed ~1 meter from the sample collects data that are more sensitive to the geometry of the unit cell. The evolution of “far-field” diffraction patterns reveal *changes in the distribution of orientation and strain within the polycrystalline sample*. HEXD can capture diffracted X-rays from an evolving polycrystal many times each second during loading to quantify the progress of deformation.

MHEXD is giving the research community our first opportunities to probe the internal state of polycrystalline solids while we subject them to external stimuli.¹⁶ This pathbreaking development is enabling us to measure non-destructively the microstructure and the micromechanical state of a polycrystalline solid *in situ* as we deform it thermo-mechanically. For the first time, we can observe the key characteristics and phenomena associated with polycrystalline structural materials – e.g., the three-dimensional grain structure, the crystallographic orientations with sub-grain resolution, the elastic strain state of individual grains or individual layers of grains, and the formation of voids and cracks – dynamically and in real time as we subject the material to loading conditions that mimic processing or in-service conditions.

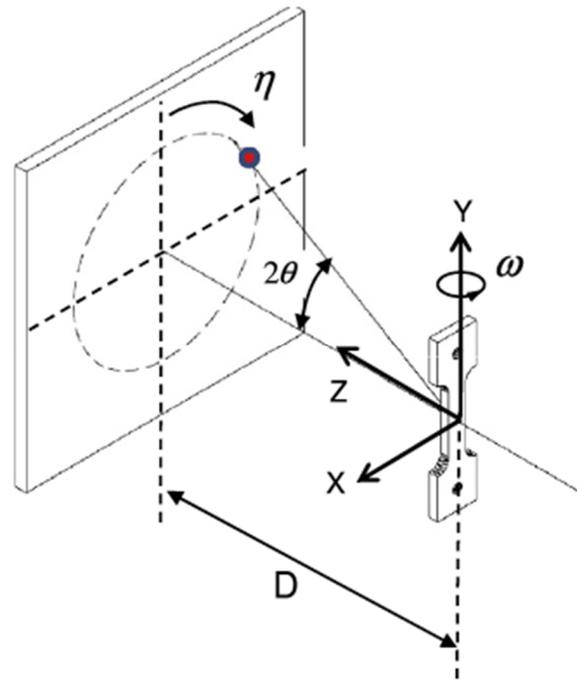


Figure 3: Schematic Diagram of Monochromatic High-Energy X-Ray Diffraction Microscopy

Only MHEXD can provide real time, quantitative, three-dimensional data for a process such as fatigue crack growth. Figure 4 contains images taken in real time from the fracture surface within Ti-55531 (another titanium alloy).¹⁷ The researchers interrupted a fatigue crack growth experiment periodically to conduct an HEXD experiment combined with computed tomography. They thereby obtained not only the crack growth rates but also the underlying crystal orientations and stress states.

Figure 5 shows a full 3D grain map of 316L austenitic stainless steel¹⁸ measured *in situ* at the CHESS F2 beamline with detail revealing (b) grains that have a special crystallographic relation (twins) and (c) the boundary between two neighboring grains.

MHEXD will help us to understand the kinetics of plasticity (the term *plasticity* refers to the deformation of a solid that is irreversibly changing shape in response to mechanical forces). For example, alloys with hexagonal close packed structures have different slip modes, and the rate of slippage as a function of strain likely varies from slip mode to slip mode.¹⁹ MHEXD will enable us to discriminate among different slip modes and to measure how the deformation under each mode varies as a function of an applied force.²⁰ At any given point in the material, MHEXD will enable us to measure the *strain and rotation of the atomic lattice structure*. It will enable us to characterize the interactions between adjacent parcels of the material over time and in response to a given mechanical force.

MHEXD is also enabling us to validate modeling techniques with experimental data. Over the past 50 years, scientists have developed many physics-based models that describe the responses of structural materials to deformation processes over many length scales. Practicing engineers rarely apply these multiscale models because a lack of experimental data has made it difficult or impossible to validate them. MHEXD provides

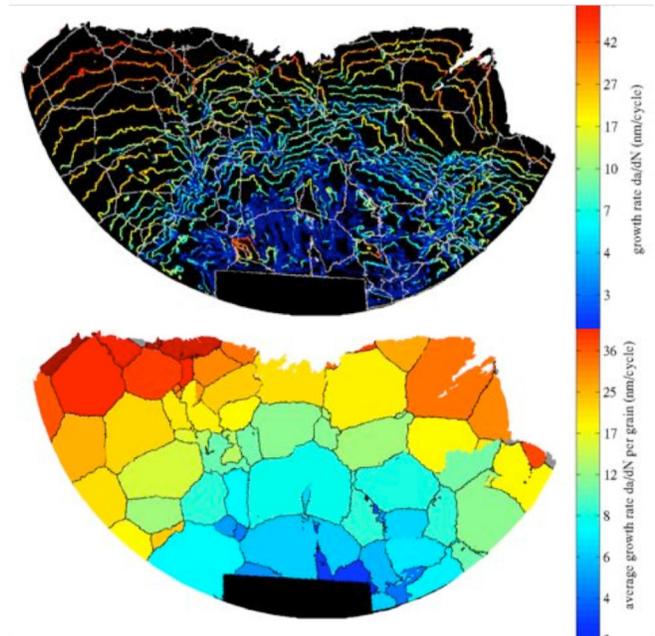


Figure 4: Crack growth rates in Ti-55531, a BCC titanium alloy measured via Diffraction Contrast Tomography, an HEXD technique. The top figure shows local rates. The bottom image depicts grain-averaged rates.

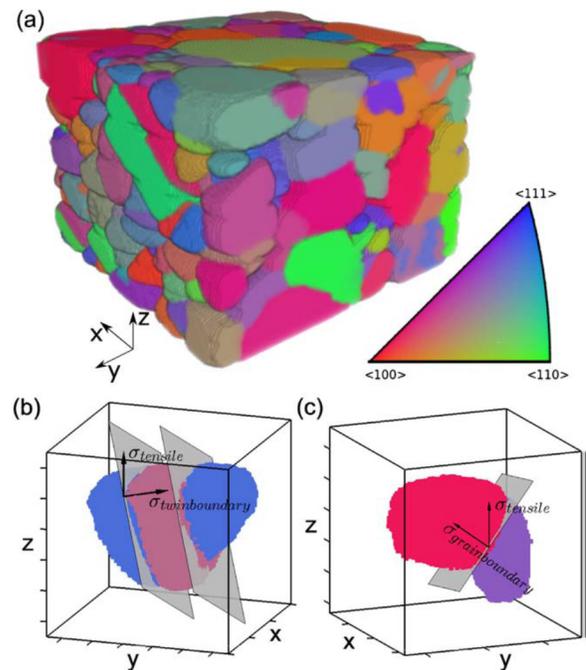


Figure 5: 316L Austenitic Stainless Steel: Full 3D Grain Map Acquired *In Situ* by HEXD

data from the Ångstrom to the millimeter. These data give us the unprecedented and powerful ability to validate, from the microscale to the macroscale,²¹ modeling techniques such as crystal plasticity finite element modeling.^{22,23} MHEXD enables us to test the accuracy of these models at the length scales where they predict the response.²⁴ The models will then allow materials scientists and engineers to understand the mechanical performance of known structural materials and to accelerate the development of new ones. The timing is opportune for this pursuit: computational power and MHEXD experimental techniques are both enjoying rapid development.

In August of 2016, the National Science and Technology Council called out the development of HEXD in its report on the Materials Genome Initiative's 5th Anniversary Accomplishments.^{25,26}

Researchers from AFRL, ANL, Lawrence Livermore National Laboratory (LLNL), Carnegie Mellon University, Petra III (Germany), PulseRay, and Cornell University have developed a revolutionary way of using high-intensity x-rays to measure the detailed structure of a material while it is being bent, compressed, or stretched. The measurement method provides new insights into how materials fail—insights that are critical for creating more accurate models needed to rapidly optimize, predict and improve the performance of light-weight, high-strength materials for aircraft and automobiles.

Energy Dispersive X-Ray Diffraction

Synchrotron based energy dispersive X-ray diffraction (EDXRD) is emerging as a complementary technique to MHEXD for analysis of residual stresses, particularly in large or complex parts. In EDXRD, an undulator provides an intense and collimated ‘white’ beam source which, when used in conjunction with an energy resolving detector, makes it possible to detect many Bragg lines simultaneously.²⁷

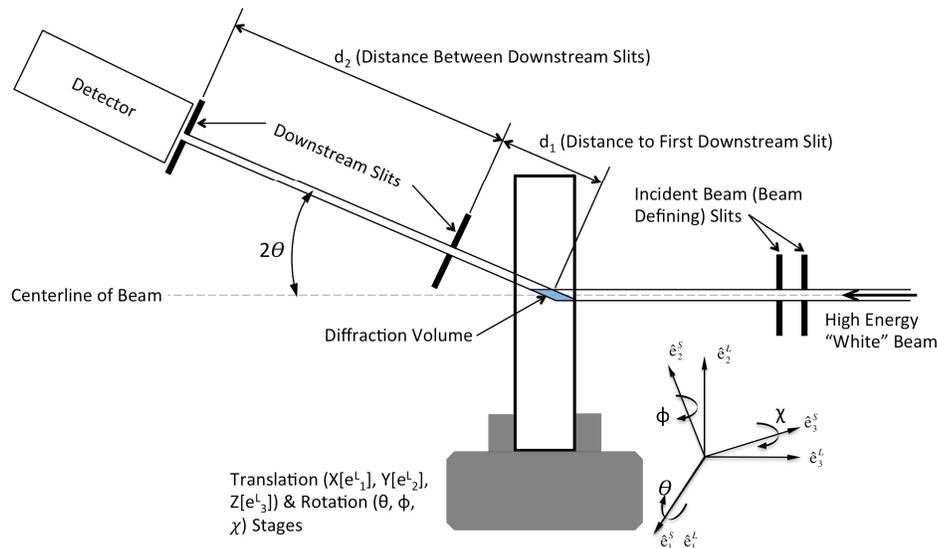


Figure 6: Schematic of Energy-Dispersive X-ray Diffraction (EDXRD) Apparatus

As shown in Figure 6,²⁸ an intense beam of X-rays with energies between 30 and 150 keV enters from the right. Slits narrow the incident beam and the diffracted beam, thereby defining the gauge volume, shown in blue. A micro-positioning x-y-z stage sweeps the specimen through the

gauge volume. An energy-dispersive Ge-detector collects the EDXRD spectra. Data from a transmitted beam detector enable the system to construct a radiographic profile, which in turn makes it possible to position the sample precisely relative to local structures. The system can then measure strain field as a function of position near locations where fatigue cracks may initiate and grow. It can measure gradients in the strain field as the stage sweeps the target volume through the beam. A variation on the EDXRD technique makes it possible to construct 2D and 3D tomographic images that reveal voids, cracks, and crystal structures, all of which are key components needed to build accurate constitutive models.

Taken together, EDXRD and MHEXD are giving the research community new capabilities for three-dimensional profiling of residual stress.²⁹ Figure 7, courtesy of the Caterpillar Corporation, shows an experimental apparatus at CHESS A2 to measure residual strain in a carburized ring sample to characterize a heat treatment process. Accurate measurements of residual stress will enable engineers to avoid overdesigning structures at high costs and also enable researchers to initiate their models correctly.

Advantages of CHESS-U

Data from MHEXD and EDXRD have begun to validate models that provide the foundations for the *Materials Genome Initiative* and for *Integrated Computational Materials Engineering*. The demand for MHEXD and EDXRD is increasing. CHESS and APS 1ID, the only two user facilities that offer MHEXD and EDXRD, are already oversubscribed. As a result, scientists who qualify to apply these techniques at CHESS and APS have limited access to beamtime. It is therefore important to learn the techniques quickly and to implement them successfully the first time. Since Cornell is a university that offers workshops and training, CHESS serves as part of the educational infrastructure for developing users of MHEXD and EDXRD.

The wide beam at CHESS-U will give us the unique capability to conduct MHEXD and high-energy computed tomography (HECT) experiments simultaneously. Researchers will combine these techniques to gain information about the topology and the evolution of voids, cracks, and important interfaces. High-precision registration of the MHEXD and HECT data will provide a comprehensive picture of crystal structure, stress, and damage within a deforming polycrystalline material.

MHEXD and EDXRD are evolving from the development stage, in which we have looked at model materials, to the practical stage, in which we are beginning to look at real engineering materials and components. Sample handling capabilities at CHESS-U will support the practical study of relatively large engineering components critical to building the bridge between discovery science and practical application to structural design and manufacturing. The high flux

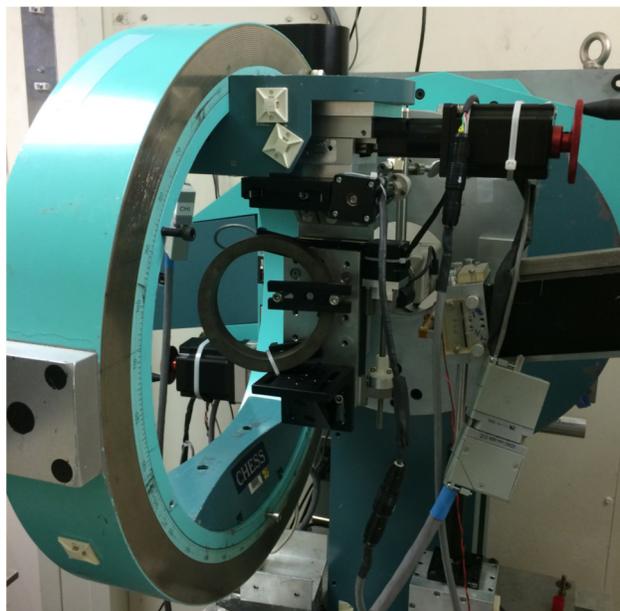


Figure 7: Measurement of Residual Strain in Carburized Ring Sample at CHESS A2

of our beam will give CHESS-U the unique capability to map residual stress in steel components up to 4 cm thick via EDXRD. Our research community will measure stress and stress gradients in engineering components *in situ* at multiple scales under load.

Fast detectors with high dynamic range (such as the Mixed-Mode Pixel Array Detector), combined with high-temperature *in situ* testing facilities (such as the Rotational and Axial Motion System), will enable the CHESS-U research community to study slip-system-dependent rate sensitivity at temperatures and stress states that are relevant to applications. We need detectors with high speed because the strain transients developed under changing loads occur on the order of milliseconds. We need detectors with high dynamic range because information in the evolving dislocation structure appears in both the strong and weak parts of the signal.

Impact of CHESS-U

CHESS-U will advance the mission of NSF's initiative entitled Designing Materials to Revolutionize and Engineer Our Future (DMREF):³⁰

DMREF will support activities that accelerate materials discovery and development by building the fundamental knowledge base needed to design and make materials with specific and desired functions or properties from first principles. This will be accomplished by understanding the interrelationships of composition, structure, properties, processing, and performance. Achieving this goal will involve modeling, analysis, and computational simulations, validated and verified through sample preparation, characterization, and device demonstration.

The *InSitu* (Integrated Simulation and X-Ray Interrogation Tools and Training for μ -Mechanics) center at CHESS supports structural materials research. The mission of *InSitu* is to understand and model the crystal-scale behavior of engineering alloys. The principal tools at *InSitu* are MHEXD and finite element-based polycrystal modeling (FEpX). Recently, the Office of Naval Research has provided funding for *InSitu* to help industrial engineers apply these techniques productively for analysis and design. *InSitu* will continue to manage CHESS-U's research relationships and technology transfer relationships with Caterpillar and other companies. It will also coordinate our collaborations with academic scientists and with representatives of government research labs such as the Air Force Research Laboratory, Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Sandia National Laboratories, and the National Institute of Standards and Technology.

CHESS-U will enable the research community to gain a long-sought *quantitative* understanding of the interrelationship among properties, processing, external loads, and microstructure. It will allow us to measure stress quantitatively throughout the volumes of structural materials. The high-energy, high-flux beam at CHESS will make it possible to collect data necessary to verify and qualify sophisticated models of structural material behavior. Software suppliers will then develop new simulation tools that integrate these models with computer-aided design software. The new computer-aided design software will enable engineers to design safe structures with optimal microstructure and minimal macro-scale over-design. The models and the integrated software will also help researchers to develop new lightweight, high-strength structural materials.

V. High-Precision Plant Phenotyping

Abstract

About 30% of the human population lacks adequate nutrition. Population growth and climate change will exacerbate this problem. New crop varieties with enhanced resistance to pests, droughts, floods, diseases and, especially, enhanced nutrient content, must become part of the solution. Plant biologists have sequenced the genomes of at least 41 food crops, but the research community's understanding of the link between a plant's genetic sequence and its observable traits – collectively referred to as its phenotype – lags far behind. As a result, it is difficult to know what genes to modify in order to increase the nutritional value and the robustness of food crops. Our overarching goal is to discover how instructions from a single gene or network of genes, combined with environmental factors, translate into the full range of phenotypic traits of an organism. Synchrotron-based x-ray microscopy will support systematic studies of plant phenotypes and help researchers to associate them with genotypes. High-flux, high-energy beams will make CHESS-U an ideal location to address three aspects of plant biology: 1) mineral distribution and mineral ligand environment, 2) genetic and environmentally-induced structural changes, and 3) the interplay between structural changes and mineral distribution, all at organ, tissue, and cellular scales. CHESS-U will have broad impact on worldwide efforts in plant genetics and breeding and hence on the urgent problem of global food security in the 21st century.

Today almost 800 million people lack access to enough food to conduct active and healthy lives.³¹ Micronutrient malnutrition constitutes one of the most serious nutritional disorders, with serious impact on global health.^{32,33} Iron-deficiency anemia affects over 30% of the world's population and causes 0.8 million deaths per year, primarily in poor populations across the globe.^{34,35} Zinc deficiency is similarly common.³⁶ Rice and other cereals can satisfy daily caloric needs, but these grains are inherently low in Fe and Zn, particularly when grown in nutrient-poor soils. Climate change, decreasing agricultural land resources and population growth will exacerbate these problems. The Grand Challenge of Agriculture is to produce enough food and nutrition for 9.6 billion people by 2050³⁷ with less water³⁸ and less energy³⁹ than today, and to do so sustainably.

To address this challenge, we must breed new crops that can provide higher yields and higher nutritional content, not only in soils cultivated today but also in marginal soils under increasingly extreme environmental conditions. Breeding requires in-depth understanding of a plant's *genotype* – the genetic instructions encoded in its DNA – as well as its *phenotype* – the vast number of physical and functional traits of a plant that result from both its genotype and environment.⁴⁰

To achieve these goals, the scientific community has acquired a broad understanding of plant genomics. In 1998, the *Interagency Working Group on Plant Genomics*, represented by USDA, DOE, NIH, NSF, OSTP, and OMB, formed the *National Plant Genome Initiative*, a research program targeted to discover the structures and functions of plant genomes.⁴¹ The research community sequenced the *Arabidopsis*⁴² and rice⁴³ genomes by 2005 and the entire genomes for at least forty-one crops in the decade that followed.⁴⁴

The next step is to apply this genetic understanding to breed more nutritious, more robust crops. Efforts to do so must confront two related challenges. The first challenge is to explain the mechanisms by which plants carry out their many functions. The only direct information a genotype provides is knowledge of what proteins it can produce. A genotype does not describe how those proteins interact to determine the many traits and characteristics of a plant's

phenotype, such as how a plant will grow, absorb nutrients and toxins, fight disease, and reproduce.

A second challenge, then, is to identify and catalog plant *phenotypes* over the vast range of plant varieties in a manner useful to geneticists and breeders. The research community has only recently begun to address this problem systematically. Relative to genotyping and plant genome sequencing, plant phenotyping has progressed slowly, creating a *genotype-to-phenotype gap*. We don't understand the complex phenotypes of crop plants well enough to know which anatomical or physiological features we should change in order to improve nutritional yield and robustness, much less which genes influence which traits. We understand little about how diverse plant phenotypes interact to influence yields, nutrition, and tolerance to drought, flood, and pests. The next steps are to quantify structural and functional phenotypic variation at the cellular, tissue, organ and whole plant levels and to associate measureable phenotypic variations with genotypic variations observed at the sequence level.⁴⁵

Plant phenotypes encompass a large variety of behaviors, properties, and parameters, any of which may interest plant breeders. Many of these characteristics do not require sophisticated technology to measure. The research community has initiated a large effort to develop rapid phenotyping techniques for use in the field. However, many other phenotypes, such as those related to cell- and tissue-scale function, or transport and control of nutrients and toxins, require advanced characterization tools. An important technical barrier to rapid progress in plant phenotyping is the absence of optimal tools, or the lack of access to optimal tools, for studying plant phenotypes.⁴⁶

X-ray-based probes offer several advantages for plant phenotype studies:

- X-rays transmit through air, making it possible to simplify sample preparation techniques and to study hydrated or even live samples.
- X-rays can directly map the distributions of many elements, without staining or other sample preparation.
- X-rays penetrate bulk materials, making it possible to gain 3D information.

In addition to these inherent features, advances in x-ray methodologies, instrumentation, and availability have dramatically increased X-ray-based plant studies. In preliminary experiments, synchrotron-based X-ray investigations have emerged as key enabling technologies for plant phenotyping.⁴⁷ This document illustrates the state of the art of X-ray-based plant imaging tools and shows how CHESS-U can improve both their capabilities and their availability.

The State of the Art: Synchrotron-based X-ray Imaging of Plants

X-Ray Fluorescence Microscopy

One of the most important priorities for plant phenotyping is to study the distribution of the elements (ions) within a plant. For example, within the wheat grain, Fe, Cu and Zn reside mainly in the aleurone layer and embryo, which are lost during milling.^{48,49,50,51} It is critical to understand how nutrients are taken from the roots, transported to the body of the plant, then localized in specific cells, tissues and organs. Even further, we must understand how these nutrients participate in internal signaling, support the functioning of proteins, and maintain the proper osmotic and electrochemical potential necessary for the life of the plant.^{52,53,54,55}

Synchrotron X-ray fluorescence microscopy (SR-XRF) probes the location of elemental distributions in a heterogeneous sample and can therefore measure directly the distributions of metal nutrients in a plant. In this method, a focused X-ray beam, typically between 0.1 and 10 microns in size, scans a sample in a raster pattern. Detectors collect the secondary emission (x-ray fluorescence) from the sample and resolve the emission into a spectrum, which we can analyze to determine the concentration of elements at each position on the sample.⁵⁶ The spatial resolution of the image depends on the size of the incident beam. SR-XRF makes it possible to create 2D images of quantitative elemental distributions across the sample at concentrations of 1 milligram per kilogram and below.^{57,58,59} For example, researchers have relied on this approach to obtain the distributions of P, S, K, Ca, Mn, Fe, Ni, Cu, and Zn in rice^{60,61} wheat, mycorrhizal plant roots, and fungi.⁶² By combining XRF microscopy with X-ray absorption spectroscopy, it is possible to speciate an element at points of interest within the 2D map.⁶³ These studies reveal critical information such as the toxicity of metals in the plant and the mechanisms by which plants transport nutrients.

X-Ray Fluorescence Studies of Genotype Control of Elemental Distributions in Arabidopsis Seed

Researchers have begun applying X-ray fluorescence microscopy to understand precisely how plants control and organize the distributions of nutrients.^{64,65} In Arabidopsis, for example, a family of proteins called endomembrane cation exchangers (CAXs) transports Ca^{2+} and other cations. However, the research community lacks a detailed understanding of this and related transport activity. In one study, researchers applied SR-XRF to observe how genetic modifications in the activity of different CAX proteins altered the distribution of metals in the seed of the plant.⁶⁶ Figure 1, in which brighter colors indicate higher concentrations of Mn, Fe, and Zn, shows a clear difference in both the Fe and Mn distributions between the “*cax1cax3*” genetic variant of Arabidopsis and the wild type. From these data, researchers obtain specific, mechanistic insight into how proteins CAX1 and CAX3 localize Mn within the seed. This work relates directly to the challenge of genetic biofortification.

Measurements of Toxic Metals in Crops by SR-XRF

Arsenic, a human carcinogen, contaminates soils and groundwater worldwide, particularly in south and southeast Asia.⁶⁷ To reduce arsenic contamination in rice grains, researchers must understand the basic mechanisms that govern arsenic accumulation in rice. One research group tested the hypothesis that Fe plaque around rice roots limits the uptake of arsenic.⁶⁸ They studied rice roots with synchrotron X-rays via X-ray fluorescence imaging, XANES, transmission X-ray microscopy, and tomography. They discovered that in roots covered with Fe

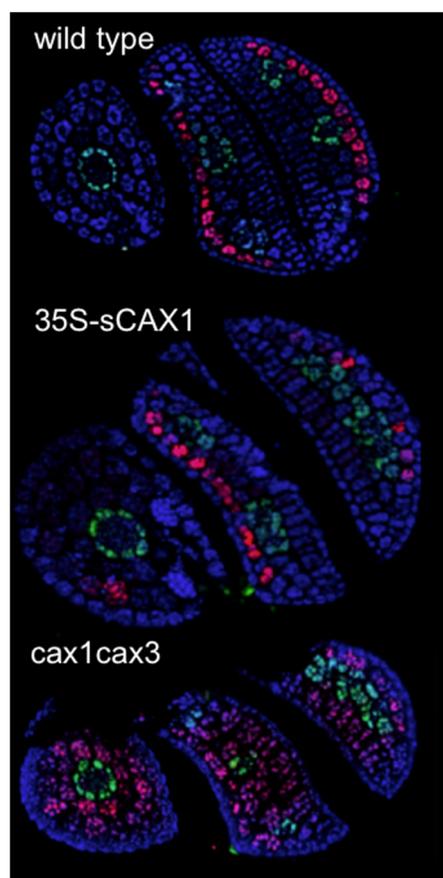


Figure 1: XRF Images of the Distribution of Mn (red), Fe (green), and Zn (blue) in three genetic variants of Arabidopsis Seed.

plaque, As(V) is strongly collocated with the plaque. An exterior coating of arsenite covers the plaque and the As(V). However, they also found As(V) on the interior of the roots. The research team concluded that Fe plaque serves as a bulk scavenger of As, predominantly near the root base, but it does not directly restrict nor intercept the uptake of arsenic by rice roots. Furthermore, Fe plaque does not coat young roots or younger portions of mature roots. In the absence of Fe plaque, As(V) and As(III) confronting rice roots find few barriers to entry.

X-Ray Fluorescence Tomography

2D XRF maps typically require thinned samples, which exact costs in time and efficiency and can also limit the scientific questions we address.⁶⁹ XRF-tomography, a 3D technique, overcomes this limitation. In this method, we collect data in much the same way as in 2D-XRF, except we rotate the sample by 180 degrees at each lateral position of the spatial scan. This approach generates an image corresponding to a complete 2D slice of an unthinned sample. Figure 2 illustrates the capability of fluorescence tomography to examine metal uptake in *alyssum murale*, a nickel hyperaccumulator.⁷⁰ It maps region-specific metal concentrations (micrograms per gram) for nickel, zinc, and iron in cross sections of the leaf, the stem, and the root.

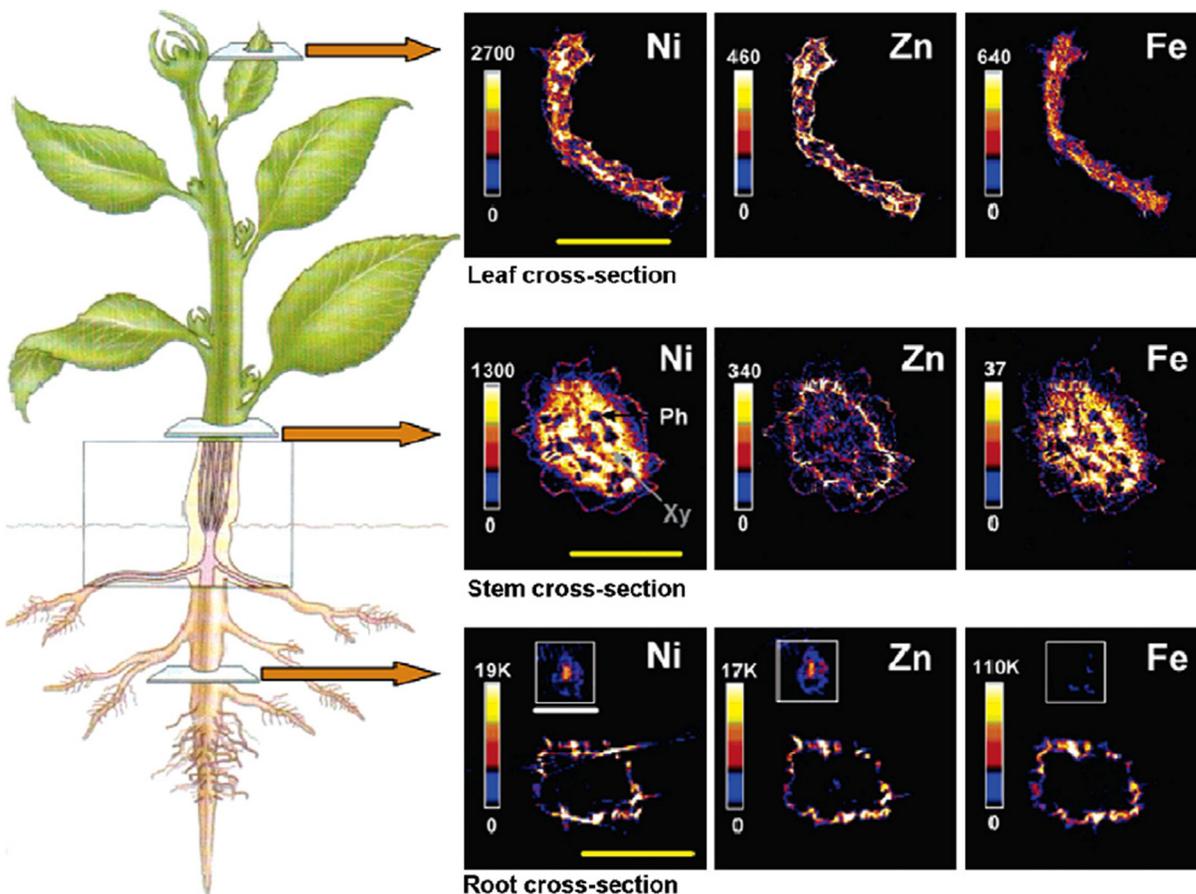


Figure 2: Nickel, Zinc, and Iron Fluorescence Computed Microtomography Images of Leaf, Stem, and Fine Root Cross Sections from *Alyssum Murale*

X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) exploits the absorption of X-rays at energies near the electron core-level binding energies characteristic of a given element. A full XAS spectrum typically incorporates measurements of X-ray absorption near-edge structure (XANES) and X-ray absorption fine structure (XAFS). XANES can measure the oxidation state of a given atom and also identify the atomic species of its nearest neighbors. XAFS studies identify the local structure of a given atom, including its coordination number, the interatomic distances, and the degree of local disorder. Plant biologists have studied the speciation of arsenic in the fronds of the fern *Pteris vittata* via XANES and discovered that it accumulates in the fronds as As(III). XAFS spectra showed that the plant can store arsenic in the leaf vacuoles.^{71,72}

XAFS can assess the ligand environment of the mineral and thereby help to evaluate the bioavailability of minerals for human diets. For example, in grains of cereal crops, only a small fraction (5–10%) of Fe and Zn is bioavailable in human diets because these minerals form complexes with phytic acid, a strong chelator of metal ions.⁴⁸ Therefore, we must not only increase the concentration of these minerals in the endosperm rather than the aleurone layer but also increase their bioavailability by enriching grains with other Fe ligands such as nicotianamine or organic acids. XAFS will facilitate our efforts to isolate crop genotypes with increased mineral bioavailability in grains.

Phase Contrast Imaging

Phase contrast imaging (PCI) exploits the *refraction* of X-rays. Synchrotron-based phase contrast imaging (SR-PCI) is emerging as a fast, minimally invasive way to visualize the complex internal structures of plants.⁷³ At X-ray energies greater than 5 keV, the phase signal from low-density material exceeds the absorption signal by about 3 orders of magnitude.^{74,75} The earliest SR-PCI studies of plants focused on dried parts and artificial soils.^{76,77}

A more recent investigation showed that SR-PCI achieves higher resolution than X-ray absorption in images of the cotyledon and stem of a 10-day-old canola plant (see Figure 3).⁷⁸

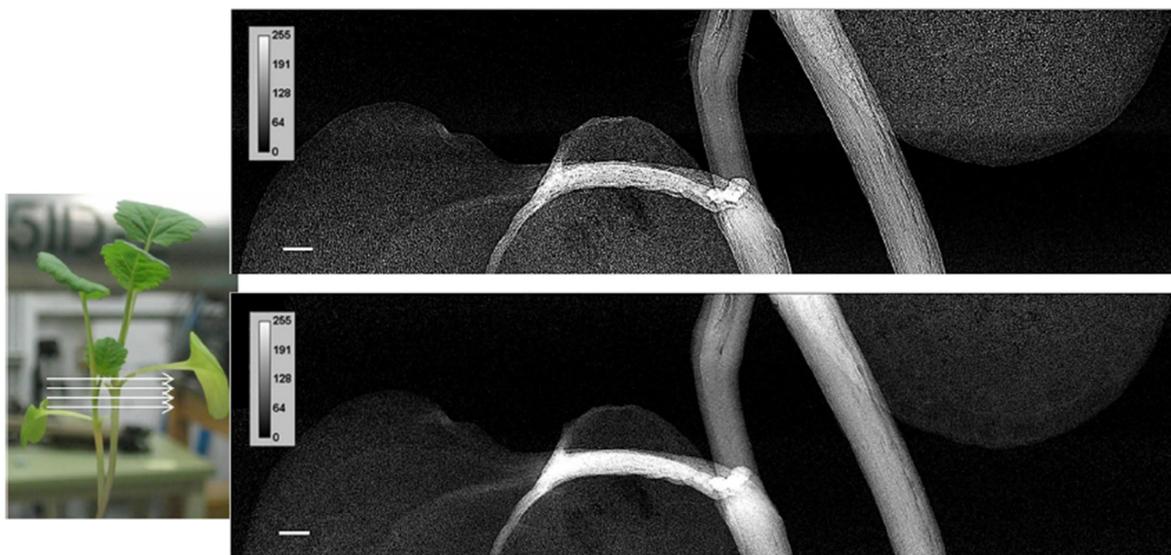


Figure 3: Images of Canola Plant via SR-PCI (top) and X-ray Absorption (bottom)

Figure 4 below confirms that the SR-PCI images (A and B) display individual vessels in the canola stem with higher resolution than the X-ray absorption images (C and D). The SR-PCI images also display more clearly not only the cavitation (marked by red arrows in Figure 4B) in the vessels but also the structures that connect the vessels. These studies identified 18 keV as the optimal X-ray energy, 8.75 microns as the optimal pixel size, and 85 centimeters (the maximum travel range of the sample table in this particular beamline) as the optimal sample-to-detector distance for imaging plant seedlings. The authors pointed out that “the beam parameters used in this work can be improved by beamlines optimized for plant research.” The low radiation dose absorbed by the samples may allow future longitudinal studies in which researchers image the same living plant in a series of time-separated exposures.

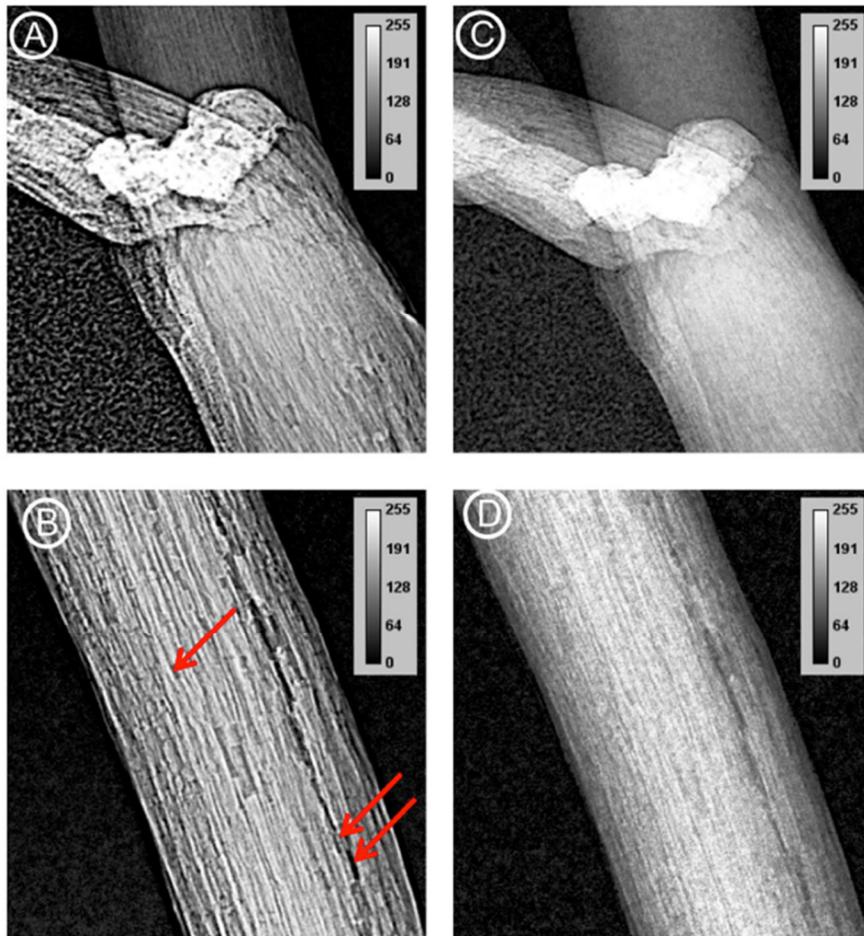


Figure 4: X-Ray Phase Contrast Images (A and B) and X-ray Absorption Images (C and D) of Canola Cotyledon and Stem

Opportunities for High-Resolution Plant Phenotyping at CHESS-U

To offer new opportunities and methodologies for the study of plant phenotypes, CHESS-U will focus on several related goals:

- Tailor the CHESS-U beamline layout and optics for plant imaging. For example, users will be able to select beam sizes from 1 micron to over 1 cm and select beam energy from 6 to 60

keV. These settings will enable the beams to support both X-ray fluorescence microscopy and phase contrast imaging at multiple spatial scales, as dictated by the scientific question at hand.

- Develop confocal X-ray fluorescence microscopy (CXRF) to allow direct 3D imaging and XAS on live and/or extended samples, such as plant leaves, roots, and stems.
- Develop plant husbandry and capabilities *on-site*, as well as environmental control capabilities at the beamline, allowing researchers new opportunities to study whole plants and plant tissues.

Each of these goals would build upon strengths of CHESS and CHESS-U to satisfy the emerging needs of plant research. Researchers need to tailor the beam size, bandwidth, beam energy, and imaging method to the sample at hand in order to study the different material types and length scales associated with roots, leaves, and seeds.

The development of confocal XRF for 3D imaging builds on in-house research at CHESS. CXRF is a 3D imaging technique that, in contrast to XRF tomography, does not require computation to extract 3D information. CHESS has invented and developed collimating channel arrays (CCAs) that improve the spatial resolution of CXRF to 1 micron, a 10-fold advance.^{79,80} Researchers are already applying this technology at CHESS and the APS,^{81,82} but the combination of resources and expertise to produce and enhance this technology currently exists only at CHESS. This effort leverages the Cornell Nanoscale Science and Technology Facility. To our knowledge, CHESS's effort in CXRF is unique in the world.

CHESS will realize a new opportunity for X-ray microscopy by combining CXRF with Maia, a new detector technology comprising an array of 384 small silicon-diode detectors, each with associated signal processing. The Maia improves the throughput of SR-XFS systems by acquiring data photon-by-photon in streaming mode.⁸³ CXRF with the Maia detector will enable plant phenotype researchers to conduct large-area 2D scanning on a live or unthinned sample, then switch quickly to 3D imaging to analyze particular regions within a structure in great detail.

On-site capabilities for plant husbandry and environmental would represent a worldwide first in synchrotron-based plant research. Transporting plants to a synchrotron can impose stress on the plant, and the stress can influence the phenomena to be studied. We need either to transport seeds to CHESS and allow them to germinate on site or to establish a controlled facility in which plants can recover before we study them.

CHESS will develop one or both of these capabilities with help from Cornell's *School of Integrative Plant Science*. U.S. News & World Report recently ranked Cornell as the #1 university in the world in plant and animal science.⁸⁴ CHESS's strong relationships with local biologists, *The Agricultural Research Center* at the University of Saskatchewan, and the *Donald Danforth Plant Science Center* in Creve Coeur, Missouri, guarantee that our work will address the needs of the wider user community.

Advantages of CHESS-U

CHESS-U creates a timely opportunity to create a beamline specifically targeting the study of plant phenotypes. This beamline will significantly enhance the plant biology community's capabilities for and access to synchrotron X-ray techniques. An optimized beamline will enable the research community to image plant structure, elemental distributions, and chemistry systematically and routinely. It will facilitate detailed studies of the interactions among genotype,

phenotype, and the environment. Researchers need this beamline to address urgent challenges in global food security and nutrition.

Among U.S. synchrotrons, only CHESS-U will provide high-flux, high-energy X-rays for both X-ray fluorescence microscopy and phase contrast imaging, tailored to the challenge of plant biology. High-energy X-rays offer three practical advantages for studies of plant phenotypes. First, they penetrate more deeply into materials and thereby allow researchers to study large plants (up to several centimeters thick), or even to image roots within soil. Second, high energy X-ray fluorescence provides an advantage for studying plant uptake of heavy metals such as lead, cadmium, tin, and barium. The uptake of these elements bears relevance not only to plant toxicity but also to bioremediation; e.g., to remove metals and toxins from soils. Third, high-energy X-rays damage biological samples less severely than low-energy X-rays.⁸⁵ Furthermore, researchers need a large field of view to image macroscopic regions of plant anatomy.

Scientific Questions that CHESS-U Researchers Will Answer

Researchers will come to CHESS-U to answer these questions:

- What phenotypic variation can we associate with improved yields and nutrition? How do plants take up, distribute, utilize and store nutrients and toxins as they grow and reproduce? How do environmental factors affect this behavior?
- How do nutrients and toxins interact or compete within a plant?
- How do genetic and environmental variations impact the phenotype of a plant, including its physiology, health, and behavior?
- What genes or networks of genes control the transport, localization, and speciation of key elements within a specific crop plant?
- What genes or networks of genes control root system architectures?
- How can we exploit genetic variation to improve the phenotypic performance of crop plants?
- How can we engineer root systems to increase their ability to take up nutrients without increasing their uptake of toxic metals?

Impact of High-Precision Plant Phenotype Studies at CHESS-U

Researchers at CHESS-U will lead the international effort to quantify phenotypes and to associate phenotypic variation with specific genes and gene variants. Our overarching goal is to discover how instructions from a single gene or network of genes, combined with environmental factors, translate into the full range of phenotypic traits of an organism. The work at CHESS-U may support molecular breeding efforts to develop not only crops that achieve higher yields in cultivated soils but also crops that grow successfully in marginal soils.

CHESS-U staff will work with users to develop instruments and methodologies that enable plant biologists with minimal X-ray expertise to conduct productive synchrotron experiments in plant phenotyping. As a result, synchrotron X-ray facilities may influence plant functional genetic and genomic studies in much the same way that X-ray crystallography influenced molecular biology.

The interdisciplinary work that integrates plant functional genomics with state of the art analytical synchrotron-based tools for plant biology will appeal to a wide group of students. Undergraduate and graduate students will receive training, conduct synchrotron experiments, and thereby gain experience that advances their careers.

Plant phenotype studies at CHESS-U will support the mission of NSF's Directorate for Biological Sciences, "to enable discoveries for understanding life." CHESS-U will also support the aims of the *Genetic Mechanics* cluster within the BIO directorate's Division of Molecular and Cellular Biosciences: "Theoretical and experimental research is welcome that integrates structural, biochemical, genetic, and "omic" (genome, transcriptome, interactome, phenome, etc.) data to understand the mechanistic relationship of genotype to molecular phenotype."

In summary, CHESS-U will give plant biologists consistent and sustained access to a synchrotron beamline optimized to investigate plant phenotypes. CHESS-U may thereby emerge as a key player in the broad-based worldwide scientific effort to feed mankind.

VI. Nanocrystal Superlattices

Abstract

Nanocrystal superlattices are 3D ordered arrays of nanocrystals that exhibit not only the size- and shape-dependent properties of the individual nanocrystals but also exciting new collective properties resulting from the optical and electronic interactions between nanocrystals. Going beyond our traditional periodic table of the elements, materials scientists and engineers are beginning to see hundreds of thousands of nanocrystal superlattices – either individually or in combination – that they can apply to design innovative materials with custom tailored properties. CHESS has pioneered techniques for studying nanocrystal superlattices, and a nascent research community has coalesced. The CHESS-U project will enhance by a factor of 1000 the high-energy (>30keV) x-ray intensity needed to collect SAXS/WAXS and spectroscopic data simultaneously from specimens inside diamond-anvil cells. The enhanced beam intensity will enable us to examine smaller samples, samples within processing chambers or reaction vessels, or samples that change rapidly as we vary experimental conditions. The research community will come to CHESS to explore new frontier areas of condensed matter physics and solid state chemistry, to discover novel phenomena associated with nanocrystal superlattices, and to accelerate the design of new materials with applications in communications, sensing, diagnostics, pharmaceutical delivery, energy conversion and storage, and environmental monitoring and remediation.

Nanocrystals are crystals of metallic, semiconducting, magnetic, or insulating materials that typically range in size from 2 to 20 nm. They contain a few hundred to a few thousand atoms. Their electronic, optical, and magnetic properties depend on their size and shape. They can exhibit unique emergent phenomena such as size-dependent magnetic properties, size-dependent bandgaps,^{86,87} and surface plasmonic resonance.⁸⁸ These emergent phenomena give design engineers and device fabricators new degrees of freedom, such as the opportunity to tailor the electronic structure of a material without changing its chemical composition.⁸⁹

Nanocrystal superlattices consist of 3D ordered arrays of metallic, insulating semiconducting, or magnetic nanocrystals. Researchers often refer to nanocrystal superlattices as “artificial solids” in which nanocrystals take the place of atoms.⁹⁰ Figure 1 illustrates the analogy between an *atomic solid* in which carbon atoms occupy sites on a diamond lattice and a *nanocrystal superlattice* in which nanocrystals occupy sites on a diamond-type lattice.⁹¹ We can think of the list of available nanocrystals as a new “periodic table” with which we can build new materials.

Nanocrystal superlattices occur in natural systems such as opals and virus

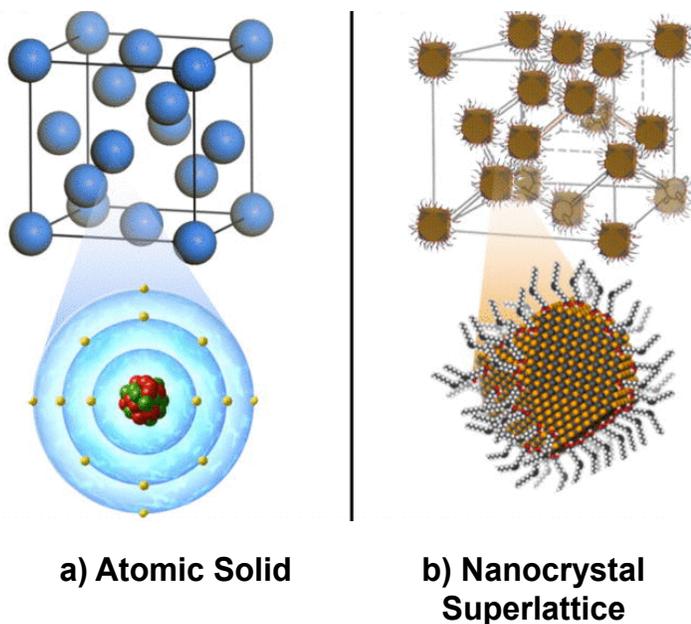


Figure 1: a) Atomic solid with carbon atoms on a diamond lattice; b) Nanocrystal superlattice with nanocrystals in a diamond-type lattice.

Note dimension scale difference: 0.1 nanometer on left, 2-20 nm on right.

crystals. Opals (Figure 2a) are iridescent because a regular lattice of silica particles diffracts light. Similarly, tobacco mosaic virus crystals (Figure 2b)⁹² contain a regular lattice of rod-shaped virus particles.

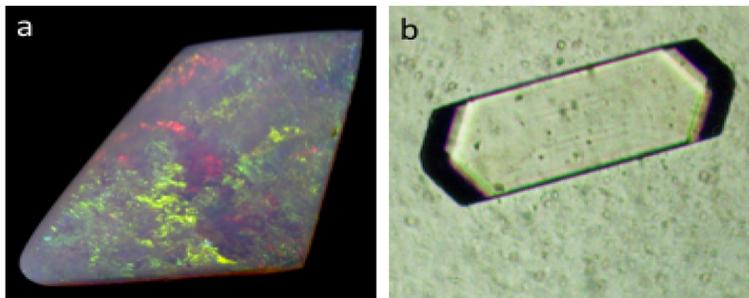


Figure 2: Natural Nanocrystal Superlattices, a) Brazilian opal, b) virus crystal (tobacco mosaic virus)

Benzton and his colleagues published the first report of a man-made nanocrystal superlattice in 1989.⁹³ They placed a colloidal solution

containing iron oxide nanocrystals on a transmission electron microscope (TEM) grid and allowed the solution to evaporate.⁹⁴ They later observed that iron oxide nanocrystals spontaneously formed an ordered 3D array. In this way, they serendipitously discovered that monodispersed nanocrystals in colloidal solutions can self-assemble into superlattices with long-range order. In this context, *monodispersed* means that the nanocrystals have the same surface chemistry, the same internal structure, and a narrow distribution of size and shape.

Nanocrystal superlattices can range in size from 2D thin films on substrates to 3D free-standing millimeter-sized bulk samples. Nanocrystals exhibit both orientational and positional ordering. The spacing between the nanocrystals can vary from less than 1 Ångstrom to more than 100 Ångstroms. When the spacing is less than 5 Ångstroms, exchange interactions can cause insulating superlattices of nanocrystals to become semiconducting, metallic, or even superconducting, depending on their composition.⁹⁵ When the spacing ranges from 5 to 100 Ångstroms, electrons can either hop or tunnel between adjacent nanocrystals.

The dimensions of the superlattice unit cell depend on the packing symmetry of the nanocrystals. Spherical nanocrystals typically self-assemble into a face-centered cubic (FCC) or a hexagonal close packed (HCP) lattice. Nanocrystals with shape anisotropy can adopt other symmetries, such as body-centered cubic (BCC) phases.⁹⁶ Superlattices composed of crystallographically aligned polyhedral or rod-like nanocrystals exhibit strongly anisotropic properties.

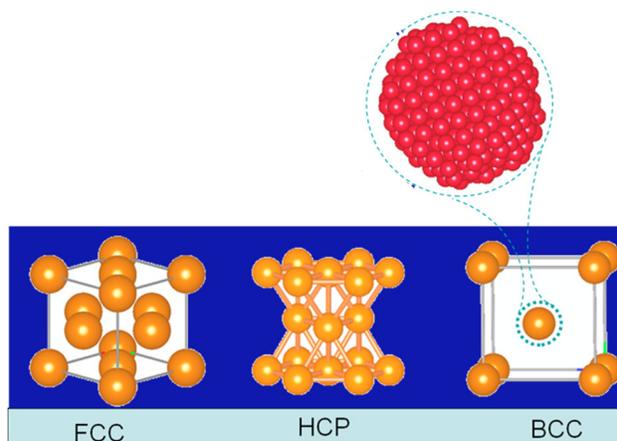


Figure 3: Common Nanocrystal Superlattice Packing Schemes

Figure 3 illustrates the most common packing symmetries. The top of the image shows a spherical nanocrystal building block composed of atoms. The bottom illustrates the face-centered cubic (FCC), hexagonal close packed (HCP), and body-centered cubic (BCC) nanocrystal superlattice structures.

The crystallographic symmetry of the superlattice often depends strongly on the composition of the nanocrystal. To overcome this limitation, various research groups have engineered

superlattices in which DNA linkers (i.e., the long flexible “tails” shown in figure 1b) control nanocrystal position and inter-nanocrystal spacing.⁹⁷ This approach separates the identity of the nanocrystal from the variables that control its assembly. It enables researchers to control particle size, lattice parameter, and crystallographic symmetry independently. It also enables them to design complex functional superlattices with absolute control over the placement of each nanocrystal in order to optimize properties for plasmonics,^{98,99,100} photonics,¹⁰¹ catalysis,^{102,103} and other applications.

A Rich Variety of Binary Nanocrystal Superlattices

Research groups have demonstrated that mixing colloidal solutions of nanocrystals with different sizes and functionalities can create rich phase diagrams. Figures 4 and 5 show a remarkable diversity of structures that results, we presume, when particles of different sizes and types adjust to space constraints in a variety of ways. For example, scientists have identified binary superlattices with cubic, hexagonal, tetragonal, and orthorhombic symmetries and with AB, AB₂, AB₃, AB₄, AB₅, AB₆, and AB₁₃ particle stoichiometry.^{104,105,106,107,108} By combining nanocrystals with various compositions, researchers have also synthesized binary superlattices that are isostructural with NaCl, NiAs, CuAu, AlB₂, MgZn₂, MgNi₂, Cu₃Au, Fe₄C, CaCu₅, CaB₆, NaZn₁₃, and *cub*-AB₁₃.^{109,110} It is possible to fabricate nanocrystal superlattices with equal stoichiometries but different symmetries by varying the size of the nanocrystals and the nucleation and growth conditions. Figure 4 shows examples of binary nanocrystal superlattices.

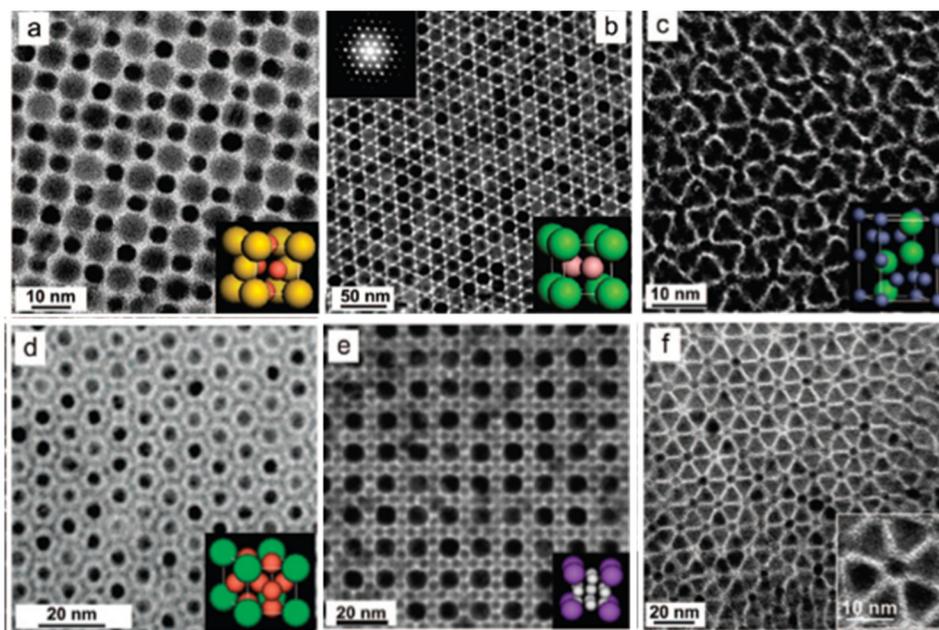


Figure 4: Binary Nanocrystal Superlattice Structures TEM (001) projection images, with unit-cell inserts (lower right) and select electron diffraction patterns (top left). a) 7.6-nm PbSe and 5.0-nm Au; b) 13.4-nm Fe₂O₃ and 5.8-nm PbSe; c) 6.2-nm PbSe and 3.0-nm Pd; d) 3.4-nm CdSe and 7.3-nm PbSe; e) 8.1-nm CdTe and 4.4-nm CdSe; f) (not (001)) BNSL with 5.0-nm spherical Au and 9.0-nm LaF₃ triangular nanoplates.

The research community has also discovered binary nanocrystal superlattices with quasicrystalline symmetry. For example, one group observed self-assembled binary nanocrystal

superlattices with dodecagonal quasicrystalline order in three different systems: 13.4-nm Fe₂O₃ and 5-nm Au nanocrystals, 12.6-nm Fe₃O₄ and 4.7-nm Au nanocrystals, and 9-nm PbS and 3-nm Pd nanocrystals.¹¹¹ Figure 5 shows ordered binary superlattices with quasicrystalline symmetry self-assembled from 13.4-nm Fe₂O₃ and 5-nm Au nanocrystals:

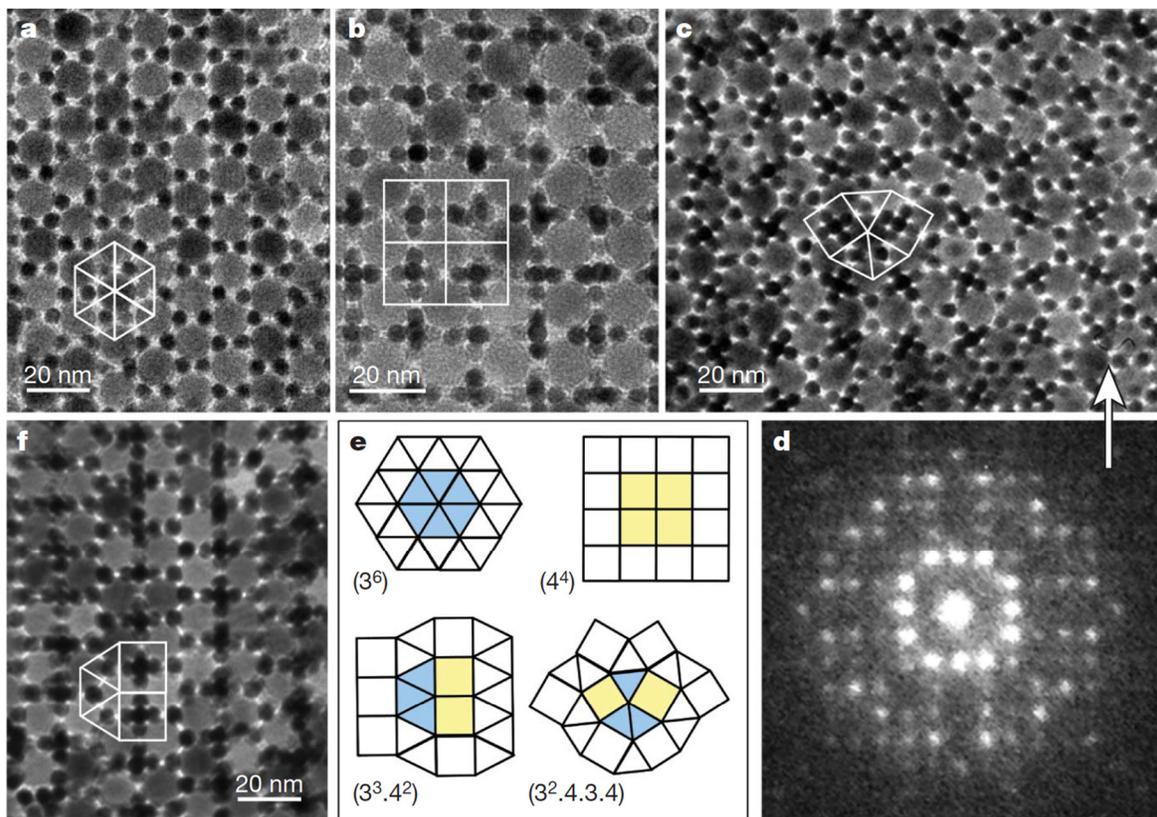


Figure 5: Binary Nanocrystal Superlattices with Quasicrystalline Symmetry using 13.4-nm Fe₂O₃ and 5-nm Au nanocrystals. a) AIB₂-type, b) CaB₆-type, c) AB₄ stoichiometry and the structural motif of the 3.2.4.3.4 Archimedean tiling (the integers refer to the number of sides of the polygon; the subscripts indicate the quantities of those polygons), d) electron diffraction pattern from a ~6 mm² domain of AB₄ shown in c), e) tilings that describe the structure of the binary nanocrystal superlattices, and f) a superlattice corresponding to the 3.3.4.2 tiling.

With precise control of stoichiometry and symmetry of constituent nanocrystals, researchers can create a multitude of binary superlattices. Scientists have just begun to fabricate ternary superlattices,^{112,113,114} and we expect that the research community will soon synthesize quaternary and much more complex superlattices.

Engineering Devices from Nanocrystal Superlattices

Nanocrystal superlattices vastly expand the range and variety of materials that engineers can select to solve technological problems. Today engineers can choose any of about 100 elements from the periodic table, either individually or in combination. In the future, engineers will be able to select from hundreds of thousands of nanocrystals to make superlattice materials. They will be able to design and synthesize new nanocrystal superlattices with properties tailored by changing one or more variables.^{115,116} Each change will yield a new nanocrystal superlattice with

traditional properties of the constituent elements (metals, semiconductors, and insulators), *size- and shape-dependent properties* of the constituent nanocrystals, and *new optical and electronic properties* that emerge from communication among the nanocrystals and that depend on inter-nanocrystal distances, packing symmetries, and densities.¹¹⁷

Various research groups have exploited these properties to fabricate electronic^{118,119,120,121} and optoelectronic^{122,123,124,125} devices in which nanocrystal superlattices formed either the metallic interconnecting layer or the active semiconducting layer. In these early devices, the nanocrystal superlattice formed only a single element; the rest of the device architecture consisted of traditional materials deposited at high vacuum by conventional slow and costly techniques.

Recently a team of researchers designed and fabricated high-carrier-mobility field-effect transistors (FETs) in which all the layers – metals, semiconductors, and insulators – consist of solution-processed nanocrystal superlattices (see Figure 6).¹²⁶ Superlattices with metallic silver and semiconducting CdSe nanocrystals make up the thin film electrodes and the FET channel layers. Indium nanocrystals co-dispersed with the silver nanocrystals passivate and dope the CdSe channel layer. Superlattices with Al₂O₃ nanocrystals assembled layer-by-layer with polyelectrolytes form a gate insulator with a high dielectric constant, enabling the devices to operate at low voltages. The FETs achieved high electron mobilities of 21.7 cm²/volt-sec. Since the team fabricated these devices on plastic substrates, nanocrystal superlattices may compete with organic semiconductors to serve emerging markets for large-area, low-cost, flexible electronics.

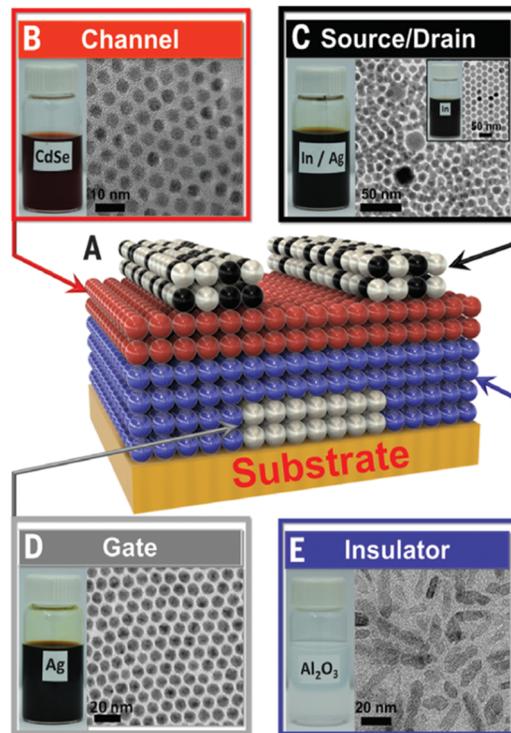


Figure 6: High-Carrier-Mobility FETs in which All Layers Consist of Nanocrystal Superlattices

Invention of X-ray “Supercrystallography” Methods at CHESS

Nanocrystal superlattices exhibit long-range order on multiple length scales. The packing arrangement of the nanocrystals assures a common crystallographic orientation. As a result, they diffract X-rays in the same manner as a single crystals.¹²⁷ Researchers study nanocrystal superlattices with synchrotron X-rays to identify the atomic-level structure of the individual nanocrystals and the packing arrangements of the unit cells.¹²⁸ SAXS studies reveal with greater confidence than any other analytical technique not only the size and size distribution but also the translational symmetry of monodispersed nanocrystals.^{129,130,131} WAXS studies reveal the size and shape of the nanocrystals with typical orientation, as well as the internal structure of the average nanocrystal core.^{132,133,134}

CHESS pioneered a unique capability to conduct SAXS and WAXS studies simultaneously from the same volume of specimens (Figure 7). Researchers gain experimental efficiency and

precision because the two techniques are always probing the same material volume under identical conditions. This approach eliminates pressure gradients and sample inhomogeneities. Referring to their methods as *supercrystallography*, they developed specimen handling and data collection and analysis methods to determine the atomic scale, nanoscale, and mesoscale structures of nanocrystal superlattices with

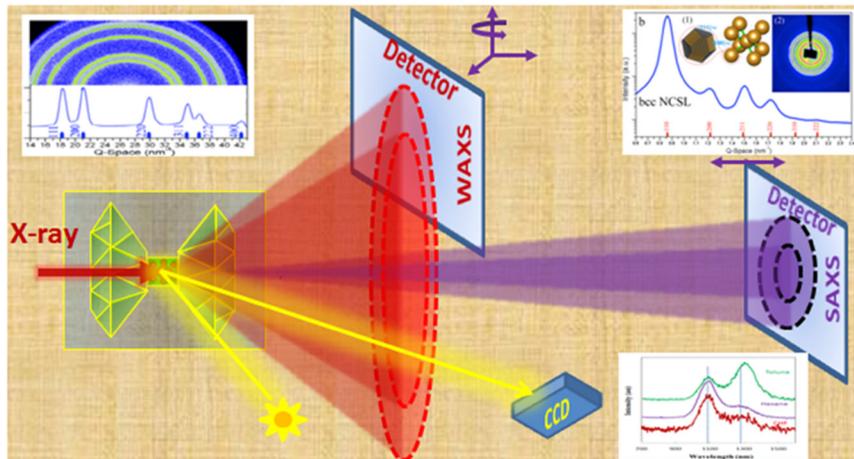


Figure 7: CHES Experimental Apparatus for Simultaneous SAXS, WAXS, and Spectroscopic Studies of Nanocrystal Superlattices at High Pressures

unprecedented spatial resolution.¹³⁵ In the first experiments, they grew nanocrystal superlattices from platinum nanocubes suspended in hexane, then applied high-energy (25 keV) X-rays and a two-circle diffractometer to obtain unprecedented detail from full sets of SAXS and WAXS data. They indexed the SAXS data via a procedure common in protein crystallography to identify the superlattice symmetries that best fit the data, then simulated appropriate superlattice structures to fit scattering spots with experimentally collected SAXS data sets.

By acquiring full sets of SAXS and WAXS data simultaneously, the team gained the ability to identify the orientation of nanocrystals within the superlattice. Supercrystallography makes it possible to understand the nucleation, growth, and transformation of nanocrystal superlattices. Supercrystallography with high-energy synchrotron X-rays has become an essential tool for learning to design transformative materials with targeted mesostructures and properties for device applications.

After the CHES team reported the first synchrotron-based SAXS/WAXS studies of nanocrystal superlattices at high pressure,¹³⁶ many experiments demonstrated how these studies offer fast and easy ways to discover advanced materials with novel structures and useful properties. For example, CHES developed a mechanical annealing technique in which high pressure from the diamond anvil cell transformed polycrystalline superlattices of gold nanocrystals into a quasi-single-crystalline superlattice at ambient temperature.¹³⁷ Researchers applied pressure to transform a superlattice of PbS nanocrystals into a large two-dimensional single-crystal nanosheet (Figure 8).¹³⁸ The CHES team applied pressure to transform a superlattice of cubic PbS nanocrystals into a metastable *strained-but-interconnected* phase with a 3D porous architecture.¹³⁹ After they released the pressure, the metastable phase persisted under ambient conditions. Other researchers working at CHES created nanowire arrays by compressing a face-centered-cubic superlattice of gold nanocrystals in a diamond anvil cell.¹⁴⁰ These studies showed that pressure-induced phase transformations can provide new ways to realize nanocrystal architectures and to fabricate nanostructured materials.

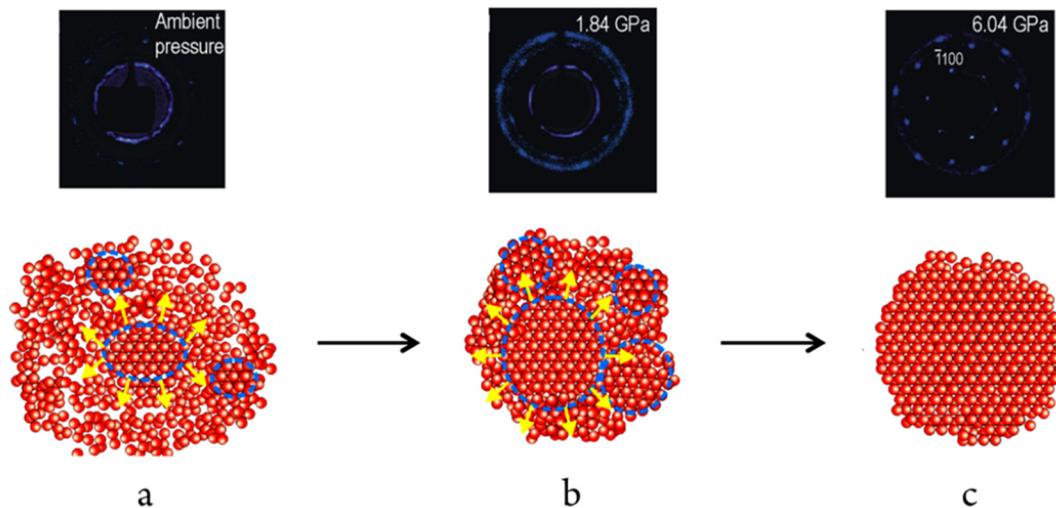


Figure 8: Mechanical Annealing to Remove Vacancies and Defects from Nanocrystal Superlattices at Ambient Temperature. Top images show the X-ray scattering patterns that reveal the growing perfection of the nanocrystalline lattice.

Grand Challenges and Scientific Questions

The growing community of CHESS researchers will elucidate the basic science and applications of nanocrystal superlattices. For example, they will answer these questions:

- How do nanocrystal superlattices assemble?
- How do nanocrystals interact with surface-coating ligands and solvent molecules in various environments? How do they nucleate into ordered structures, grow to large mesostructures, and eventually grow into bulk materials?
- What forces drive the assembly of nanocrystal superlattices (inter-nanocrystal van der Waals interactions, steric repulsions of surface-coating molecules, evaporation-induced capillary forces, attractive depletion forces, surface-charge-induced or electric-dipole-induced Coulomb forces, entropic forces, etc.)? Which of these forces are most important?
- How do the electronic and optical couplings among nanocrystals in a superlattice depend on the distance between them? How do the couplings depend on the nanocrystal orientation?
- How do the phase diagrams of nanocrystal superlattices change as a function of nanocrystal size, shape, pressure, and temperature?
- What crystalline symmetries manifest in nanocrystal superlattices with various chemical compositions? What orientations do the nanocrystals assume in each crystallographic site?
- How do superlattices transform from one crystallographic symmetry to another?
- How can we controllably increase the size of nanocrystal superlattices to mesoscale and then to macroscale? As their sizes increase, do their properties improve or degrade? What new collective properties will manifest? What architectures and interactions are responsible for enhancing their properties or creating new collective properties?
- Can we apply high pressure to create new metastable structures with new properties? Will the structures remain stable and the properties persist under ambient conditions?

- How do atomic and superlattice structure change when we control nanocrystal superlattices in a device? How do these changes develop as a function of time?

By answering these questions, we will enable rational design of novel devices that exploit the novel phenomena and unique properties of nanocrystal superlattices.

New Opportunities Provided by CHESS-U

Over the next few years, the research community will graduate from straightforward studies of superlattice phase and structure to functional studies of superlattices made from *semiconductor nanocrystals* that absorb and emit light, *metal nanocrystals* that interact with light and emit strong plasmonic signals in the visible spectrum, and *magnetic nanocrystals* that absorb radio frequency energy and emit radio-frequency signals under external magnetic fields. These studies will push the experimental envelope in these directions:

- *In situ* high-energy x-ray SAXS /WAXS / spectroscopy inside reaction vessels.
- *In situ* high-pressure and high-temperature SAXS / WAXS measurements through larger diamond anvil cells that only high-energy, high-intensity X-rays can penetrate.
- Time-resolved measurements of the nucleation, growth, and transformation of nanocrystal superlattices in controlled physical and chemical conditions (e.g., temperature, moisture, flow, evaporation, pH, hydrostatic pressure, deviatoric pressure, etc.).
- Imaging and structural studies of nanocrystal superlattices at lengths ranging from atomic scale to bulk.
- Studies of structure-property and structure-operation relationships of nanocrystal superlattices over a wide range of environmental conditions.

CHESS-U will provide high-energy (> 30 keV), high-flux X-ray beams with 1000 times higher intensity than we can currently deliver. These beams will enable researchers to extend studies of nanocrystal superlattices to these regimes:

- smaller volume samples (1 to 100 microns).
- samples with light elements that scatter X-rays weakly.
- samples within processing chambers (including diamond anvil cells) or reaction vessels.
- samples that change rapidly as we vary experimental conditions; e.g., as we increase pressure.

Potential Scientific Impact

The large number of publications emanating from a single bend magnet beamline at CHESS provide evidence for the research community's strong interest in nanocrystal superlattices and for the benefits of building a state-of-the-art supercrystallography facility. A large fraction (near 50%) of those publications appeared in high profile journals. CHESS-U will transcend current capabilities and deliver scientific impacts in the following ways:

- Open new frontier areas of condensed matter physics and solid state chemistry in which scientists explore the novel phenomena associated with nanocrystal superlattices.
- Identify the physical and chemical rules that control the formation of nanocrystal superlattices.
- Explore the new types of chemical bonding among nanocrystals within superlattices.

- Explore the new non-equilibrium, many-body physics of electrons in nanocrystal superlattices.
- Explore the new behavior of electrons in *s*, *p*, and *d* molecular orbitals and their interactions within nanocrystal superlattices.
- Determine which architectures and interfaces enable nanocrystal superlattices to manifest novel properties and functionalities.
- Determine how the electrons in adjacent or nearby nanocrystals interact with each other to produce new physics and new chemistry.
- Determine how the interactions among quantized nanocrystals vary as we extend the volume of superlattices to the mesoscale state and eventually to the bulk state.
- Articulate useful design rules to accelerate the materials design process and to reduce the time from materials discovery to manufacturing for applications.
- Elucidate the interactions among the organic and inorganic components of superlattices. The knowledge we acquire will help us to understand natural biomineralization processes and to design bio-inspired lightweight materials with enhanced toughness and hardness.
- Provide datasets to computational materials scientists, thereby improving their ability to model nanocrystal superlattice behavior and to predict materials structures and properties.

“Arrays of single crystals of order 1-15 nm in diameter are a promising route to mesoscale manufacturing. The arrays themselves can be mono- or polydisperse, and be assembled in one-, two-, or three-dimensional configurations. The diversity of programmable behavior in these arrays is enormous, and the opportunity for applications in biological diagnosis and therapy, polymer-based nanocomposites, energy storage and conversion, environmental monitoring and remediation, and electronic and optoelectronic devices is virtually limitless. The capability of synthesis and characterization of nanocrystal arrays is in its infancy, with far more phenomena remaining to be discovered than have yet been found.”

***From Quanta to the Continuum:
Opportunities for Mesoscale Science,
US Department of Energy,
Basic Energy Sciences
Advisory Committee, 2012***

Potential Technological Impact

Nanocrystal superlattices are a new class of building blocks for creating innovative designer solids; they vastly expand the capabilities offered by the periodic table of the elements. Materials scientists and engineers of the future will be able to design and synthesize new nanocrystal superlattices with desired properties by customizing the composition, size, shape, orientation, or packing density of the constituent nanocrystals, the electronic or optical communication among the nanocrystals, or the length or chemical functionality of the organic ligand capping layer. CHESS has pioneered the studies of nanocrystal superlattices and provided a leading research facility. The CHESS-U upgrade to higher-energy, high-intensity X-rays will deliver unique new capabilities that will enhance our research community’s ability to explore, understand, and exploit these promising materials.

VII. *In-situ* Processing of Organic Semiconductors

Abstract

Organic semiconductor devices have the potential to generate annual markets valued at hundreds of billions of dollars and to address national needs related to human health and welfare, clean energy, infrastructure, consumer goods, and national security. The rate of progress in the field suffers because the research community lacks a thorough understanding of the interrelationships among processing, microstructure, and device performance. Device materials typically consist of organic thin films with significant amounts of processing-related disorder. To gain the fundamental understanding required to design high-performance materials and devices rationally, the research community needs to study materials and processing *in situ* and in real time by X-ray scattering with high-flux, high-energy synchrotron beams. CHESS-U will provide the requisite x-ray beams and sample environments required for rapid progress, as demanded by the Materials Genome Initiative.

Organic semiconductors combine the electronic properties of inorganic semiconductors with the mechanical properties of plastics. They absorb light, emit light, or conduct electricity.^{141,142} In most cases, their bandgap lies within the visible spectrum. They are soft, flexible, conformable, and lightweight. Since they are soluble in standard organic solvents, we can process them via industrial coating and printing techniques in which temperatures do not exceed 200°C.

These materials contain carbon, hydrogen, and, in some cases, heteroatoms such as sulfur, oxygen, or nitrogen. They derive their electrical properties from their atomic structure, a network of sp_2 -hybridized carbon atoms in which the sp_2 orbitals occupy a single plane. The p_z orbitals, perpendicular to the plane, undergo hybridization and form a π bonding system (see Figure 1). Loosely bound electrons can travel over significant portions of the molecule.¹⁴³

The scientific community classifies organic semiconductors into two large families: *polymer semiconductors* and *small-molecule organic semiconductors*. Polymer organic semiconductors can contain tens of thousands of atoms; they consist of long chain-like molecules with a repeating monomer unit. Small-molecule organic semiconductor molecules typically contain tens of carbon atoms. Figure 2 on the next page shows typical examples of each family.

In laboratory experiments, both families of organic semiconductor have exhibited excellent electrical properties.¹⁴⁴ Some researchers have referred to conjugated polymers as “synthetic metals” because of their high electrical conductivity.¹⁴⁵ In highly ordered films of small-molecule organic semiconductors, overlap of the π -orbitals leads to high carrier mobility, sometimes exceeding that of amorphous silicon.^{146,147,148} Some research groups have fabricated high-performance organic field effect transistors (OFETs) from single crystals of small-molecule organic semiconductors^{149,150,151,152,153,154,155} with carrier mobilities as high as $16.4 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$.¹⁵⁶

The fabrication techniques for printed electronics vary dramatically from those of conventional electronics. Conventional wafer fabs manufacture circuits from inorganic semiconductors at high

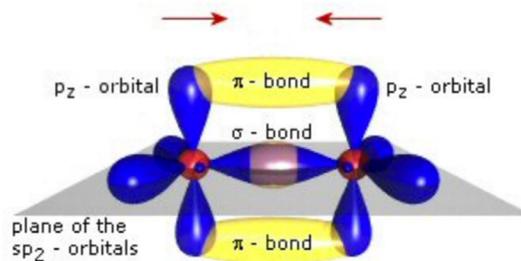


Figure 1:
 sp_2 Hybridized Carbon Atoms

temperatures in a controlled vacuum environment via a subtractive batch process with high equipment costs and high material costs. They optimize processes for long runs of identical products. By comparison, printed electronics manufacturing facilities could create circuits from organic electronics at ambient temperature and pressure¹⁵⁷ by continuous additive processes with substantially lower equipment and energy costs. For example, they could fabricate organic semiconductor devices and circuits by low-temperature thermal evaporation^{158,159} or by solution-deposition techniques such as coating¹⁶⁰ (spin, spray, dip, knife, roll-to-roll, or slot-die) or printing¹⁶¹ (screen, gravure, inkjet, or offset). They could optimize their processes for short, flexible production runs.¹⁶²

All these factors suggest that organic semiconductors could enable new generations of low-cost, flexible, rugged, stretchable,¹⁶³ lightweight¹⁶⁴ electronic devices and circuits. These products would consume little energy and generate little heat. They would operate over large areas and serve other applications that rigid devices and circuits cannot address.

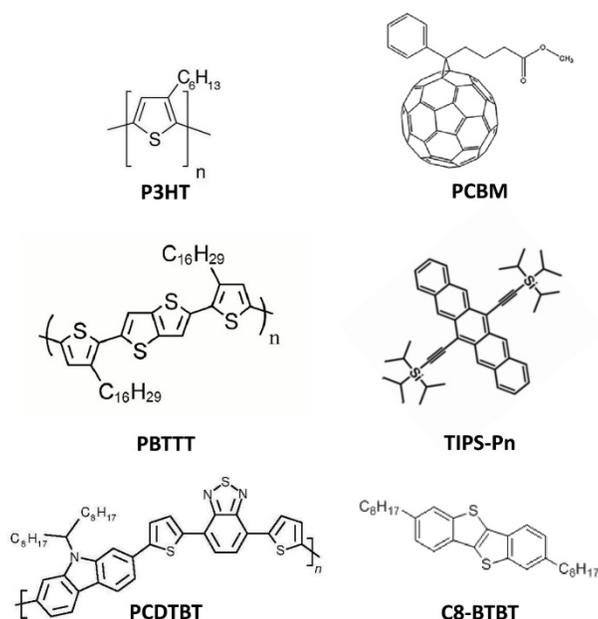


Figure 2: Organic Semiconductors

Examples of Polymers (left column):

poly(3-hexylthiophene) (P3HT),
 poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT),
 and poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT)

Examples of Small Molecules (right column):

Phenyl C60 butyric acid methyl ester (PC₆₀BM), Bis(triisopropylsilyl)ethynylpentacene (TIPS-Pn),
 and 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C₈-BTBT)

Novel products enabled by organic semiconductors would target national needs identified in the Materials Genome Initiative Strategic Plan:

- *Human Health and Welfare* (biomedical monitoring, biomedical implants, artificial skin for burn victims¹⁶⁵)
- *Clean Energy* (lighting, photovoltaics,¹⁶⁶ batteries)
- *Infrastructure* (sensors for non-destructive evaluation)
- *Consumer Goods* (logic / memory, wearable electronics, displays, smart packaging)
- *National Security* (communication technologies and displays integrated with warfighters' uniforms, lightweight photovoltaics, flexible sensors mounted on aircraft and vehicles, etc.).

The Market Potential

Germany's National Academy of Science and Engineering concluded in a 2011 study that "organic and large area electronics are forecast to have a global market volume of several hundred billion euros in the medium and long term, corresponding to the economic importance of current conventional silicon-based electronics."¹⁶⁷

IDTechEX, a consulting firm that has covered the field of printed, flexible, and organic electronics since 1999, has predicted that the market for printed and flexible electronics could be "larger than the silicon semiconductor industry, which is not a surprise given that it is applicable to so many things." In 2016, Grand View Research predicted that the global market for organic and flexible electronic products will grow from about \$8 billion today to \$87 billion by 2024.¹⁶⁸ IDTechEX recently forecast that the annual market for printed, flexible, and organic electronics would grow to \$340 billion by 2030, including \$100 billion in logic and memory, \$100 billion in organic light emitting diode (OLED) displays, \$70 billion in organic photovoltaics, and \$30 billion in OLED lighting.¹⁶⁹



**Figure 3: 65-inch OLED TV
(Panasonic)**

Current Products

OLED displays for televisions and smart phones have achieved early success in the marketplace. They consist of a layer of organic semiconductor material (either small molecules or polymers) sandwiched between two electrodes (e.g., indium tin oxide), all mounted on plastic or another substrate material. OLED pixels emit colored light via electroluminescence and therefore do not require backlighting. As a result, they are thinner, lighter, and more energy efficient than liquid crystal displays, they display more brilliant colors, and the image quality remains independent of the viewing angle.

Today's OLED televisions, manufactured by Panasonic and by LG Electronics, achieve the best contrast of all TV technologies: the darkest blacks (because the pixels switch completely off) and the brightest whites (see Figure 3). In June of 2016, LG forecast that global sales of its OLED televisions would triple from about 300,000 units in 2015 to about 900,000 units in 2016.¹⁷⁰

The new Samsung Galaxy smart phones contain 5.1-inch high-resolution OLED displays with arrays of 2560 x 1440 pixels (577 pixels per inch). On the Galaxy S6 Edge (see Figure 4), Samsung fabricated the OLEDs on a flexible plastic substrate that bends around both sides of the phone, providing two independently configurable regions that are visible not only from the front but also from the sides, even when the phone lies face down. When the main display turns off, the curved regions exhibit a rotating carousel of screens that show the time, weather, tweets, news feeds, e-mail messages, voice mail messages, and missed calls. Samsung sold 6 million Galaxy S6 and Galaxy S6 Edge smart phones during the first month after their release in 2015.



Figure 4:
Galaxy S6 Edge
with OLED Display
on Flexible Substrate



**Figure 5: TempTraq
Flexible
Thermometer
with Wireless
Transmitter**

Other products that exploit the advantages of organic, flexible, and printed electronics have recently entered the commercial marketplace. Cooper Atkins of Middlefield, Connecticut is marketing *TempTraq* (see Figure 5), a flexible electronic thermometer that measures skin temperature continuously and transmits data to mobile devices via Bluetooth. Enfucell of Vantaa, Finland has introduced a soft battery (see Figure 6) with printed electronics to power other flexible electronic products, such as wearable electronics, RFID tags, and smart functional packaging. Konica Minolta, DuPont, Philips, and LG Chem now manufacture and sell flexible OLED lighting panels (see Figure 7).

Another wave of flexible electronics products is moving through the R&D pipelines of companies worldwide. At the 2016 Consumer Electronics Show,



**Figure 7: OLED Lighting Panels
from LG Chem**

Samsung exhibited a prototype OLED display measuring 18 inches corner-to-corner and less than 1 millimeter thick that could roll up as tightly as a newspaper (see Figure 8). Heliatek of Dresden, Germany is

developing roll-to-roll-processed organic photovoltaics that integrate with buildings. The company claims world-record efficiency of 13.2% for opaque or translucent organic solar cells¹⁷¹ and 6% efficiency for transparent organic solar cells. Some experts have forecast that organic photovoltaics will reach efficiencies of 15% to 20%.¹⁷²



**Figure 6: Soft Battery
by Enfucell**



**Figure 8: Flexible, Bendable
18-inch OLED Display
by Samsung**

Experienced observers recognize the uncertainty of these forecasts. It remains to be seen whether sales will grow to the predicted values and whether some of the envisioned products will ever reach the marketplace. However, 20 to 30 years ago it was hard to imagine the diversity and complexity of silicon-based microelectronics that we now take for granted. Organic electronics are positioned to evolve along a similar trajectory and to revolutionize our interactions with electronic devices.

The State of Knowledge

Today the charge carrier mobility of organic semiconductor devices remains modest compared to that of single-crystalline silicon devices. The research community does not understand how to fabricate organic semiconductors with reproducible properties for most device structures. Scientists usually fabricate prototypes on small scales via techniques that cannot scale to industrial production. These factors limit the range of potential applications and the rate at which products can advance toward commercialization. OLED televisions have achieved early commercial success because only the light emitters contain organic materials; responsibility for the electrical conduction and switching fall to inorganic indium tin oxide transparent electrodes and to arrays of metal oxide thin film transistors (MOS-FET).

The fundamental knowledge gap is that the research community lacks a thorough understanding of the processes by which organic semiconductors self-assemble. For example, we have no consistent picture of the mechanisms of solution deposition, which is inherently a non-equilibrium process – the material

dries quickly, molecular mobility and diffusion diminish as the solvent evaporates, and kinetic trapping prevents the material from reaching its equilibrium structure. Recent work indicates that the materials pass through several previously unknown transient phases as they crystallize.¹⁷³ Since we don't know how thin films nucleate, we cannot yet control the nucleation;

“For all organic materials, chemists need to be able to model structure-property relationships at the molecular level so that they can design systems with more controlled self-assembly, regardless of whether that self-assembly occurs in solution (i.e., in ink) or on a surface. In other words, they must develop a more predictive science of organic electronics. Otherwise, synthesis will continue to yield decidedly non-uniform mixtures of structures that behave in unpredictable ways.”

*Organic Electronics for a Better Tomorrow:
Innovation, Accessibility, Sustainability
A White Paper from the Chemical Sciences and Society Summit,
San Francisco, 2012*

therefore, it is difficult to create single crystals with uniform size and shape. Even devices fabricated within the same batch exhibit different properties.^{174,175} Some design rules for small-molecule self-assembly are beginning to emerge, but chemists are still proceeding via trial and error. Our challenges are to elucidate the self-assembly process, then to control grain morphology as the materials crystallize while maintaining a reasonable production speed.

Crystallinity, grain size,¹⁷⁶ grain alignment,^{177,178} and grain boundaries^{179,180,181,182,183,184,185,186} influence the charge transport properties of organic semiconductor materials and devices.¹⁸⁷ We find higher carrier mobility in materials with larger grains and fewer grain boundaries. Spin-coated PBTTT grows with larger grains when spun onto octadecyltrichlorosilane (OTS) than when spun onto bare silicon oxide.¹⁸⁸ Groups fabricating organic transistors have grown larger grains by decreasing the roughness of the underlying gate dielectric.^{189,190} In both instances, the materials with larger grains exhibit higher mobility.

Grain *misalignments* can reduce carrier mobility in organic semiconductors. Models of transport suggest that the electrical properties of grain boundaries depend on the relative orientation of adjacent grains.¹⁹¹ Experimental data confirm these predictions.¹⁹² Misaligned grain boundaries induce anisotropic charge transport in thin films of polythiophene.^{193,194,195} Grain orientation also plays an important role in the performance of organic field-effect transistors.¹⁹⁶

The grain morphology of thin films of organic semiconductors depends sensitively on the vapor-phase and solution-based processing techniques by which researchers prepare devices. The solution-based techniques include *drop casting*, *spin coating*, *spray coating*, *meniscus-guided coating* (e.g., dip coating, zone casting, hollow pen writing, blade coating, slot die coating, and solution shearing), and *printing* (e.g., offset printing, inkjet printing, and screen printing).¹⁹⁷ Looking forward, there may also be opportunities to process organic electronic materials via advanced additive manufacturing (i.e., 3D printing). Still, the research community lacks a complete understanding of how these processing techniques influence thin film microstructures.

“A much more detailed understanding of the process steps used to fabricate devices and their influence on thin-film material structure and device performance is an essential prerequisite for accelerating the development of this nascent industry and further broadening its scope.”

Materials Genome Initiative Strategic Plan, 2014

However, it is clear that processing techniques can dramatically influence device performance. For example, we can change a material’s ability to carry electrical charge by several orders of magnitude by annealing it,^{198,199,200} processing it with a different solvent,²⁰¹ or depositing it onto a different substrate.^{202,203,204} Processing can also determine which polymorph forms, and polymorphic structures of the same molecule can display very different charge mobility.²⁰⁵

Although the research community’s fundamental understanding continues to advance, the interrelationships among processing, microstructure, and electronic properties remain poorly understood. It will be impossible to design and process high-performance organic semiconductor devices rationally until we elucidate these relationships. Moreover, we must develop a tool for characterizing the morphology in 2D patterned thin films. *Grain mapping* can determine the size, shape, location, and orientation of grains and grain boundaries in such films. No suitable thin film grain mapping tool for patterned thin films exists today. CHESS-U provides the rare opportunity to develop such a tool.

The Crucial and Enabling Role of Synchrotron X-ray Scattering Studies

X-ray scattering with high-flux, high-energy synchrotron radiation is the most effective tool for studying the microstructure of organic semiconductors *in situ* and in real time.^{206,207,208} X-ray scattering studies have revealed interfacial effects, intermediate metastable phases,^{209,210} grain morphology,²¹¹ and other microstructural factors that control the electrical performance of organic semiconductor materials and devices. Only high-energy, structure-sensitive X-ray scattering tools will enable us to examine subtle effects such as small-angle grain boundaries.

Researchers have recently combined small-angle X-ray scattering with tensor tomography to create three-dimensional images of bones²¹² and teeth²¹³ on both macroscopic and nanoscopic scales. This new technique, known as diffraction tomography, can visualize the structure and

orientation of mineralized collagen fibrils in each pixel of the scan. We plan to adapt this methodology to image grains and grain orientations within organic semiconductor thin films and devices.

Goals of the Organic Electronics Research Community

The overarching goals of the research community are to understand and eventually to eliminate all factors that compromise the performance of organic electronic devices. They plan to elucidate the relationships among processing, molecular and mesoscopic structure, and performance. Enabled by CHESS-U, the research community will develop new techniques to map grains and to characterize their orientation in patterned organic thin films, in 2D organic circuits, and possibly in 3D organic circuits. Today no national synchrotron source provides such a capability. A thorough fundamental understanding must begin with knowledge of how the structure forms. Researchers will elucidate the self-assembly process and learn to control the ways in which domains nucleate and grow.^{214,215} They will conduct spatially resolved *in situ* X-ray scattering studies to reveal grain morphology and also time-resolved studies to reveal the kinetics of structure formation. The research community will investigate the microstructural impacts of all materials processing techniques in order to acquire a detailed and holistic fundamental understanding.

A key issue will be to understand self-assembly of organic semiconductors in device structures produced by coating or printing methods that are suitable for mass production. We need suitable and scalable *in situ* sample environments to understand sample processing in real time. We need high-energy beams to penetrate overlayers, high-flux beams to achieve the required temporal resolution (1 to 100 milliseconds), and beamlines designed to accommodate *in situ* processing tools. Researchers will study materials and devices *operando* to determine the optimal structures for specific applications, then identify the optimal processing techniques for creating those structures.

Scientific Questions to Address

CHESS-U will enable the research community to address the following scientific questions:

- How do molecular and mesoscopic structure form in organic semiconductors?
- What mechanisms govern the self-assembly of organic semiconductors under different processing conditions?
- How do molecular and mesoscopic structure influence the performance of organic semiconductor devices?
- How do processing conditions influence molecular and mesoscopic structure?
- How do molecular and mesoscopic structure affect device performance?
- What industrially relevant processing techniques will enable us to optimize molecular and mesoscopic structure and device performance with high yield and uniformity?

These questions are important because future applications for organic devices and circuits such as light-emitters,^{216,217} transistors,^{218,219} and photovoltaics^{220,221,222} depend on our ability to mass-produce materials and devices with grain morphologies that allow consistently high performance.

Unique Enabling Capabilities at CHESS

To answer these scientific questions, we will need to study organic semiconductor materials and devices via X-ray microbeam grazing-incidence scattering techniques (including grain mapping and diffraction tomography) with *in situ* chambers and coaters. We will study industrially relevant processing conditions in real time with high spatial and temporal resolution. We will design *in situ* sample chambers that we can scale for volume production and make these chambers available to the general user community. We will need high-energy (10-30 keV) X-ray microbeams (1-10 microns) with high flux ($>10^{13}$ photons per second on the sample or $>10^{12}$ photons per second in the microbeam).

The combination of high-energy X-rays and microfocusing with a grazing-incidence scattering beamline provides a unique national opportunity to enhance our understanding of soft materials processing. Such a beamline would complement other national facilities' soft-x-ray beamlines, such as scanning transmission x-ray microscopes (STXM), which offer higher spatial resolution and spectroscopic information but would not be optimal for manufacturing environments because they require vacuum conditions.

CHESS already offers a unique combination of microfocusing X-ray optics, sample chambers, fast detectors, and staff expertise. CHESS has developed and made available to our user community a variety of sample environments to investigate thin film processing techniques such as knife coating and *in situ* solvent vapor annealing.²²³ We possess cutting-edge X-ray scattering equipment, such as microfocusing optics and fast detectors. This equipment has enabled us to demonstrate the importance of *transient phases* that no other technique would have revealed.^{224,225} We possess laboratory space in which to develop next-generation sample chambers that can support optical spectroscopy and transport measurements simultaneously with X-ray scattering.

It would be time consuming and expensive to duplicate CHESS's capabilities elsewhere. Furthermore, it takes time to develop sample chambers. For example, we needed two years of effort to refine the knife coater so that we could conduct experiments with the required control. The first publication appeared three years after the start of the project.

Broader Impacts of Organic Semiconductor Research

The research community will develop a fundamental understanding of self-assembly under processing conditions that are scalable to industrial production. They will create a rational basis for designing new organic semiconductor materials and devices. For example, they will identify the optimal coating speed and temperature to create high-performance films with minimum material consumption. Our insights will help engineers to develop organic semiconductor manufacturing techniques that reduce costs, solvents, emissions, and energy consumption.

CHESS-U research on organic semiconductor materials and devices will help U.S. scientists and engineers to develop new products that address national needs for human health and welfare, clean energy, infrastructure, consumer goods, and national security. It will help U.S. companies to establish a strong market position in organic and flexible semiconductor devices despite strong competition from East Asia and Europe. It will support the *Materials Genome Initiative's* overarching goal: to deliver the next generation of materials into products in half the time at a fraction of the cost. It will advance the objective of NSF's *Designing Materials to Revolutionize and Engineer Our Future* program: "to accelerate materials discovery and development by

building the fundamental knowledge base needed to design and make materials with specific and desired functions or properties from first principles. This will be accomplished by understanding the interrelationships of composition, structure, properties, processing, and performance.”

VIII. Atomically Thin Films and Interfaces

Abstract

Over the last decade, two-dimensional thin films of complex oxides, graphene, and transition metal dichalcogenides have displayed an astonishing array of unexpected properties. CHESS-U will enable the research community to address the grand challenge of characterizing the atomic structure of these materials and explaining how their structure determines their properties. This work will advance the fundamental understanding of two-dimensional materials and accelerate their commercialization for electronics, optoelectronics, data storage, sensing, communications, photovoltaics, and other applications. CHESS-U will provide critical atomic structural characterization to help two NSF-funded Materials Innovation Platforms – the *Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials* (PARADIM) at Cornell and the *Two-Dimensional Crystal Consortium* (2DCC) at Penn State – to fulfill their missions.

We are witnessing an extraordinary increase in interest and investment to understand and exploit novel thin film systems such as high-K dielectrics, III-V nitride semiconductors, complex oxides, and two-dimensional materials. The scientific community wants to explore how and why the properties of known materials change dramatically when we reduce their dimensions. Technology industries need ultra-thin films to make future products smaller, faster, and cheaper. To accelerate our progress in understanding and exploiting these materials, we must improve our ability to understand and control the properties of interest. We need advances in thin film growth and in post-growth processing to create higher-quality materials. We need advances in theory and characterization to elucidate their atomic structures. The research community needs broad access to these advances.

X-ray beams from synchrotron light sources can improve our understanding of atomically thin films and interfaces. High-energy X-rays can probe buried interfaces. Data from X-ray experiments can enhance theoretical modeling tools that help us understand truncated surfaces, reconstructions, impurities, and defects. In complex experimental setups that mate beamlines with growth chambers, high-energy X-rays penetrate complex vacuum vessels and travel through gaseous atmospheres or liquids to capture information about thin film growth *in situ*. High-flux beamlines can gather time-sensitive data on tiny fractions of an atomic monolayer or on atomically clean surfaces in ultra-high vacuum. CHESS-U will provide both the thin film research community and the technology development community with advanced characterization capabilities that will drive advances in electronics, optoelectronics, data storage, sensors, communications, photovoltaics, and more.

Examples of Thin Film and Interface Systems with Technological Potential

Thin Films and Interfaces of Complex Oxides

Oxides exhibit electronic, optical, and magnetic behavior. Structurally compatible oxides can serve as insulators,^{226,227} semiconductors,²²⁸ metals,²²⁹ superconductors,²³⁰ ferroelectrics,²³¹ pyroelectrics,²³² piezoelectrics,²³³ ferromagnetics,²³⁴ multiferroics,^{235,236,237} and nonlinear optical materials.²³⁸ These compounds can exhibit structural instabilities, electronic correlations, and complex phase diagrams with competing ground states.²³⁹

Oxides with the perovskite structure (ABO_3 ; see Figure 1) can exhibit high-temperature superconductivity and colossal magnetoresistance.²⁴⁰ Since perovskites can be chemically and structurally compatible, this large and diverse family of materials offers an opportunity to

combine electronic, magnetic, and optical properties in ways we cannot achieve with conventional semiconductors.

Films with nanometer-scale thickness exhibit quantum size effects, including a wide range of surprising and unexplained phenomena.²⁴¹ For example, thin films of LaNiO_3 undergo a metal-to-insulator transition when researchers reduce the film thickness to only two unit cells.²⁴²

FeSe monolayers grown on an oxide (SrTiO_3) substrate lose all resistance to electricity above 100K, ten times higher than the superconducting transition temperature of bulk FeSe .²⁴³ This result stimulates us to imagine that one day materials scientists will engineer high-temperature superconductivity by tailoring the electron pairing at the interfaces between two different materials.²⁴⁴

The interfaces between complex oxide surfaces also exhibit new and unexplained phenomena.^{245,246} For example, the interface between LaAlO_3 , a Mott insulator, and SrTiO_3 , a band insulator, undergoes gate-tunable insulator-to-metal^{247,248} and insulator-to-superconductor^{249,250} transitions. It also exhibits a large interfacial spin-orbit effect.^{251,252} Ferromagnetism coexists with superconductivity at the interface.^{253,254} The research community continues to debate the mechanisms responsible for these phenomena.^{255,256,257}

Scientists have also reported superconductivity at 300 mK at the interface between SrTiO_3 and LaTiO_3 , a Mott insulator.²⁵⁸ Another group reported a 2D electron gas between LaTiO_3 and the band insulator KTaO_3 .²⁵⁹ At the interface, they observed metallic conduction over the range from 2K to 300K and carrier mobilities as high as $21 \text{ cm}^2 / \text{volt-second}$ at 300K, three times higher the mobility of doped bulk SrTiO_3 . Another group found a two-dimensional electron gas with high carrier mobilities at the interface between SrTiO_3 and GdTiO_3 , a Mott insulator.²⁶⁰

Yet another group discovered configuration-dependent conductivity at the interface between SrTiO_3 and the Mott insulator LaVO_3 .²⁶¹ The (001) oriented n-type $\text{VO}_2 / \text{LaO TiO}_2$ interface exhibits a LaVO_3 thickness-dependent insulator-to-metal transition and an anomalous Hall effect at low temperatures. The (001) p-type $\text{VO}_2 / \text{SrO} / \text{TiO}_2$ is insulating, as is the (110) heterointerface.

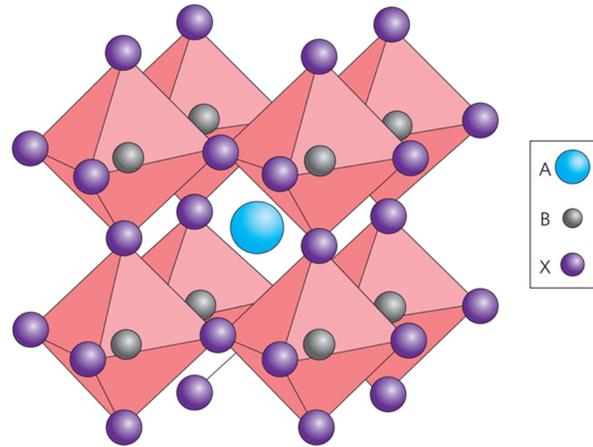


Figure 1:
The Perovskite Crystal Structure

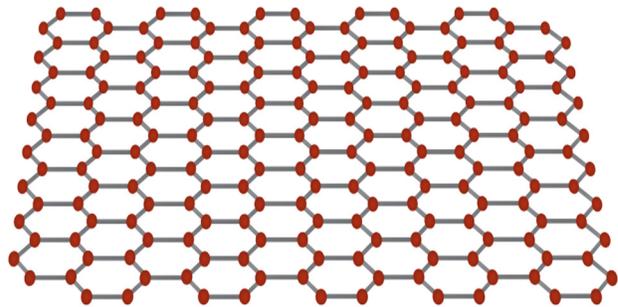


Figure 2: Schematic of the Structure of Carbon Atoms in Graphene

In other experiments, researchers have observed ferromagnetism at the interface between the antiferromagnetic oxides LaMnO₃ and SrMnO₃.²⁶²

In the aggregate, these experiments suggest that interface engineering is an attractive approach to creating novel two-dimensional states in systems with correlated electrons. However, the research community cannot engineer devices rationally today because we lack a mechanistic understanding of how these phenomena occur.

Graphene

Graphene,^{263,264} the monolayer form of graphite (see Figure 2),²⁶⁵ is an excellent electrical and thermal conductor²⁶⁶ with high carrier mobility and surprising molecular barrier properties.²⁶⁷ Graphene has stimulated an abundance of new physics because its electronic band structure has a linear dispersion near the K point and because its charge carriers act as massless Dirac fermions.^{268,269}

Scientists have proposed a broad range of devices and applications, including flexible electronics, high-frequency transistors, logic transistors, photodetectors, optical modulators, mode-locked lasers, composite materials, paints, coatings, solar cells, batteries, sensors, metrology, drug delivery, tissue engineering, regenerative medicine, and microscopy.²⁷⁰ In devices encapsulated in BN dielectric layers, the carrier mobility of graphene exceeds 10⁶ cm² / volt-second at 2K and 10⁵ cm² / volt-second at room temperature.^{271,272} Since pristine graphene lacks a bandgap, field-effect transistors (FETs) made from graphene cannot switch off effectively. Researchers have engineered bandgaps in graphene via nanostructuring,²⁷³ chemical functionalization,²⁷⁴ or applying a high electric field to bilayer graphene,²⁷⁵ but these techniques increase complexity and diminish carrier mobility.

A monolayer graphene membrane is impermeable to standard gases, including helium;²⁷⁶ it can support pressure differences greater than 1 atmosphere. This property may enable a broad range of physical, chemical, and biological applications that range from cellular compartmentalization to pressure sensing. Sub-micron membranes of graphene oxide are completely impermeable to liquids, vapors, and gases, with one counterintuitive, provocative, and still controversial exception: it may allow unimpeded permeation of water.²⁷⁷

At room temperature, the thermal conductivity of graphene varies from $\sim(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W/mK.²⁷⁸ This value suggests that graphene can outperform carbon nanotubes in heat conduction. It enhances graphene's potential for electronic applications and suggests that graphene will be an exceptional material for thermal management.

Two-Dimensional Transition Metal Dichalcogenides

Transition metal dichalcogenides^{279,280} (TMDs) are a class of materials with the formula MX_2 , where M is a transition metal element from group IV (Ti, Zr, or Hf, etc.), group V (V, Nb, or Ta, etc.) or group VI (Mo or W, etc.), and X is a chalcogen (S, Se, or Te). These materials form layered structures of the form X–M–X, with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms. Figure 3 shows a schematic representation of a typical MX_2 structure, with the chalcogenide atoms (X) in yellow and the metal atoms (M) in black. The combination of strong in-plane bonding and weak out-of-plane interactions makes it possible to exfoliate two-dimensional layers with thickness of a single unit cell.

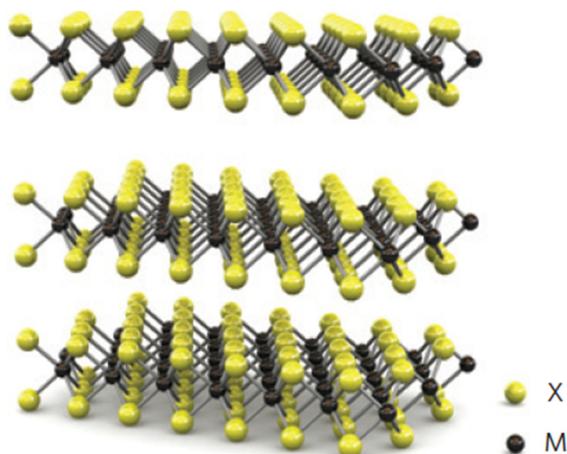


Figure 3: Typical Structure of a Transition Metal Dichalcogenide

The niobium and tantalum dichalcogenides (NbS_2 , NbSe_2 , NbTe_2 , TaS_2 , TaSe_2 , and TaTe_2) are metals^{281,282} that superconduct at low temperatures.^{283,284,285} The molybdenum and tungsten dichalcogenides (MoS_2 , MoSe_2 , MoTe_2 , WS_2 , WSe_2 , and WTe_2) are semiconductors with bandgaps that range from 1.0 eV to 2.1 eV.^{286,287,288,289,290,291} The bandgaps are wider in the monolayer materials than in the bulk.

Single-layer TMDs have interesting and potentially useful electronic,²⁹² optical,^{293,294} mechanical,²⁹⁵ and magnetic properties.^{296,297,298} Researchers have integrated these materials into prototype field-effect transistors,²⁹⁹ thin-film solar cells,³⁰⁰ and photodetectors.³⁰¹ The sizable bandgaps of WS_2 and WSe_2 change from indirect in the bulk to direct in monolayers, opening the possibility of applications in transistors, photodetectors and electroluminescent devices.³⁰²

In MoS_2 , the indirect bandgap of the bulk material also shifts to a direct bandgap of 1.9 eV in a monolayer,³⁰³ making it an attractive material for electronic applications.³⁰⁴ The MoS_2 monolayer is the first atomically thin material that emits light strongly; it exhibits a thousandfold increase in luminescence quantum efficiency compared with the bulk material. Monolayer MoS_2 also exhibits an effective Young's modulus of 270 ± 100 GPa, comparable to that of steel. It can deform up to 11% before breaking.³⁰⁵

Experimental Capabilities at CHESS-U

Engineers cannot yet exploit the full technological potential of ultra-thin complex oxide films, graphene, and two-dimensional dichalcogenides because the research community does not fully understand the precise conditions that bring their properties into existence. The properties depend sensitively on the detailed atomic structure of extraordinarily thin films – in some cases a single atomic layer – as well as the detailed stoichiometry and arrangements of atoms at atomic-layer interfaces in buried materials. They depend on the interplay among strain, temperature, crystallographic phase, and the properties of the substrate. It is difficult to investigate these features and relationships in films that are only one or two atomic layers thick.

In 2000, CHESS created a new beamline end station with reactive gas handling and high-power lasers to serve the pulsed laser deposition thin film growth research community. CHESS designed the end station so that we could easily mount vacuum vessels and reaction chambers (including those from other laboratories) on a multi-circle diffraction instrument. To collect data on ultra-thin specimens and/or rapidly evolving systems, we commissioned a wide-energy bandpass X-ray optic with double focusing to maximize beam flux. Research groups from Brookhaven National Laboratory, Boston University, the University of Vermont, Cornell University, and the Naval Research Laboratory have exploited these capabilities.

CHESS-U will augment these current capabilities. CHESS-U's high-energy, high-flux X-ray beams, combined with our custom broadband X-ray optics and hazardous gas handling infrastructure, will enable researchers to measure film thickness, crystalline phase, and strain by X-ray scattering and also to measure the atomic composition of films by X-ray fluorescence, all *in situ* and in real time. Researchers will conduct rapid structural characterization studies and also rapid phase diagram studies as a function of temperature and environmental conditions with high-energy (40 to 70 keV) X-rays and large-area 2D detectors. CHESS-U will motivate our user community to develop new *in situ* growth environments where they can study thickness-dependent structure transitions, surfactant effects, strain, surface morphology, and other growth phenomena at ambient pressure and in UHV, during atomic layer deposition and chemical vapor deposition.

Experimental Objectives at CHESS-U

The CHESS-U research community will take advantage of our experimental infrastructure to pursue these scientific objectives:

- Characterize the atomic structures of ultra-thin films and heterostructures of complex oxides, graphene, and transition metal dichalcogenides.
- Monitor thickness, crystalline phase, strain, and composition in these materials *in situ* during thin film growth.
- Elucidate the interrelationships among structure, properties, and processing.
- Provide experimental data to theorists to help them refine their models.
- Identify growth conditions that optimize the desired structure and the desired properties.
- Collaborate with industry to realize the commercial potential of 2D materials.
- Explore the potential of realizing unexpected properties in heterostructures of these materials.

Scientific and Technological Impacts

CHESS-U will support two major NSF-funded Materials Innovation Platform (MIP) user facilities: PARADIM (*Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials* at Cornell) and 2DCC (the *Two-Dimensional Crystal Consortium* at Penn State). These MIP facilities seek to harness the transformative potential of complex oxides, graphene-inspired structures such as BN and MoS₂, and heterostructures that combine these systems. CHESS-U will augment the in-house characterization facilities of these MIP centers by providing high-flux, high-energy X-ray beams that allow higher spatial and temporal resolution.

Proximity to the MIP centers is an important advantage because ultra-thin samples can be extremely sensitive to contamination. A few atoms striking the surface can destroy the sample. Even at pressures as low as 10⁻¹¹ Torr, samples may only survive one to two days. PARADIM

resides near CHESS on the Cornell campus, and researchers from 2DCC can drive to Cornell in about 3 hours (as compared with 5.5 hours to NSLS-II or 11 hours to APS). CHESS will design a sample carrier to transfer samples from deposition chambers at PARADIM and at 2DCC into compatible UHV characterization chambers at CHESS without breaking vacuum. CHESS-U will enable users to study two-dimensional materials by crystal truncation rod analysis, coherent Bragg rod analysis, X-ray standing wave analysis, resonant / anomalous diffraction, and pole-figure analysis. Researchers will conduct these experiments at ambient pressure and under vacuum, at high and low temperatures, generally with X-ray energies of 10 to 60 keV.

Studies at CHESS-U will help the research community to understand the mechanistic origin of the properties of two-dimensional materials. Researchers will gain critical new insights into the ways in which material performance depends on atomic structure, strain, temperature, and the substrate. By watching films grow in real time, researchers will learn to synthesize two-dimensional materials with optimized properties. The research community needs this knowledge to accelerate the commercialization of two-dimensional materials for electronics, optoelectronics, data storage, sensing, communications, photovoltaics, and more.

Researchers will conduct *in situ* experiments at other synchrotrons, but CHESS-U will maintain a competitive advantage in the total intensity of X-ray energy on the sample, which will enable time-resolved experiments with the shortest possible time intervals. We can achieve this high intensity because of CHESS-U beam characteristics, wide-energy-bandpass multi-layer monochromator technology, and high-flux undulator sources. No other synchrotron in the U.S. will optimize a high-energy, high-flux beamline to characterize thin film growth *in situ*. CHESS-U will provide a unique capability to accelerate the basic understanding and the commercial applications of two-dimensional materials.

IX. Catalysts, Man-Made and Biological

Abstract

CHESS-U will enable the research community to acquire a fundamental understanding of the mechanisms and dynamics of catalyzed transformations. Industrial processes for manufacturing chemicals, polymers, and pharmaceuticals all depend on catalysts that increase the rates of chemical reactions, lower the temperatures at which they occur, and enhance the yields of desired products. High performance catalysts would enable more efficient use of materials and energy, minimize the environmental footprint of chemical transformations, and enable processes for harvesting renewable energy. Biological systems have evolved sophisticated enzyme catalysts that can serve as models and provide insights into catalyst design.

The research community lacks an atomic-level understanding of how most man-made and biological catalysts operate. An understanding of reaction mechanisms would enable chemists and chemical engineers to design efficient, selective, environmentally benign catalysts for any application.

CHESS-U will enable researchers to study catalysts *operando* with unprecedented electronic state selectivity and temporal resolution. Our X-ray beams will enable the research community to identify the catalytically relevant species and intermediate steps in chemical and biochemical transformations, relate structure and composition to catalytic activity and product distribution, and connect experimental observables with theoretical and computational predictions.

A catalyst is a substance that accelerates a chemical reaction without itself being consumed.³⁰⁶ Catalysts facilitate chemical transformations by providing alternative lower-activation energy pathways. They enable specific chemical transformations via a sequence of intermediate reactions, “an intricate dance of chemical bond-breaking and bond-forming steps.”³⁰⁷ A catalyst can increase the rate of a chemical reaction, lower the temperature required for the reaction to occur, increase the selectivity of a reaction (i.e., increase the yield of the desired product), or even change the reaction pathway to yield a different product.³⁰⁸

Catalysts control processes that dominate the pharmaceutical, petroleum, and energy industries. They limit the environmental impacts of these industries and optimize their utilization of limited resources. Chemists, materials scientists, biologists, and engineers study catalysts to understand nature and to address industrial requirements. They typically evaluate catalysts by three figures of merit: *activity* (the rate of the reaction at a given temperature), *selectivity* (the percentage yield of the desired product), and *stability* (the ability of the catalyst to sustain its activity over time).³⁰⁹ A broad range of materials can serve as catalysts, including solids, porous frameworks, nanoparticles, and enzymes.

Technologically Important Classes of Catalysts

Catalysts distinguish between *heterogeneous catalysts*, which are in a different phase from the reactants, and *homogeneous catalysts*, which are in the same phase as the reactants. *Enzymatic catalysts* represent an important category of homogeneous catalysts. We need a detailed fundamental understanding of all areas of catalysis in order to improve our economy, meet humanity’s energy needs sustainably, protect the environment, and develop more sustainable chemical transformation processes.

Heterogeneous Catalysis

Since heterogeneous catalytic reactions occur at solid surfaces, heterogeneous catalysts tend to be porous materials with high surface area.³¹⁰ Heterogeneous catalysts offer several advantages:

- They are relatively easy to separate from the reaction products.³¹¹
- They typically operate for several years before they require replacement.
- They can withstand temperatures as high as 1600K and pressures as high as 350 atmospheres.³¹²
- They typically do not corrode standard reactor units.

The chemical industry transforms nitrogen into ammonia for fertilizers via the Haber-Bosch process, which employs an iron catalyst. The petroleum industry relies on zeolite catalysts to break up large molecules into smaller molecules and on platinum catalysts to improve the octane rating of fuels. Heterogeneous catalysts clean flue gases from power plants and remove toxic gases from industrial waste streams. Today, every new car contains a heterogeneous catalytic converter in which precious metal catalysts (e.g., platinum, palladium, and rhodium) convert carbon monoxide to carbon dioxide and water, transform hydrocarbons into carbon dioxide and water, and convert nitrogen oxide back into nitrogen and oxygen.

It is difficult to unravel the mechanistic details of many heterogeneous catalytic processes because surface reactions occur only at specific sites and because intermediate chemical species typically have short lifetimes. Photon-in / photon-out X-ray spectroscopies make it possible to study a given process *in situ* and *operando* with excellent temporal resolution.

Homogeneous Catalysis

Homogeneous catalysts may be active molecular species, or they may contain molecular components that transform to a catalytically active form in solution. They can be simple acids or bases or complex molecular (often organometallic) assemblies. Industrial engineers tend to select homogeneous catalysts less frequently than heterogeneous catalysts because it can be difficult and expensive to separate them from final products. However, homogeneous catalysts remain in industrial practice. We cite two examples:

- *hydrogen fluoride* to manufacture 2,2,4-trimethylpentane (to increase the octane rating of gasoline) and
- *sulfuric acid* to manufacture ethane-1,2-diol (for antifreeze and polyester fibers), phenol (for plastics and pharmaceuticals), propanone (a commercial solvent), and bisphenol A (for polycarbonate plastics and epoxy resins).

The research community lacks an atomic-level mechanistic understanding of the operating mechanisms of some important homogeneous catalysts, including many biological reactions.³¹³

Enzymatic and Biological Catalysis

Enzyme catalysis is a type of homogeneous catalysis that biological systems have evolved over eons and tuned to accelerate the rate of a single reaction at the active site of a protein under ambient conditions. Enzyme catalysts tend to be more active and more selective than human-engineered catalysts. At their active sites, many enzyme catalysts contain earth-abundant elements from the first row of transition metals. Enzyme catalysts with similar active sites and

metal co-factors can facilitate markedly different reactions. It is important to understand precisely how these reactions proceed so that chemists can design new catalysts rationally.

Difficulties of Probing Catalytic Reactions

It is challenging to probe catalytic reactions. During those reactions, the catalytically relevant species can change subtly or dramatically in composition, structure, and oxidation state. The reactants, intermediates, and products can resemble each other closely. They can exist in low concentrations, and the concentrations can vary as a function of time. The reactions can occur at high temperatures and high pressures (for example, the Haber-Bosch process occurs at 150 atmospheres and at 450°C). To study these reactions, we need to select experimental techniques that enable us to probe the intermediates with maximum sensitivity and selectivity, and we need to optimize those techniques for *in situ* and *operando* measurements.

Advantages of Probing Catalytic Reactions with X-Rays

X-ray spectroscopies will provide profoundly useful information for scientists who are trying to understand how catalysts operate. High-energy X-rays penetrate sample environments such as high-pressure and high-temperature cells. High-flux X-rays make it possible to probe species in low concentrations. High-energy X-ray techniques are element specific because of the large energy separation between edges and emission lines; therefore, we can study one element in the presence of others.

Goals of Catalytic Research at CHESS-U

The CHESS-U research community will seek a fundamental understanding of catalytic transformations. CHESS-U will enable researchers to:

- Study catalytic reactions *operando*.
- Correlate the composition and structure of catalysts with activity and overall performance.
- Identify active sites on solid catalyst surfaces.
- Identify the cycle of intermediate reactions, the bond-breaking and bond-forming steps by which catalysts accelerate various chemical transformations.
- Develop the ability to probe the structures of reacting molecules and catalytic intermediates in real time with high spatiotemporal and energy resolution.
- Identify the detailed electronic and geometric changes that occur over the course of a reaction.
- Identify the changes in oxidation states, spin states, and coordination number that occur at given reaction steps and at individual active sites.
- Characterize the composition, structure, and morphology of heterogeneous catalysts *operando*.
- Characterize enzyme catalysts. Gain an atomic-level understanding of how they carry out their reactions. Elucidate the geometric and electronic structures of their active sites at intermediate stages.
- Determine how enzyme catalysts selectively bind the metals with which they interact. Determine how and why their catalytic pathway optimizes chemical conversion.
- Combine experimental studies with computation and simulation to establish design rules for optimizing catalyst design and catalytic behavior.

Unique Research Capabilities at CHESS-U

CHESS-U will provide a world-class X-ray facility and develop novel capabilities to study and characterize catalysts and catalytic reactions. The facility will provide tunable high-energy beams with spectral flux exceeding 10^{13} /sec/eV. High-energy beams will enable the CHESS-U research community to study catalysts in solid phases and in solution under a range of operating conditions (e.g., at high pressure, at high temperature, in flowing solutions, and during electrochemistry). High-flux beams will enable researchers to investigate structural changes in catalysts that undergo reaction on millisecond to microsecond time scales. Standardized mounting and alignment capabilities will facilitate “plug-and-play” operations with the specialized equipment that visiting researchers will bring to CHESS-U. Researchers will monitor the electron density and chemical state of samples during reactions by combining small or wide angle scattering with spectroscopic techniques simultaneously. CHESS-U will provide the capability to trigger processes and reactions with short pulses of light. The CHESS-U X-ray beams, coupled with a dual-array valence emission spectrometer (DAVES),³¹⁴ will make it possible to monitor multiple metal centers simultaneously as reactions progress.

Spectroscopic Techniques

The CHESS-U upgrade will provide the high-flux beams required to support these and other techniques:

- *X-ray emission spectroscopy* to probe quantitatively the electronic structure of active sites, including their metal spin state, oxidation state, and ligand identity. Since this technique does not require high incident energy resolution, we can exploit undulator bandwidth and energy to enhance signals.
- *High-energy-resolution fluorescence-detected X-ray absorption near-edge spectroscopy* to study selectively the electronic properties of specific active sites. The high flux of the CHESS-U beam will make it possible to conduct these traditionally time-consuming studies within the limits of beamtime availability. These studies take advantage of high energy resolution, and they require 100- μ m spatial resolution, easily available at CHESS-U.
- *Resonant inelastic X-ray scattering (RIXS)* to probe catalytic surfaces with element selectivity, valence selectivity, and spin selectivity.
- *Valence-to-core RIXS* to provide selectivity for metal-ligand interactions.
- *X-ray Raman spectroscopy* to study low-energy edges under catalytically relevant conditions.
- *X-ray absorption fine structure spectroscopy (XAFS)* to clarify the structure and function of sites on amorphous catalytic materials, to gain information about atomic oxidation states in the near-edge region (XANES), and to gain short-range structural information such as the interatomic distances and coordination numbers of catalytic species.
- *X-ray diffraction crystallography (XRD)* to identify the long-range ordered structures of bulk catalysts and catalyst supports.

Beamline Infrastructure

The techniques described above impose stringent requirements on the beamline. We need both high flux and high resolution to optimize selectivity (e.g., *elemental sensitivity*, for which we tune the beam to probe specific absorption edges, and *electronic state sensitivity*, for which we

tune the beam to excite a core electron to a specific vacant atomic or molecular orbital and collect photons corresponding to specific final states of the electronic transition).

CHESS-U will offer a wide range of sample environments in which users can study various catalytic processes, enzymes in solution, chemical transformations under high pressure, and electrochemical interfaces. Hutch design and infrastructure will enable us rapidly to mount and align specialized equipment built by our users. CHESS-U will also leverage other existing experimental capabilities, such as the dual-array valence emission spectrometer (DAVES). This instrument helps researchers to study catalysts that employ two chemically important metals because it can simultaneously collect two XES spectra or two HERFD emission lines.

All these capabilities will enable CHESS-U researchers to study catalytic systems under real-world conditions. In the case of enzyme catalysts, our users will conduct continuous-flow X-ray spectroscopy experiments in which they interrogate an enzyme intermediate in solution under turnover conditions.

An Example Application in Enzymology and Biocatalytic Systems

CHESS-U would enable researchers to study the enzyme methane monooxygenase. Soluble methane monooxygenase (sMMO) is an iron-containing enzyme that helps bacteria to convert methane, the principal component of natural gas, into methanol, a liquid alcohol fuel. Natural gas is abundant, but difficulties associated with storing and transporting it motivate energy companies to burn off significant quantities at petroleum refineries. An inexpensive method of transforming methane to methanol would make it possible to exploit natural gas effectively and efficiently.

sMMO has attracted much interest from chemists and biochemists, but the challenges associated with this enzyme – low concentrations, incomplete accumulation of intermediates, and short lifetimes of the relevant species – have hindered studies. The CHESS-U upgrade will enable researchers to study sMMO via $K\beta$ XES and HERFD XAS in a continuous flow apparatus. This approach will enable us to study reaction intermediates selectively and efficiently by varying the time interval between the onset of the reaction and the exposure to the X-rays. Knowledge of how sMMO converts methane to methanol would give synthetic chemists a mechanistic foundation for strategies to carry out this reaction on an industrial scale. Researchers could conduct similar experiments on other enzymatic systems with two-color XES.

An Example Application in Heterogeneous Catalysis

CHESS-U will enable researchers to study heterogeneous catalysts under realistic operating conditions such as high temperatures and pressures. For example, our users will apply high-energy X-ray spectroscopic methods to understand the mechanism of nitrogen reduction to ammonia in the industrial Haber-Bosch process. We have derived our current incomplete understanding of the mechanism from soft X-ray studies of idealized iron catalytic surfaces. The research community doesn't fully understand the transformation that occurs with a real operating industrial catalyst. High-energy X-rays at a CHESS-U undulator beamline will enable our users to study the catalyst at high temperatures and pressures. We may obtain the first experimental evidence for *in situ* nitriding, which the research community has proposed on the basis of idealized model systems but has never observed in the real catalyst.

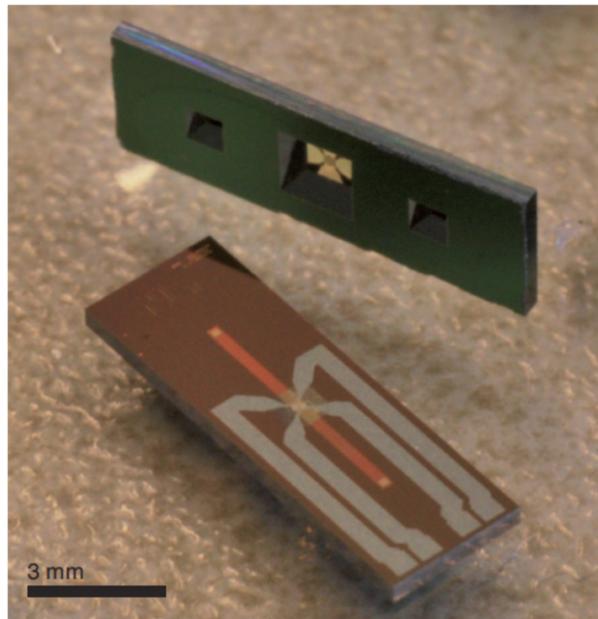


Figure 1: Prototype High Pressure, High-Temperature Cell for X-Ray Spectroscopy Measurements

Figure 1 shows a prototype high-pressure, high-temperature cell compatible with X-rays. CHESS will adapt this cell for spectroscopy. Due to the intrinsic complexity of the industrial catalyst, these experiments would benefit greatly from the ability to perform two-color XES in which we follow the roles of both the Fe (or Ru) catalyst and the K promoter at the same time. X-ray Raman scattering (XRS)³¹⁵ would provide the unique ability to obtain N K- and Fe L-edge data on an operating catalyst. A full understanding of the industrial mechanism and of the deactivation process will provide an essential knowledge base to support future catalytic design.

Scientific and Technological Impact

Catalysis researchers at CHESS-U will seek a fundamental understanding of the mechanisms and dynamics of catalyzed transformations. This understanding will make it possible to design catalysts for many chemical transformations with atomic precision. They will design catalysts that convert reactants to products with molecular precision and with high selectivity and efficiency. High-selectivity catalysts will optimize utilization of resources and will minimize capital costs, operating costs, and waste. The understanding we gain could transform the chemical and energy industries of the 21st century. Their work will make it possible to create a sustainable energy supply from domestic sources while minimizing their environmental impact.

X. Disordered Materials

Abstract

Single crystal diffraction ranks among the most celebrated and powerful of all the synchrotron x-ray techniques. It offers structural information with atomic-scale precision and bulk sensitivity. However, X-ray crystallography excels at measuring perfect order, and all real crystals contain some degree of disorder – local, non-repeating structures to which traditional crystallography is blind. Increasingly, researchers are becoming aware of the important role these local structures play in determining the useful function of materials. CHES-U will enable researchers to study local structures in crystalline materials quantitatively via unique high-energy beamlines optimized for diffuse x-ray scattering. By measuring Bragg and diffuse scattering simultaneously over expansive ranges of reciprocal space, CHES users will generate precise 3D maps of local structures in crystals efficiently and will elucidate disorder-function relationships for the first time.

We aim to develop a quantitative, robust, and even intuitive understanding of disorder in crystalline materials. Disordered structures can evoke useful properties in a wide range of complex functional materials. Silicon becomes useful for solid-state transistors only after we dope it. Diamond becomes useful for quantum computing only when it contains nitrogen vacancy centers. Exotic properties of disordered materials often arise when the disorder is correlated; i.e., when the defects interact with each other. For example, Figure 1 shows that as we intercalate Na ions into V_2O_5 , they form disordered chains that manifest as diffuse streaks in reciprocal space, halfway between the rows of Bragg peaks (left). As we decrease the temperature or increase the concentration of Na, the intercalated ions undergo an ordering transition, and the streaks coalesce into new lines of weak peaks (right).

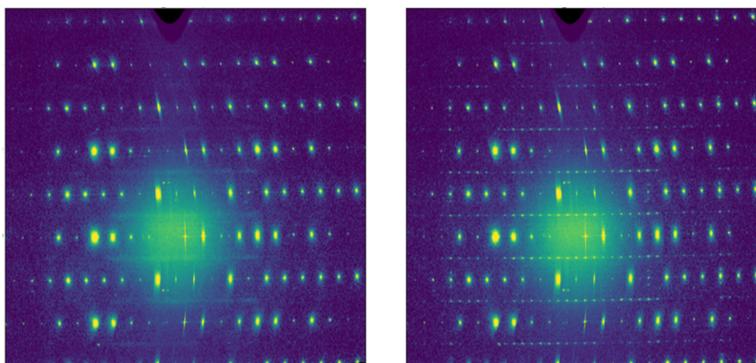


Figure 1: Defect correlations in $Na_xV_2O_5$.
Data collected at CHES A2 using 56 keV x-rays & Pilatus6M detector.
Images courtesy of M. Krogstad and R. Osborn.

Many materials, including frozen water, are intrinsically disordered but still strongly correlated, even when chemically pure.³¹⁶ In these materials, the structural building blocks cannot order in the traditional way because of *frustration*, wherein the local interactions that drive order are incompatible with the geometry of the lattice on which that order must evolve.³¹⁷

To address the grand challenge of understanding disorder, aperiodicity, and local structure, we need to create a new constructive language to describe these states of matter. Rather than defining these phases by their deficiency relative to an idealized structure, we seek to understand the underlying interactions that govern them and to learn how the properties of materials with correlated disorder depend on their structure. We must learn to control correlated disorder in

order to engineer materials with novel functionalities. To gain the required understanding, we must learn to probe correlated disorder in its various manifestations: structural, magnetic, orbital, spin, electronic, etc. We must learn to measure these properties on microsecond, nanosecond, and even picosecond time scales to understand the dynamics of local states. Critically, we need powerful, quantitative probes of the dynamics of disordered states, the most important of which is diffuse high-energy X-ray scattering.

Diffuse X-Ray Scattering

X-rays diffracting from a long-range repeating pattern of electron density, such as a perfect crystal, exhibit sharp, narrow *Bragg peaks* in the scattering intensity. When the pattern of electron density repeats imperfectly, the intensity of the Bragg peaks diminishes slightly, and we see a broad, slowly modulated background of scattering in the nominally empty space between them. Crystallographers refer to this signal as *diffuse scattering*. Diffuse scattering indicates that the X-rays are probing short-range order. It contains information about correlations spanning a spatial range from a few Ångstroms to hundreds of nanometers.

In many cases, the disordered structure of a material controls its properties.³¹⁸ For example, in cubic zirconia, oxygen vacancies provide the basis for superionic conductivity and phase stability.³¹⁹ In alloys, the details of local atomic ordering influence hardness, tensile strength, and electrical and thermal conductivity.^{320,321} In catalysts such as zeolites, the shapes and sizes of channels and cavities determine the ability to discriminate among different absorbing molecules.³²² In liquid crystals, the state of order lies intermediate between liquid and crystalline, and the types of short- and long-range translational and orientational order determine device performance.³²³ In oxide superconductors, several competing short-range orders, including oxygen vacancy correlations and charge density waves, can profoundly alter the electronic properties.^{324,325} In relaxor ferroelectrics, nanometer-sized polar domains may play a role in determining the extraordinary dielectric and piezoelectric properties.³²⁶ Diffuse scattering can help us gain a quantitative understanding of all these phenomena. Eventually, it may help us learn to design disordered materials rationally to meet the requirements for a broad range of applications.

Although scientists have observed diffuse scattering since the earliest days of X-ray diffraction, the research community has been slow to develop methods to interpret and analyze diffuse scattering data. One reason is that the diversity of disorder observed in nature has made it difficult to devise universal analysis techniques suitable for all phenomena. Another reason is that the research community lacked the extreme computing power and modern detectors required to conduct the experiments. CHESS-U will mitigate these problems³²⁷ with a state-of-the-art infrastructure of computer hardware and computer models,³²⁸ intense synchrotron sources, and improved detectors, including a 6-megapixel high-dynamic-range pixel array detector (Pilatus6M).

The State of Knowledge of Disordered Materials

The research community understands qualitatively the basic taxonomy of several kinds of disorder (crystalline defects, sublattice mixing, ice-like disorder, spin liquids, high entropy alloys, glasses, quasicrystals, phonons, polarons, etc.). We also recognize that these phases leave distinct fingerprints in the diffuse x-ray scattering.³²⁹ We know how to define some kinds of

short range order parameters, and we have applied chemical intuition to understand local structures in some specific systems on a case-by-case basis.³³⁰

The pair distribution function (PDF) technique has achieved significant success in collecting and fitting the diffuse signal between and beneath the Bragg peaks.³³¹ PDF gives the probability of finding two scatterers a given distance apart. It provides a real-space picture of interatomic separations, regardless of whether the sample contains long-range order. Researchers have applied it successfully to study disorder in polycrystalline and amorphous materials. Dedicated research groups and beamlines specialize in this technique, and it has evolved into a useful tool even for non-specialists. Unfortunately, the angular averaging required for PDF obscures subtleties and leads to ambiguities in the analysis. Thus PDF provides a first approximation of correlated disorder, but not a final answer. Furthermore, many emerging materials of interest come in the form of epitaxial thin films and heterostructures, which are fundamentally incompatible with PDF techniques.

Diffuse scattering studies of crystals and films contain much more information than polycrystalline PDF measurements, but they have not seen widespread use or achieved comparable success because of their higher degree of technological and theoretical difficulty.

Knowledge Gaps We Propose to Fill

We lack automated and prescriptive data analysis pipelines for diffuse single crystal scattering. We lack a language and a robust taxonomy to describe the symmetries and rules of local disordered structures. We require huge datasets to measure correlated disorder, and it is only now becoming technically feasible to collect, reduce, and visualize the data. We lack fast forward modelling, *ab initio* methods, and machine-learning algorithms that would enable us to analyze the large datasets we can generate.

A result of these technical limitations, we don't understand the role of disorder in important materials. Standard materials characterization protocols overlook or ignore diffuse signals. This bias against analyzing locally disordered structure may be concealing the underlying physics of a huge number of materials. For example, ubiquitous short-range charge order in cuprate superconductors evaded notice for ~25 years, despite the fact that the research community has published more than 200,000 papers about them since 1987.³³² Not until 2012 did synchrotron X-ray studies reveal the diffuse scattering associated with charge density waves in these materials.³³³

CHESS-U will overcome the aforementioned technical limitations at CHESS. It will establish a fully optimized system to study simultaneously the Bragg and diffuse scattering in single crystal systems. This system will enable the CHESS research community to realize the next generation in precision analysis, the so-called "3D-PDF" technique.³³⁴ By measuring the three-dimensional diffuse scattering without resorting to the angular averaging inherent in traditional PDF, we will recover additional information regarding the shape of local structures. We will also gain sensitivity to weak modulations that stronger signals conceal during averaging. By fitting these comprehensive datasets, we will enable model-independent reconstructions of both the average background lattice and the local aperiodic structures in unprecedented detail.

Scientific Questions We Propose to Answer

Materials researchers will come to CHESS-U to avail themselves of the only beamline optimized for high-energy diffused scattering. Users will answer these and many other scientific questions:

- ***How can local structures control global properties in strongly correlated quantum materials?***

In recent years, it has become increasingly clear that disorder creates new phenomena. The research community is showing increased interest in disorder-property relationships in unconventional superconductors, strongly spin-orbit-coupled materials, colossal magnetoresistance materials, relaxor ferroelectrics, and frustrated quantum magnets. We are also rapidly gaining the ability to nano-engineer the structure of materials. *Our goal is to develop the ability to control function by engineering aperiodically.* To succeed, we must understand how spectacular bulk properties follow from the sum of the local building blocks. The first step is to gain a quantitative understanding of real local structure.

- ***What is the nature of the various short-range orders in layered superconductors? How do they relate to pairing, the pseudogap, and the quest for higher T_c ?***

In cuprate superconductivity, various types of disorder (e.g., vortex-pinning defects, stacking faults, oxygen ordering, and phase competition with charge density waves) seem to control all the technologically relevant parameters, including the transition temperature, the critical current, and the mechanical strength. Despite decades of study, comprehensive maps of the diffuse scattering have begun to appear only recently. Given the huge number of materials families of unconventional layered superconductors, we need a high-throughput instrument to address this issue, lest it take another 10 years to understand the full impact of structural disorder.

- ***Can we understand how phonons interact with defects and with each other? Can we apply this understanding to engineer better thermoelectric materials?***

As Debye taught us ~100 years ago,³³⁵ a perfect idealized harmonic crystal would have infinite thermal conductivity. The very existence of finite thermal conductivity demonstrates that heat-carrying lattice vibrations (phonons) scatter from crystal imperfections and from each other.³³⁶ We can study both the defect populations and the phonon populations by diffuse X-ray scattering,³³⁷ and we can study their interactions by driving materials out of equilibrium with heat pulses.³³⁸ These studies may enable us to understand and then to suppress the thermal conductance of thermoelectric materials. This achievement would enable us to harvest heat more efficiently to generate electric power and thereby to increase the efficiency of hybrid vehicles.

- ***Can magnetic diffuse scattering help us to diagnose exotic interactions in topological and strongly spin-orbit-coupled materials?***

Physicists have long championed quantum materials with exotic disordered ground states in the electronic (spin, charge, orbital) degrees of freedom as sources of new emergent particles that can underlie new technologies.^{339,340,341} In Kitaev systems, for example, the predicted

spin liquid ground state exhibits exotic fractionalized excitations that may be useful for fault-tolerant quantum computing.^{342,343} However, it has proven difficult even to show that a material exhibits Kitaev interactions, let alone fractionalized excitations. Resonant magnetic diffuse x-ray scattering may be the most powerful probe to identify Kitaev interactions in iridates and other strongly spin-orbit-coupled materials.³⁴⁴ CHESS-U will offer high flux over energy ranges spanning the K and L edges of 3d, 4d, and 5d transition metals, as well as the lanthanides and actinides. At CHESS, we are developing unique analyzer optics that will enable us to collect diffuse resonant signals efficiently with area detectors.

- ***What local correlations between mobile ions develop in battery materials as they charge? How do these correlations affect battery function?***

As batteries charge, ions intercalate into a host electrode. We can think of these intercalations as time-varying concentrations of defects. As their density increases, they will interact with each other and develop correlations (as shown in Figure 1), which will alter the material properties.³⁴⁵ By understanding the onset of these correlations and their influence on stored energy density, we will learn to design better batteries.

- ***How does epitaxial strain control octahedral rotations in perovskite thin films? How can we exploit this understanding to tune band structures (measured via ARPES) and induce novel behavior?***

Epitaxially grown perovskite films manifest a wide variety of unconventional electronic states. These structures are susceptible to symmetry-lowering octahedral rotations. These rotations leave a subtle signature in the diffraction signals, but they can exert a large effect on materials properties. For example, they can double the unit cells and drastically affect the band structures, turning, for example, a wide-band metal into a semi-metal or even an insulator.³⁴⁶ The rotations can manifest both as long range ordered patterns or as locally disordered fluctuations. Materials can undergo transitions between these two cases. CHESS researchers will study epitaxial perovskite films via comprehensive X-ray scattering to elucidate the impact of octahedral rotations on the observed band structures. We will determine how the rotations depend on epitaxial strain and thereby enable a new degree of freedom for engineering the band structure in perovskite thin films of high-temperature superconductors (cuprates), photovoltaic materials (hybrid organic-inorganic halides), colossal magnetoresistance compounds (manganites), and spin-orbit-driven insulators and semi-metals (iridates).

- ***What are the dynamics associated with local structures? How can we manipulate the dynamics on fast timescales?***

Long-range ordered states are naturally long-lived and stable. When correlation lengths are small, dynamics are more likely, and local non-equilibrium fluctuations can arise. Ultrafast measurements of diffuse scattering from local structures promise to teach us how polarizations switch in relaxor ferroelectrics, how ions diffuse in solid-state electrolytes, and how strain and heat pulses propagate through crystals.

Experiments and Experimental Techniques at CHESS-U

Members of our user community who are interested in disordered materials will conduct efficient, rapid, high-dynamic-range diffraction studies of single crystals and thin films. We will optimize these experiments for throughput and for real-time analysis of huge datasets. In non-resonant scattering experiments, we will exploit the highest-energy photons and largest-area detectors available to collect truly comprehensive data.

CHESS-U will accommodate plug-and-play sample environments that provide low temperatures, high temperature, high pressures, electric fields, magnetic fields, and uniaxial strain. Our experiments will make sub-nanosecond measurements of local dynamics by taking advantage of the large bunch charges in CHESS-U beams as well as the ultrafast detectors developed at Cornell.

When we study magnetic correlations via resonant scattering, the polarization of the X-rays leaving the sample carries important information. Furthermore, the sample simultaneously emits many unwanted low-energy fluorescence photons, which we must discriminate out of the signal. CHESS is therefore developing novel X-ray optics to analyze the polarization and energy of the scattered beam while preserving the massive efficiency increases associated with area detectors. The polarization analyzers consist of bent silicon with a special toroidal shape. We couple them with area detectors in the near field, using a 45-degree Bragg reflection geometry. They will enable us to measure about 10^5 momentum transfers simultaneously, subtending a solid angle that spans a full Brillouin zone. This coverage pales in comparison to our highest-energy non-resonant capabilities, but it will increase our efficiency dramatically because researchers typically conduct magnetic scattering measurements a single momentum transfer at a time.

Why the U.S. Research Community Needs CHESS-U to Study Disordered Materials

The studies described above require a high-flux, high-energy (7-keV to 100-keV) X-ray beam. Within this range, CHESS-U will provide world-leading capabilities. The high flux of our beam will enable us to resolve weak scattering signals. The high energy of our beam will deliver more information per image because it projects more reciprocal space into the solid angle subtended by the surface of the detector. High energies penetrate through bulk crystals and alleviate self-absorption problems, enabling us to collect data over full 360° rotations rather than narrow regions of reflection from the sample surface. As a result, we can standardize the measurement procedure from sample to sample and thereby simplify experiments. High energies allow us to study heavier elements; for example, we will be able to study compounds that contain Pb (relaxors), U (heavy fermions), Yb (frustrated magnets) without preparing extremely thin samples. High-energy photons don't interact strongly with air or with windows; this fact alleviates low-angle background scattering from images or alternatively removes strict requirements for in-vacuum operation.

CHESS is currently the only synchrotron that provides a 6-megapixel high-dynamic-range pixel array detector (Pilatus6M) for use on high-energy (> 40 keV) beamlines. This unique combination is ideal to support diffuse scattering experiments. CHESS benefits from co-location with Sol Gruner's detector research group at Cornell, which produces the best high-dynamic-range X-ray detectors in the world. Today his MMPAD detector achieves dynamic range approaching 8 orders of magnitude with single-photon sensitivity.³⁴⁷ These devices are not

commercially available to other light sources. The Gruner group is developing detectors that will achieve ~ 10 orders of magnitude dynamic range on the timescale of CHES-U.

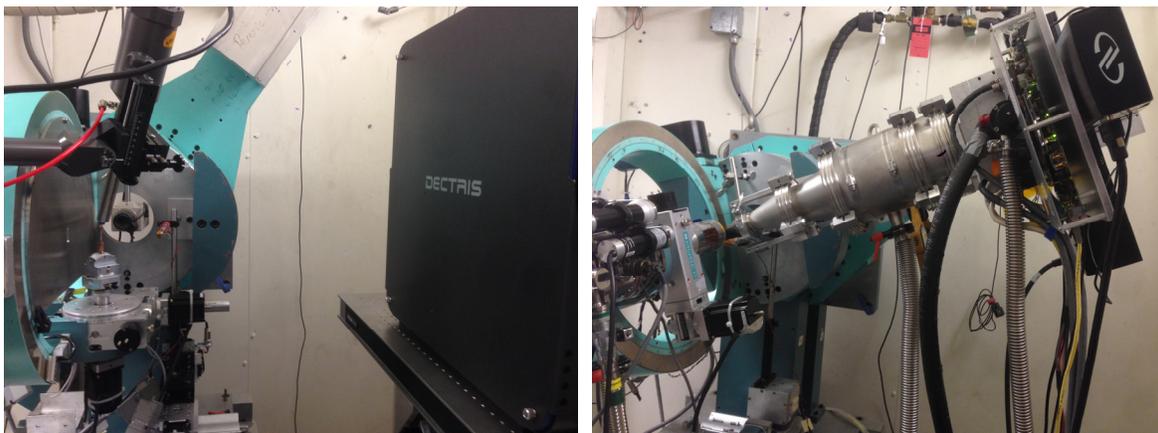


Figure 2. Unique detectors for high energy diffuse scattering available at CHES.
Left: Dectris Pilatus6M detector. Right: One-of-a-kind MMPAD detector.

CHES has invested in the computing infrastructure (high performance computing, storage, and software) required to handle big data throughout the facility. In collaboration with computer scientists from Argonne National Laboratory and the Cornell Laboratory for Accelerator-Based Sciences and Education, CHES has implemented a highly parallelized workflow for analyzing and transforming diffraction data. This workflow can handle experiments that generate > 5 TB/day.

Limitations of Other Facilities

No synchrotron beamlines have optimized to study high-energy single-crystal diffuse scattering. Certain beamlines at the Advanced Photon Source deliver comparable high-energy beams, but all currently lack the detectors and computing infrastructure that diffuse scattering experiments require. Lower-energy beamlines at APS and ESRF have established a part-time focus on diffuse scattering, but their lower energy typically limits the quality and completeness of the data collected for many systems of interest. No other beamline, regardless of its technical suitability, is likely to approach this area of science with the same depth or breadth of effort that CHES will provide. Only the mission of CHES identifies high-energy single-crystal diffuse scattering as a primary focus.

DOE funds dedicated beamlines for PDF analysis. These beamlines are excellent tools to study disorder, but DOE has not optimized them to study single crystals or thin films. No DOE-funded X-ray beamline specializes in efficient, high-energy single crystal diffraction mapping techniques at high dynamic range. This CHES-U beamline would enable 3D-PDF analysis with unrivalled levels of detail.

The Advanced Photon Source is planning a several-hundred-million-dollar upgrade to a new source design that greatly reduces the emittance. APS is also designing new beamlines exclusively to support experiments that will require and exploit low emittance. APS-U will generate beams with high transverse coherence and will focus these beams down to nanometer dimensions. Over the next 10 years, APS is unlikely to pursue new beamline ideas that don't require these properties, even if the ideas are scientifically exceptional. Disordered materials and

other fields of science that require high-energy single-crystal diffuse scattering experiments represent a unique opportunity for CHESS.

DOE recently constructed the neutron instrument *Corelli* at the Spallation Neutron Source. *Corelli* *does* focus on single-crystal diffuse scattering studies, and it aims to answer scientific questions similar to those described here, with complementary capabilities. CHESS will enjoy inherent advantages: X-ray beams are smaller (microns instead of centimeters) and brighter than neutron beams, and researchers can access extra information by tuning the photon energy to excite particular atoms. Researchers will be able to collect data more quickly at CHESS than at *Corelli* (minutes vs. hours). CHESS will enable researchers to analyze smaller samples than *Corelli* (less than 1 microgram vs. about 1 gram). Researchers at CHESS will be able to analyze thin films; researchers at *Corelli* will not. On the other hand, *Corelli* will allow better sensitivity to light elements, as well as meV-level elastic discrimination that is unavailable at CHESS. *Corelli* will also have greater sensitivity to disordered magnetic states.

Ultrafast diffuse scattering will remain a niche of free electron lasers such as the LCLS, which operates in the femtosecond regime. However, there are many interesting non-equilibrium problems to probe on nanosecond and longer timescales, all of which are better suited to a 3rd generation storage ring such as CHESS. Large bunch charges will enable CHESS-U to conduct experiments with sub-nanosecond temporal resolution.

Impact of CHESS Investigations into Disordered Materials

Scientific Impact

Diffuse scattering experiments with disordered materials will generate high-quality datasets, which will motivate new progress in theory. We will host all the leading software for diffuse scattering analysis on CHESS computing resources (DISCUS, YELL, PDFGUI, etc.) and invite our users to access them remotely. CHESS staff will maintain expertise in these codes and will train users in data analysis and modelling. CHESS will also recruit postdoctoral researchers to advance the theory and modelling of disorder.

CHESS-U will optimize a beamline to collect comprehensive datasets rapidly from single crystals. Reciprocal space mapping at CHESS via standard techniques historically took several hours. Our recent pilot program with the 6M detector allowed us to collect comprehensive data (spanning hundreds of Brillouin zones) in ~20 minutes.³⁴⁸ The optimized CHESS-U beamline will collect comparable datasets in 2 minutes. This approach will mitigate our current oversubscription.

The high throughput will enable CHESS users to explore more unique samples or the same samples under different experimental conditions (temperatures, pressures, magnetic fields, etc.). This approach will remove selection bias inherent in choosing a few samples or dopings, minimize the probability of irreproducible results, and allow serendipitous discovery of unpredicted effects. High-throughput will allow researchers to map entire phase diagrams during short time intervals that once allowed only sparse sampling. We see the potential for resonant diffraction experiments in which parallel data collection will enable us to increase efficiency by many orders of magnitude.

Many world-class researchers study disordered materials within the U.S. and abroad. Since the world lacks a dedicated “home” synchrotron beamline for studies of disorder in crystals, these groups have no center of mass. A CHESS beamline dedicated to studies of disorder could anchor

the worldwide effort here in the U.S. This home for disordered materials research would offer ideal sources and detectors, ease of use, data of the highest quality, expert training and assistance in data analysis, a significant computational infrastructure available to the users, workshops, summer schools, meetings, etc.

Technological Impact

The CHESS-U user community will study disorder in many technological materials, such as the following:

- superconductors at first to control T_c , J_c , and structural strength, then to design strong magnets.
- thermoelectrics in order to control phonon scattering rates and eventually to transform waste heat from engines into useful electrical power.
- battery materials to learn how ions correlate and interact as they intercalate into electrodes and eventually to achieve higher energy densities.
- electrochemical materials to understand local inhomogeneity at interaction sites and thereby to improve the performance of catalysts.

They will learn to correlate specific local structure (rather than average global structure) with material properties. They will learn to synthesize materials with desired local structures and to design-in disorder to promote desired functions.

How Studies of Disorder at CHESS-U Will Help NSF to Achieve Its Aims

This work addresses the NSF-DMR mission to “advance materials discovery, design, synthesis, and characterization” by bringing disordered local states into the realm of quantitatively understood materials properties. Our beamline will become a powerful new tool in materials discovery and characterization. It will provide essential feedback to facilitate materials synthesis and design. We will serve the DMR mission of “discovery of emerging phenomena of matter and materials,” specifically in relation to quantum disordered electronic phases with exotic excitations.

This work aligns with the goals of the Condensed Matter Physics program within NSF-DMR: to probe “classical and quantum phase transitions; localization; electronic, magnetic, and lattice structure or excitations; and superconductivity.” It will address these questions: How and why do complex macroscopic phenomena emerge from simple interacting microscopic constituents? What is the physics of spin systems and quantum states of matter that could lead to their coherent manipulation and control?

Our enormous datasets (today we generate 5 terabytes per day), our need for advanced data analytic tools, and the unsolved challenge of *ab initio* modelling for disordered systems will interest DMREF, the program by which the NSF participates in the Materials Genome Initiative.

XI. Technical Overview of the CHESS-U Project

Introduction

The Cornell High Energy Synchrotron Source (CHESS) is a NSF funded National User Facility located on the Cornell University campus in Ithaca, New York. Our 11 experimental stations host over 1,300 user visits a year. They support investigations by academic researchers from the physical, engineering, and life sciences, by industrial scientists and engineers, and by experts in art history and archaeology. Two partner programs enhance our support to specific topics and user communities: *MacCHESS*, funded by NIH, focuses on structural biologists, and *In-Situ*, funded by ONR, focuses on structural materials and industrial users.

CHESS originally operated parasitically to the High Energy Physics research program, which supported the Cornell Electron Storage Ring (CESR) to conduct electron-positron collider experiments. The conclusion of High Energy Physics operations in 2008 enabled CHESS to begin optimizing CESR to generate X-rays. In 2014, CHESS modified CESR, shrinking the emittance of the particle beams (see Figure 1) enough so that we could operate undulators efficiently. CHESS thereby joined the elite group of 3rd generation high-energy synchrotrons.

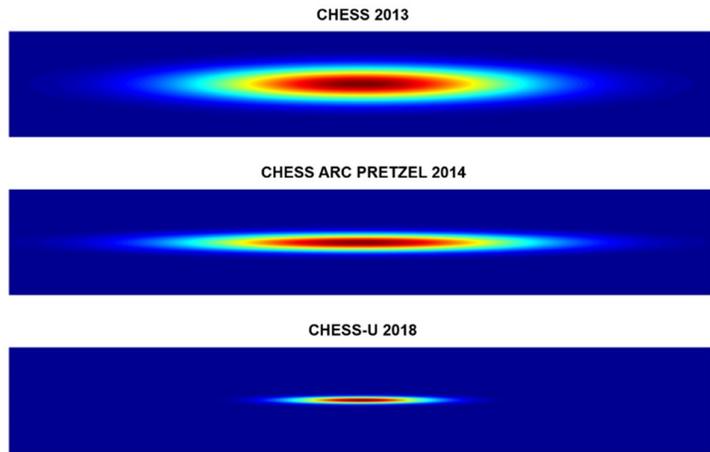


Figure 1: Electron beam size at X-ray source position.

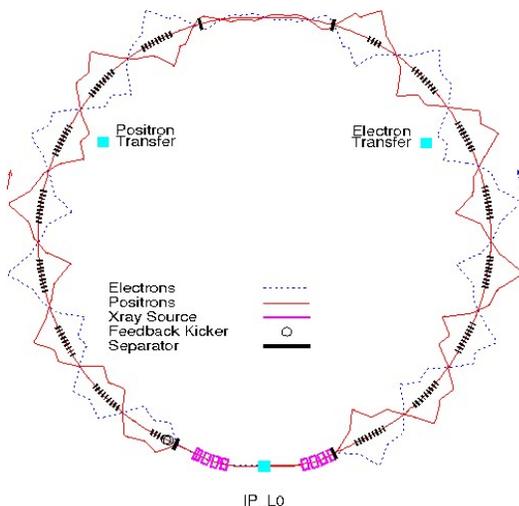


Figure 2: Current Arc Pretzel Lattice to Accommodate Electron and Position Beams

The main challenges to further improving CESR for X-ray operations are the counter-rotating beams of electrons and positrons, the massive CLEO detector, and the associated hard bend magnets. To store counter-rotating particle beams, we must assure that beams of oppositely charged particles do not run into each other. Figure 2 shows how we prevent such collisions; it displays a top view of the current arc-pretzel lattice established in September of 2014. The term “pretzel” refers to the shape of the oscillation about the central orbit required to keep the electrons and positrons from colliding. The term “lattice” refers to the configuration of magnets. To avoid collisions, the lattice separates the electron and positron beams radially when they pass each other. In the region of the X-ray source (the bottom), both the electron and positron beams occupy the central orbit (the circle).

Unfortunately, both the pretzel and the perturbations created by the proximity of electrons and positrons cause the emittance of the beam to grow. CHESS could not switch to single-beam operations because half of the X-ray beamlines were oriented to accept radiation from the electrons, the other half to accept radiation from the positrons. The massive CLEO detector required that the storage ring have a long straight section. To create space for the straight section, we replaced four of the standard dipole bending magnets with two “hard bend” magnets, each with twice the angular deflection of the standard magnets. These hard bend magnets generate most of the emittance in CESR. We are removing the CLEO detector during summer 2016, thereby gaining the ability to upgrade CESR.

The CHESS-U Project

The goals of CHESS-U are to upgrade CESR, to optimize it for X-ray production, and to reorient X-ray beamlines for single-beam operations. CHESS-U will reconfigure CESR to operate with only a single type of particle, raise the beam energy, increase the beam current, and, within those restrictions, minimize the beam emittance. CHESS-U will reorient and rebuild the A, B, C, and D beamlines to accept radiation during single-particle-beam operations. CHESS-U will provide space for up to 10 independently tunable insertion devices (undulators) that will deliver X-rays to as many as 12 experimental stations.

The CHESS-U project formally began on April 1, 2016. The major construction phase of the upgrade will occur during the summer of 2018. We will recommission CESR in the fall of 2018 and begin to ramp up X-ray user operations in early 2019.

CHESS-U Accelerator Upgrade Details

In today’s CESR, the counter-rotating electron and positron beams follow the arc-pretzel trajectory illustrated in Figure 2 on the previous page. In contrast, the CHESS-U particle beam will remain on central orbit everywhere. We will eliminate the pretzel configuration, the positron source, and the horizontal separators. We will convert the south arc (the magenta portion of Figure 2) of the CESR accelerator to a double-bend *achromat* lattice (i.e., electrons with different energies will travel on the same orbit). The new configuration will provide straight sections that will accommodate up to 10 independent insertion devices. Each insertion device (undulator) consists of a series of magnets with alternating polarity to keep the net beam trajectory along a straight line. As we reposition the X-ray beam lines and move the klystrons into the CLEO pit, we will be able to double the length of the F line, thereby improving the focusing and enabling larger experimental hutches that contain larger detectors, more equipment, etc. An external review panel of accelerator experts rigorously reviewed and approved the CHESS-U accelerator project (including electron optics and magnet design) in June 2016.

The CHESS-U upgrade will improve the quality of the particle beam. It will increase the energy from 5.3 to 6.0 GeV, increase the current from 100 to 200 milliamps, and

Synchrotron Components

Undulator magnets produce highly collimated beams of X-rays. The undulator’s parameters control the energy spectrum of the beam.

A monochromator selects X-rays with the desired energy.

Focusing optics and apertures define the beam size, shape, and angular divergence at the position of the sample.

reduce CESR's particle beam emittance from the present 100 nm-rad at 5.3 GeV to around 30 nm-rad at 6.0 GeV. The higher beam current and energy, lower emittance, and new straight sections in CESR will enable CHESS to install undulators on every X-ray beamline.

We will engineer the lattice to minimize coupling between the vertical emittance and the horizontal emittance. By keeping the coupling below 1%, we will maintain the vertical emittance of the beam below 300 picometers. As a result, the ring will emit ribbon-shaped X-ray beams (see the lowest image in Figure 1).

By operating with a single beam rather than counter-rotating electron and positron beams, CHESS-U will eliminate many performance limitations associated with the present 2-beam pretzel operation. These limitations derive from *a*) the pretzel's *angular deflection* of the beam, which increases emittance, and *b*) the *Coulomb interactions* between the electrons and the positrons, which excite various modes of oscillation.

CHESS-U will begin operation with a positron beam to minimize the dark time for X-ray users. During a regularly scheduled maintenance period, we will switch to a more easily sourced, more reliable electron beam. To implement the change, we will modify the injection system and change the polarities of the magnet power supplies. Detailed tables of parameters appear in the Appendices.

CHESS-U X-Ray Performance

The properties of the storage ring, the undulator, and the X-ray optics all contribute to the characteristics of the X-ray beam at the sample position. Scientists typically compare synchrotrons with respect to two figures of merit: flux and spectral brightness.

Flux is the number of photons per second in the X-ray beam at a given X-ray energy. Flux depends completely on the energy and current of the electron beam and the undulator. The size, angular distribution, and spectrum of the photons in the X-ray beams vary from storage ring to storage ring.

Spectral brightness is flux divided by emittance. Clearly, the spectral brightness increases as the emittance decreases. Spectral brightness is the quantity most useful for comparing the ability of sources to produce spatially coherent X-ray beams.

A third quantity that captures aspects of both the flux and spectral brightness is the *pinhole flux*. Pinhole flux is the flux through an aperture (typically 1 mm x 1 mm) located a given distance (typically 30 m) from the source of the X-ray beam. Qualitatively, one can think of pinhole flux as the amount of useful flux incident on the first optical element of an X-ray beamline. If the beam is too large because either the source size or the divergence is too large, the optic will reject some portion of the beam. Conversely, once the emittance is small enough for the beam to fit through the aperture, further decreases in the emittance no longer improve the pinhole flux. Thus, pinhole flux frequently serves as a good surrogate for the amount of flux delivered to the sample. This quantity is rapidly gaining favor as a useful measure for comparisons.

Figure 3 compares the performance of various combinations of storage ring and undulator source. The vertical axis represents the calculated flux (SPECTRA v10.0) through a 1 mm x 1 mm pinhole (see inset) placed 30 meters from the source. The horizontal axis represents the

Definitions of Beam Parameters

Emittance is the product of beam size times angular divergence. Low-emittance beams are small and highly collimated.

Flux is the number of photons per second.

Flux density is the number of photons per second per unit area.

photon energy. The magenta and green curves trace the performance of two possible choices of undulators for CHESS-U. For comparison, the dashed line shows the performance of the standard undulator A at the current APS. The figure confirms that CHESS-U can operate undulator sources that compete with the world's finest.

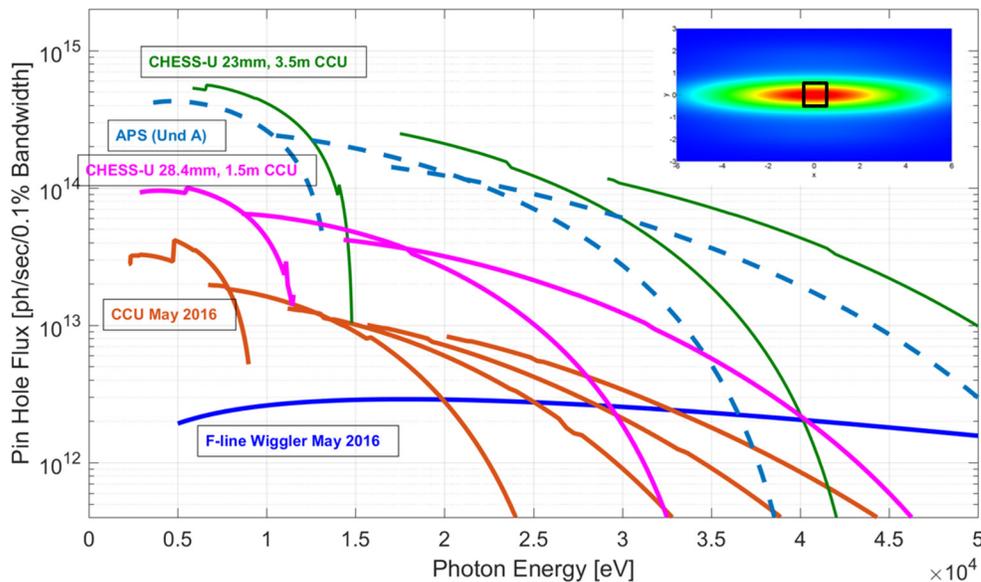


Figure 3: Calculated Pinhole Flux for Various Combinations of Storage Ring and Undulator Source

The table below compares the calculated performance of a conceptual beamline at CHESS-U with the calculated performance of the new ISR beamline at NSLS-II, a low-emittance 3-GeV synchrotron coming online at Brookhaven National Laboratory. NSLS-II has optimized ISR for *in situ* and resonant scattering studies of thin film growth. A 2.8-m in-vacuum undulator powers the ISR beamline. It utilizes a Si(111) double-crystal monochromator and a focusing mirror. For CHESS-U, we assume a design based on the current CHESS G3 beamline, including a 1.5-m CCU undulator, a focusing mirror, and a synthetic multilayer double-crystal monochromator. The table below shows the calculated performance of both beamlines.

	ISR at NSLS-II	CHESS-U G3 (CCU, 1:1 focusing, multilayer monochromator)
Flux [photons/second] (10 keV)	10^{13}	6×10^{14}
Focal Spot Size [μm^2]	40 x 200	25 x 300
Energy Bandwidth	1.4×10^{-4}	1×10^{-2}

The X-ray spot sizes at the sample position are very similar. As expected, the flux on the sample scales with the energy bandwidth. These two X-ray beamline designs serve complementary purposes. ISR supports *resonant diffraction studies* of thin-films. These studies require a narrow energy bandwidth. G3 supports *time-resolved diffraction studies* of thin-film deposition which require high flux.

The ribbon-shaped particle beams of CHESS-U will enable us to operate state-of-the-art undulator X-ray sources. Each beamline will optimize its undulator design for specific types of experiments by taking advantage of either conventional undulators, cryo-cooled superconducting undulators, or the customizable and cost-effective Cornell Compact Undulator (CCU). Designers will be able to vary the lengths of the undulators over a range from 1.5 to 4.0 meters. We can optimize the radiation field for specific applications by tuning the strength of the magnetic field and the length of the magnetic oscillation. Designers will also be able to control the energies of the undulator harmonics. We can choose between one long undulator or two shorter canted undulators to create multiple beamlines from the same straight section.

We have begun to design X-ray beamlines that support the science themes identified in this document. We plan to hold an external design review for the X-ray beamline designs in December 2016.

Optimizing for Spatial Coherence vs. High Flux

The other four high-energy synchrotrons in the world will pay a price for decreasing the electron beam emittance to the ultimate limit. Coulomb repulsion will ultimately limit their ability to squeeze a given number of electrons into a small volume. To minimize the bunch volume (i.e., to decrease the emittance), it will be necessary to reduce the bunch charge, thereby reducing the X-ray flux generated per bunch. They will be able to maintain the average flux (the stored current) by increasing the number of bunches, but fundamental physics will limit the number of X-rays that a given bunch of electrons can generate.

Capabilities Created by the CHESS-U Upgrade to CESR

- CHESS-U will support electron bunches with up to 60 nanoCoulombs – the same bunch charge in the large bunch of APS’s current hybrid mode. These large bunches enable pump/probe experiments with ~100 picosecond time resolution. APS-U, in the current design, will limit the charge per bunch to about 2 nanoCoulombs, thereby sacrificing the capability of these experiments.
- CHESS-U will generate a ribbon-shaped X-ray beam; APS-U will generate a nearly round beam. CHESS-U’s ribbon-shaped beam will serve exceptionally well all experiments that require a large, incoherent X-ray beam.

Example: Time-Resolved X-ray Diffraction of a Transient Strain Pulse

The structural evolution of materials under sudden, high-impact deformation is critically important in many applications, particularly in the automotive and aerospace industries. However, existing methods to probe such events, involving strain rates of 10^3 - 10^5 s⁻¹, provide only limited or indirect information about the atomic-scale rearrangement that materials undergo. By combining the high X-ray intensity of synchrotron radiation with a novel high-speed pixel array detector developed at Cornell, researchers from six different institutions demonstrated a new approach to this critical area of materials science.³⁴⁹ Using a Kolsky bar apparatus in the G3 hutch at CHESS (see Figure 4), the group obtained *in situ* diffraction patterns of magnesium undergoing shock-wave induced strain, with useful exposures as short as 70 nanoseconds. In this experiment, the striker bar rams into the sample, generating a strain pulse which propagates down the sample bar at the speed of sound. As the strain pulse passes through the specimen

volume, the lattice compresses and expands. A novel detector records a series of diffraction patterns as the strain pulse passes.

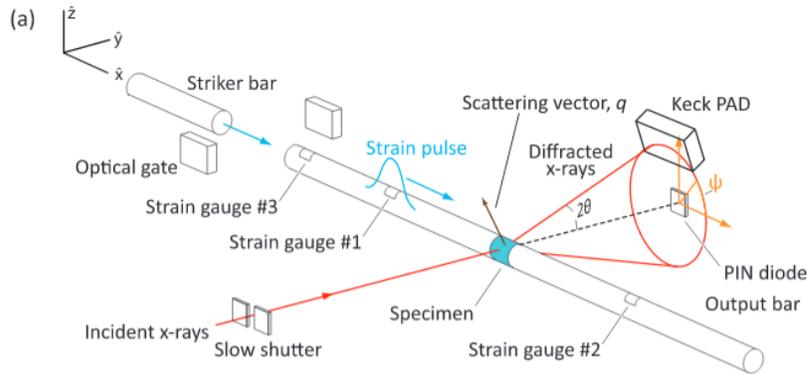


Figure 4: Schematic Illustration of Kolsky Bar Experiment

CHESS-U will make it possible to extend these experiments from 8 keV X-rays to high-energy X-rays, thereby achieving greater penetration, extending these measurements to faster time scales, and enabling researchers to study technologically relevant metals.

Example: Time-Resolved X-Ray Diffraction of Thin Film Deposition

Figure 5 shows how we can exploit the ribbon-shaped X-ray beam to achieve a valuable new capability: capturing an X-ray diffraction movie of a thin-film being deposited on a substrate. In this demonstration experiment, we deposited (La,Sr)MnO₃ on SrTiO₃ (001) via pulsed laser deposition. A commercially available polycapillary focusing device converts the ribbon-shaped beam to a converging beam. When we place the sample at the focus of the polycapillary, X-ray photons approach the sample from a range of incident angles. This advantage eliminates the need to rotate the sample, enabling us to collect data simultaneously from a range of $(\theta, 2\theta)$ points with a single detector exposure, as we do in energy dispersive diffraction. An energy dispersive detector has a total count rate limit due to pileup. In our experiment, however, each pixel in the area detector is an integrating detector without a maximum count rate. As a result, we can achieve much higher integrated signal rates. Each trace on the right side of Figure 5 represents a 0.1-second exposure.

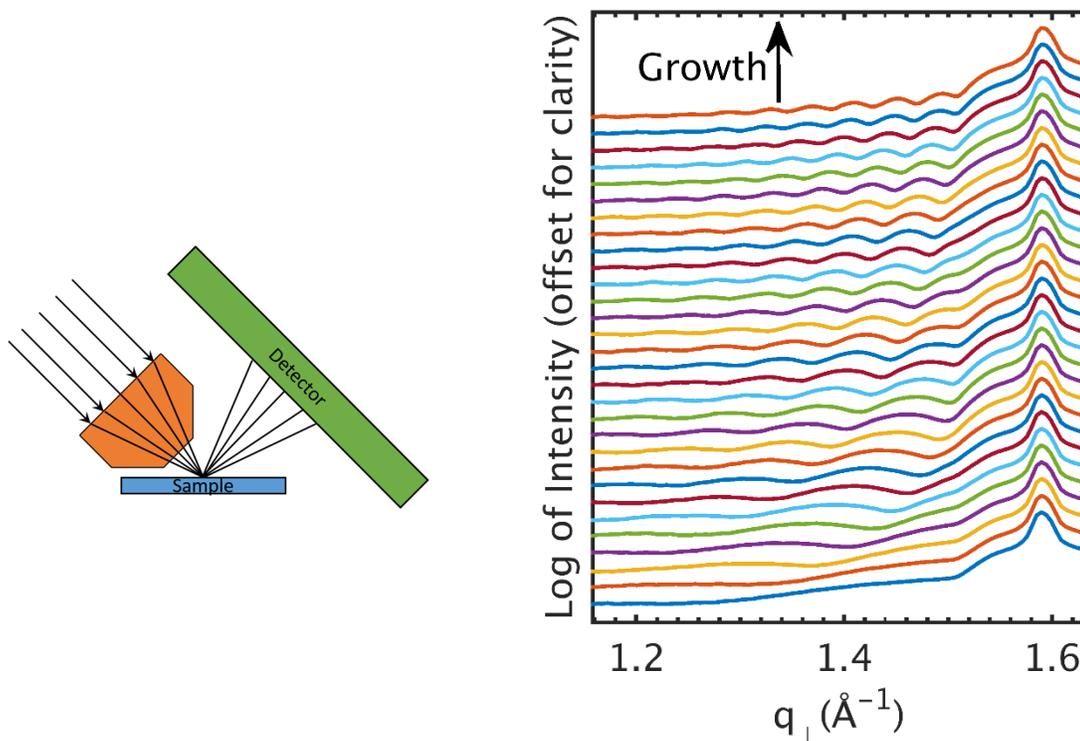


Figure 5: Time-Resolved Diffraction of Thin Film Growth

Relation of CHES-U to APS-U and NSLS-II

The only other high energy synchrotron in the United States is the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). ANL is optimizing the X-ray optics at APS to generate a low-emittance (high spatial coherence) beam. This change drives the APS toward very small, round electron beams and very small electron bunch charges. It will not support measurements that require large (> 5 mm) beam sizes, incoherent x-ray beams, or large numbers of photons per pulse. DOE has also optimized NSLS-II for high-coherence applications.

Figure 6 compares various characteristics of CHES-U, APS-U, and NSLS-II. Both CHES-U and APS-U will run at 6.0 GeV. Cornell will optimize CHES-U for high flux; ANL will optimize APS for spatial coherence. CHES-U and NSLS-II will begin to operate by the end of 2018. APS-U will not come on line until at least 2023.

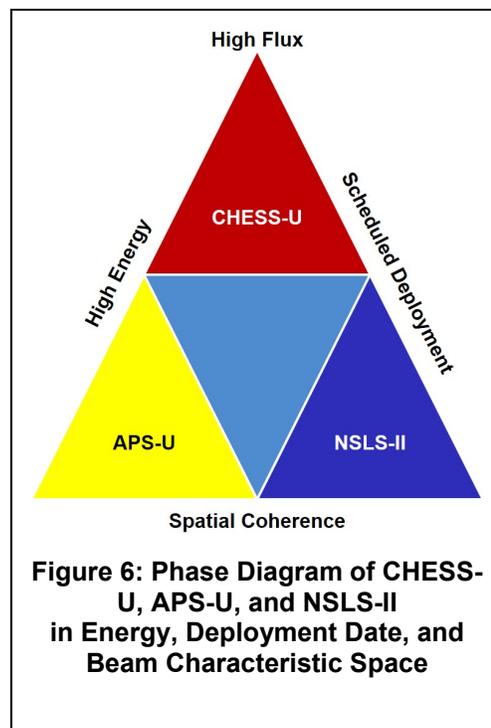


Figure 6: Phase Diagram of CHES-U, APS-U, and NSLS-II in Energy, Deployment Date, and Beam Characteristic Space

Partner Organizations

MacCHESS

A significant fraction of CHESS users are structural biologists who come to CHESS primarily to conduct macromolecular crystallography (MX) and biological small-angle X-ray scattering (BioSAXS) studies. Work in these areas originated in the early days of CHESS. It has produced breakthroughs such as the first structure of an animal virus³⁵⁰, a picture of ions moving through a transmembrane channel³⁵¹ (MacKinnon won a Nobel prize for this work in 2003), an explanation of how anti-AIDS drugs work (the Arnold group, in a series of experiments continuing over decades³⁵²), and the mechanism of DNA synthesis³⁵³.

NIH supports structural biology at CHESS through the MacCHESS facility, providing approximately \$2,400,000 per year for support staff, equipment, and technical R&D. Developments at MacCHESS benefit the entire biomedical community. For example, one research group at CHESS developed the technique of cryocooling protein crystals in a microloop to reduce radiation damage³⁵⁴. Another group at CHESS developed CCD³⁵⁵ and pixel-array detectors³⁵⁶. The combination of these two techniques promoted the spectacular growth in identifying macromolecular crystal structures that began around 1995 and continues to this day. The pressure-cryocooling technique developed recently at MacCHESS³⁵⁷ can improve the quality of diffraction from certain crystals and can also trap a gaseous reactant in a crystal, such as CO₂ in carbonic anhydrase (McKenna group, 2008 to the present^{358,359}). Software developments such as a click-to-center graphical interface for centering a crystal in the X-ray beam stimulated other synchrotron sources to implement similar software. Hardware, software, and training for BioSAXS developed at MacCHESS have greatly expanded the use of this relatively new approach to understand how macromolecules function in solution.

Structural biologists are eagerly exploiting cryo-electron microscopy (cryoEM) to determine the structures of large macromolecules and complexes. The research community will combine MX, BioSAXS, and cryoEM to obtain a deep understanding of biological processes. Scientists will rely on MX to determine the structures of small-to-medium-sized macromolecules, including components of large complexes, with atomic-scale resolution. They will select CryoEM to determine the ensemble of conformations adopted by larger structures at resolutions of 0.2 to 1.0 nm. They will choose BioSAXS to monitor conformation (at a lower resolution of 1 to 2 nm) and oligomeric state in solution under a variety of conditions.

CHESS is committed to maintaining state-of-the-art facilities for MX and BioSAXS. The improved beam characteristics of CHESS-U will make it possible to collect high-quality data from smaller samples. The ability to work with smaller samples constitutes a huge advantage because BioSAXS experiments currently require high quantities of expensive protein that is time-consuming to produce. The high brilliance of the beam will allow shorter exposure times, which lower the probability of radiation damage and support time-resolved BioSAXS studies of protein folding and protein function. We expect to study processes that occur on the millisecond time scale.

In Situ @ CHESS

High energy synchrotron x-rays can pass through bulk thicknesses of most engineering alloys and interrogate every crystal within a multi-grain sample. Over the past decade, high-speed area detectors and *in situ* sample environments have spawned a new generation of synchrotron X-ray-

based alloy characterization experiments in which scientists probe the lattice orientations, lattice strains, and topology for each crystal within a deforming polycrystal under various processing and loading conditions. The new techniques – including high-energy X-ray diffraction, diffuse scattering, and computed tomography – have demonstrated the ability of synchrotron X-rays to examine macroscopic engineering materials under real engineering conditions. They provide quantitative structural information at the size scales most relevant to materials such as structural alloys. They have created an opportunity to accelerate the engineering application of new alloys and processing pathways.

However, industrial scientists and engineers rarely apply these new techniques, perhaps because synchrotron facilities emphasize academic studies and because the sophisticated instruments and techniques are difficult to master. The overarching goal of *In Situ @ CHESS* (Integrated Simulation and X-ray Interrogation Tools and Training for μ -mechanics) is to provide detailed material characterization that will advance practical engineering design. *In Situ @ CHESS*'s mission is to achieve these long-range goals:

- Create an enhanced user support structure (based on the successful NIH-supported Mac-CHESS model) wherein a scientific and engineering staff provides state-of-the-art specimen handling, in-hutch instrumentation for high-energy x-ray beams, data collection software, and computational tools to analyze, visualize, and interpret data.
- Develop strong industrial linkages to identify challenging materials problems that can benefit from synchrotron data and analysis tools, then co-develop and refine software that will enable industrial engineers to analyze synchrotron data.
- Train personnel from industry and academia to become proficient users of synchrotron tools. Involve Masters and Ph.D. students in all aspects of the facility.
- Acquire feedback from industrial users to identify their needs. Involve them as active participants and partners to develop future tools and capabilities.

In Situ @ CHESS is creating a new materials characterization paradigm that combines *in situ* real-time high-energy synchrotron X-ray data with multiscale material models to address questions such as these: How can we integrate synchrotron data with modern material models and design tools to provide the greatest value to engineers who are working on important structural materials problems? How can we develop future analysis tools that satisfy the needs of industry? How can we train industrial and academic scientists and engineers efficiently to apply novel and sophisticated synchrotron techniques? What technology delivery pathway will best enable materials suppliers and OEMs to apply the results of a synchrotron study? *In Situ @ CHESS* addresses these challenges by enabling researchers to investigate a broad range of structural and engineering materials questions with high energy x-rays, *in situ* specimen environments, and high-fidelity computational capabilities.

XII. Conclusion

CHESS-U will provide unique capabilities that will accelerate the pace of science in key fields of science. In this section, we recapitulate the scientific, technological, and societal impacts that we expect.

Structural Materials

The CHESS-U research community is poised to make transformative discoveries about the processes by which structural materials deform. High-energy X-ray diffraction will enable us to characterize the interactions between adjacent parcels of the material over time and in response to mechanical forces. Energy-dispersive X-ray diffraction will enable us to construct 2D and 3D tomographic images that reveal internal voids, cracks, and crystal structures. Taken together, these two techniques are enabling the research community to conduct our first three-dimensional profiling of residual stress. The information we gain will enable researchers to initiate their models correctly, enable engineers to avoid overdesigning structures, and enable materials scientists to develop new structural materials that reduce costs and environmental burdens.

High-Precision Plant Phenotyping

CHESS-U will give plant breeders and botanists sustained access to a synchrotron beamline optimized to investigate plant phenotypes. Our staff members and users will develop tools and methods that will enable biologists with minimal X-ray expertise to conduct synchrotron experiments in plant phenotyping. As a result, synchrotron X-ray facilities will influence plant phenotyping in the same way that X-ray crystallography influenced molecular biology. From the standpoint of basic science, our work will help researchers to understand the relationships among genotypes and phenotypes and thereby to unravel the complex networks that control basic life processes. From the standpoint of applied science, our insights will help plant breeders to increase crop yields. In that sense, CHESS-U might play a key role in the global effort to feed mankind.

CHESS-U research in plant phenotyping will support the mission of NSF's Directorate for Biological Sciences, which is "to enable discoveries for understanding life." We will also support the *Genetic Mechanics* cluster within the Division of Molecular and Cellular Biosciences: "Theoretical and experimental research is welcome that integrates structural, biochemical, genetic, and "omic" (genome, transcriptome, interactome, phenome, etc.) data to understand the mechanistic relationship of genotype to molecular phenotype."

Nanocrystal Superlattices

Research at CHESS-U will accelerate the development of a new category of designer solids that will vastly expand the capabilities offered by the periodic table. Materials scientists and engineers will learn to design and synthesize nanocrystal superlattices with new properties by changing the composition, size, shape, orientation, or packing density of the nanocrystals, the electronic or optical communication among them, and the length or chemical functionality of the organic ligand capping layer. Each alteration will yield a new superlattice with the *traditional properties* of the constituent elements, the size- and shape-dependent properties of the constituent nanocrystals, and new optical and electronic properties that depend on inter-nanocrystal distances and packing densities.

The high-energy, high-intensity synchrotron X-ray beams available at CHESS-U will open new frontiers for physics and chemists who wish to explore the novel phenomena associated with nanocrystal superlattices. The CHESS-U research community will identify the physical and chemical rules that control the formation of nanocrystal superlattices. We will determine which architectures and interfaces convey novel properties and functionalities. We will articulate useful design rules to accelerate the materials design process and to reduce the time from materials discovery to manufacturing for applications.

***In situ* Processing of Organic Semiconductors**

The CHESS research community will work to develop a fundamental understanding of self-assembly under processing conditions that are scalable to industrial production. We will endeavor to create a rational basis for the design of new organic semiconductor materials and devices. Our work will help U.S. scientists and engineers to develop new products that address national needs for human health and welfare, clean energy, infrastructure, consumer goods, and national security. Our insights will help engineers to develop organic semiconductor manufacturing techniques that reduce costs, solvents, emissions, and energy consumption. CHESS-U will support the *Materials Genome Initiative's* overarching goal: to deliver the next generation of materials into products in half the time at a fraction of the cost. It will advance the objective of NSF's *Designing Materials to Revolutionize and Engineer Our Future* program: "to accelerate materials discovery and development . . . by understanding the interrelationships of composition, structure, properties, processing, and performance."

Atomically Thin Films and Interfaces

CHESS-U will design a user facility to optimize structural characterization of two-dimensional materials and heterostructures. Our studies will reveal the mechanistic origin of the properties of these materials. We will explain how their performance depends on their atomic structure, strain, and temperature, as well as the substrate. We will learn to synthesize two-dimensional materials with optimized properties. Our work will accelerate the commercialization of two-dimensional materials in multiple high-tech applications. CHESS-U will also support two major NSF initiatives: PARADIM (*Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials* at Cornell) and 2DCC (the *Two-Dimensional Crystal Consortium* at Penn State).

Catalysts: Man-Made and Biological

CHESS-U researchers will endeavor to acquire a fundamental understanding of catalytic transformations. This understanding will enable chemists to design optimized catalysts for any chemical transformation with atomic precision. Highly selective catalysts will reduce utilization of resources, capital costs, operating costs, and waste, while increasing atom economy and energy efficiency. The understanding we gain will improve the sustainability and the profitability of the petroleum, chemical, and pharmaceutical industries. It will enable scientists and engineers to create a sustainable energy supply from domestic sources while reducing the release of carbon dioxide into the atmosphere. Over the long term, chemists will exploit CHESS-U discoveries to design and manufacture catalysts that convert reactions to products with the efficiency and selectivity of biological catalysts that have evolved over billions of years.

Disordered Materials

CHESS-U will provide the worldwide research community with a home for the study of disordered materials. This home will offer ideal sources and detectors, ease of use, high-quality data, expert training and assistance in data analysis, a significant computational infrastructure available to the users, workshops, summer schools, meetings, etc. CHESS-U researchers will characterize disorder experimentally and develop the theory required to understand it. We will learn to correlate specific local structure (rather than global average structure) with material properties. We will learn to design-in disorder to promote desired function.

A Final Word: Convergence

The simultaneous and co-located studies at the cutting edge of these fields – organic semiconductors, thin-films and interfaces, disordered materials, catalysts, plant phenotyping, nanocrystal superlattices, and structural materials – will render CHESS-U one of the most intellectually rich environments on Earth. CHESS-U will host a high degree of convergence as staff members, users from industry and academia, postdocs, and students work shoulder-to-shoulder, compare notes, realize synergistic opportunities to transfer tools and techniques from one field to another, and open new fields of scientific endeavor by discovering new applications for high-energy, high-flux synchrotron radiation, which will remain the unique domain of CHESS-U for many years to come.

XIII. Appendices

Comparison of X-ray Performance: Current CHESS and CHESS Upgrade

	CHESS-U Baseline (1.5m CCU)	CHESS-U Low β (1.5m CCU)	APS Und. A Now	CHESS CCU Now	CHESS F-line Now	Units
e Beam Energy	6.0	6.0	7.0	5.3	5.3	GeV
e Beam Current	200	200	100	100	100	mA
Natural Emittance	30	28.0	3.3	94	94	nm- rad
Emittance Ratio	0.01	0.01	0.012	0.01	0.01	
Horizontal Beam Source Size (rms)	510	323	313	871	1,229	μm
Horizontal Divergence (rms)	57.9	96.4	14.1	136	258	μrad
Vertical Beam Source Size (rms)	28.3	25.2	10.9	54.1	126	μm
Vertical Divergence (rms) (K=1)	13.0	13.8	6.6	19.7	227	μrad
Spectral Brightness – 20 keV	4.7e+17	4.6e+17	1.2e+19	1.4e+16	7.2e+15	(*)
Total Flux – 20 keV	1.9e+14	1.9e+14	1.5e+14	6.8e+13	1.5e+15	(^)
Pinhole Flux – 20 keV	4.7e+13	3.2e+13	1.3e+14	7.2e+12	2.9e+12	(#)
Total Power (K=2.53)	6.12	6.12	4.686	2.39	12.0	kW

(*) photons/second/0.1%BW/mm²/mrad²

(^) photons/second/0.1%BW

(#) photons/second/0.1%BW in 1 x 1 mm² pinhole @ 30 m

Storage Ring Beam Parameters at ID Source Points

		CHESS- U Baseline	CHESS- U Low β	APS Now	CHESS CCU Now	CHESS F-line Now	Units
κ	Coupling factor	0.01	0.01	0.012	0.01	0.01	
σ_t	Pulse length	0.016	0.016	0.005859	0.016	0.016	m
ϵ_x	Horizontal emittance	30	28	3	94	94	nm
ϵ_y	Vertical emittance	0.3	0.23	0.039	0.94	0.94	nm
β_x^*	Horizontal beta function at center of straight section	8.8	3.0	19.4	7.69		m
β_y^*	Vertical beta function at center of straight section	2.5	2.0	3.0	3.07		m
η_x	Horizontal dispersion	0.0	0.165	0.168	0.45	0.522	m
η'_x	Horizontal dispersion gradient				0.108	-0.073	
η_y	Vertical dispersion	0.0	0.0	0.0001	0	0	m
β_x	Horizontal beta function at center of insertion device	8.91	3.19	19.4	7.21	14.89	m
β_y	Vertical beta function at center of insertion device	2.73	2.28	3.0	3.14	10.67	m
α_x	Horizontal alpha at center of insertion device	-0.085	-0.250	-0.009	0.202	1.047	
α_y	Vertical alpha at center of insertion device	-0.300	-0.375	0	-0.281	-1.121	
σ_x	Electron beam size in horizontal	510.1	298.0	312.9	871	1,227	μm
σ'_x	Electron beam divergence in horizontal	57.5	87.1	13.0	136	124	μrad
σ_y	Electron beam size in vertical	28.2	22.8	10.9	54.1	100	μm
σ'_y	Electron beam divergence in vertical	10.8	10.7	3.8	17.9	14	μrad
σ_δ	Energy spread of electron beam	7.7e-4	7.7e-4	1.1e-2	6.6e-4	6.6e-4	

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