

**X-ray Scattering
Principal Investigators' Meeting**

Marriott Washingtonian
Gaithersburg, Maryland
November 7 & 8, 2012

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Foreword

This abstract book summarizes the scientific content of the 2012 X-ray Scattering Principal Investigators' (PIs) Meeting sponsored by the Division of Materials Sciences and Engineering (DMSE) of the Office of Basic Energy Sciences (BES) of the U.S. Department of Energy. The meeting, held November 7&8, 2012, at the Washingtonian Marriott in Gaithersburg, Maryland, is the third in the series covering the projects funded by the BES DMSE X-ray Scattering Program. In addition to x-ray scattering, the Program and meeting include PIs involved in ultrafast techniques and instrumentation as applied to materials science research. BES DMSE has a long tradition of supporting a comprehensive scattering program in recognition of the high impact these tools have in discovery and use-inspired research. Ultrafast sources have entered the x-ray regime, and time-resolved experiments on the femto-second time scale involving radiation across a broad energy spectrum have become an important part of the Program, and many ultrafast projects are now included in the x-ray scattering portfolio.

The DMSE X-ray Scattering Program supports basic research using x-ray scattering, spectroscopy, and imaging for materials research, primarily at major BES-supported user facilities. X-ray scattering serves as one of the primary tools for characterizing the atomic, electronic and magnetic structures and excitations of materials. Information on structure and dynamics becomes the basis for identifying new materials and describing mechanisms underlying their unique behavior. Other key aspects of this activity are the development and improvement of next-generation instrumentation and data analysis tools, including the development of ultrafast techniques involving pulsed radiation sources.

The purpose of the PI meeting is to bring together researchers funded by BES in the x-ray scattering and ultrafast materials research area, to facilitate the exchange of new results and research highlights, to foster new ideas and collaborations among the participants, and to identify the needs of the research community. The meeting will also help DMSE to assess the state of the Program and chart future directions. The success of the meeting results from the active contributions of Program PIs in sharing their ideas and research accomplishments.

AGENDA

DOE BES DMSE X-ray Scattering Principal Investigators' Meeting
Marriott Washingtonian, Gaithersburg MD
November 7 & 8, 2012

Wednesday, November 7

7:00 - 8:00 Breakfast (also poster set-up, presentation loading on DOE computer)

8:00 - 8:40 **BES Welcome**

Linda Horton, BES

Lane Wilson, BES

8:40 - 9:45 **Panel A** (8 minutes for each presentation)

Erik Johnson, NSLS II

Jo Stohr, LCLS

Brian Stephenson, APS

Mike Toney, SSRL

Steve Kevan, Oregon/ALS

Zahid Hussein, ALS

Dave Mao, Carnegie Inst. Washington

Matt DeCamp, Delaware

9:45 - 10:50 General questions and panel discussion followed by small group discussions at each panelist poster

10:50 - 11:55 **Panel B** (8 minutes for each presentation)

Henry Kapteyn, Colorado/JILA

Rick Averitt, BU

Joe Orenstein, UC-Berkeley/LBNL

Rohit Prasankumar, LANL

Ki-Yong Kim, Maryland

Aaron Lindenberg, Stanford/SLAC

David Cahill, UIUC

Xiaodong Xu, Washington

11:55 - 1:00 General questions and panel discussion followed by small group discussions at each panelist poster

1:00 - 2:00 Lunch with discussion: Participating User Arrangements at Light Sources

2:00 - 2:50 **Panel C** (8 minutes for each presentation)

Hoydoo You, ANL

Roy Clarke, Michigan

Dillon Fong, ANL

Stuart Wilkins, BNL

Oleg Shpyrko, UCSD

Peter Fischer, LBNL

2:50 - 3:40 General questions and panel discussion followed by small group discussions at each panelist poster

3:40 - 6:00 Afternoon break for interactive discussion and free time

6:00 - 7:00 Dinner with discussion: Mix of X-ray Experiment and Theory Support

7:00 - 8:05 **Panel D** (8 minutes for each presentation)

ZX Shen, Stanford/SLAC

J-C Campuzano, UIC/ANL

Tai Chiang, UIUC

Chuck Fadley, UC-Davis/LBNL

Zahid Hasan, Princeton

Nuh Gedik, MIT

Tom Devereaux, SLAC

Jian-Xin Zhu, LANL

8:05 - 9:10 General questions and panel discussion followed by small group discussions at each panelist poster

9:10 - 9:30 End of day remarks, general discussion of meal time topics

Thursday, November 8

7:00 - 8:00 Breakfast (presentation loading on DOE computer)

8:00 - 9:05 **Panel E** (8 minutes for each presentation)

Robert Schoenlein, LBNL

Robert Kaindl, LBNL

Hermann Durr, SLAC

David Reis, Stanford/SLAC

Margaret Murnane, Colorado/JILA

Tom Silva, NIST

Paul Evans, Wisconsin

Paul Fuoss, ANL

9:05 - 10:10 General questions and panel discussion followed by small group discussions at each panelist poster

10:10 - 11:15 **Panel F** (8 minutes for each presentation)

Randy Headrick, Vermont

Karl Ludwig, BU

Anders Nilsson, SLAC

John Parise, Stony Brook

Tom Russell, Massachusetts

Simon Mochrie, Yale

Jeff Kortright, LBNL

Franz Himpel, Wisconsin

- 11:15 - 12:20 General questions and panel discussion followed by small group discussions at each panelist poster
- 12:20 - 1:30 Lunch with discussion: Participating User Arrangements at Light Sources (cont.)
- 1:30 - 2:20 **Panel G** (8 minutes for each presentation)
Bob Suter, Carnegie Mellon
Tony Rollett, Carnegie Mellon
John Budai, ORNL
Simon Billinge, Columbia/BNL
Emil Bozin, Columbia/BNL
Valeri Petkov, Central Michigan
- 2:20 - 3:10 General questions and panel discussion followed by small group discussions at each panelist poster
- 3:10 - 5:30 Afternoon break for interactive discussion and free time
- 5:30 - 6:00 Circulate to posters of members of your Panel, share dinner table with Panel members
- 6:00 - 7:00 Dinner with discussion: Discuss common equipment and infrastructure goals, suggest where strategic equipment support could push new x-ray scattering and ultrafast science frontiers.
- 7:00 - 8:05 **Panel H** (8 minutes for each presentation)
Wendy Mao, Stanford/SLAC
Viktor Struzhkin, Carnegie Inst. Washington
Jiuhua Chen, Florida Int.
Andrew Cornelius, UNLV
Clem Burns, Western Michigan
Peter Abbamonte, UIUC
John Hill, BNL
David Prendergast, LBNL
- 8:05 - 9:10 General questions and panel discussion followed by small group discussions at each panelist poster
- 9:10 - 9:30 General discussion of meal time topics, Panel reports on new opportunities and strategic equipment support
- End of meeting wrap-up

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Abstracts

Multifunctional Materials Research Using Ultrafast Optical Spectroscopy

Richard D. Averitt
Boston University
Department of Physics
590 Commonwealth Ave.
Boston, MA 02215
Email: raveritt@bu.edu

Understanding how novel behavior emerges in complex materials as a consequence of competition and interactions between microscopic degrees of freedom is a key challenge in condensed matter. Examples abound including high temperature superconductivity, ferromagnetism, heavy Fermions, negative magnetoresistance, and metal-insulator transitions. With regards to such complex materials significant experimental and experimental challenges remain. At the most fundamental level, researchers strive to gain insights regarding subtle concepts such as spontaneous symmetry breaking or the extent to which the quasiparticle concept can be applied in understanding material properties in correlated electron materials. Longer term, it will be important to harness complex materials for applications ranging from energy harvesting to low-power signal processing and data storage and read-out.

During our inaugural three-year proposal period, our investigations primarily focused on ultrafast spectroscopy of transition metal oxides (mostly the vanadates) and integrating metamaterials with complex matter to enable enhanced excitation and probing of the nonequilibrium response. During this proposal period, our effort will continue to focus on transition metal oxides and metamaterial integration.

Our work will take advantages of developments in high-field THz generation, new developments in epitaxial growth with controlled strain in the manganites, vanadates, and related materials, our ability to dynamically induce strain via excitation, and our extensive simulation, fabrication, and characterization of electromagnetic composites. We will utilize dynamic strain and high-field terahertz pulses to interrogate and control transition metal oxides. Our efforts will focus on four areas: (a) We will continue our studies of phase transition dynamics on the vanadates to explore dynamics from different starting points in the phase diagram and extend these studies to include related materials. (b) We will investigate photoinduced phase transitions in epitaxially strained manganite thin films which show considerable promise to reversibly control the ferromagnetic metallic state in samples that otherwise exhibits charge and orbital ordered insulating phases. (c) We will investigate THz driven nonlinear and coherent dynamics in charge density wave materials with emphasis on quasi-one dimensional cuprates $Sr_{14}Cu_{24}O_{41}$. (d) We will integrate metamaterials with complex oxides to extend our capabilities to interrogate and control emergent phenomena. Finally, we are part of teams at both APS and LCLS working to integrate our techniques and approaches with ultrafast x-ray probes to further extend the capabilities of time-resolved dynamics investigations of complex materials. The success of this proposal will open exciting new

opportunities to study ultrafast field driven phase transitions of transition metal oxides in general, in line with DOE Office of Basic Energy Sciences goals.

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Competition and nanoscale fluctuations in complex materials

PI: Simon J. L. Billinge (billing@bnl.gov)

Asst. Sci.: Emil Bozin (bozin@bnl.gov)

Building 510, Brookhaven National Laboratory, Upton, NY 11973

Materials with fascinating colossal responses such as high temperature superconductors and colossal magnetoresistant manganites often show great complexity at the nanometer level. Modern experiments sensitive to the local structure reveal broken local symmetries and nanoscale correlated local orders such as stripe and checkerboard structures of charge, spin and orbitals. These nano-scale modulated structures are thought to be intrinsic responses of the system and may play a vital role in determining the properties of the material. However, they are very difficult to study experimentally because of the complexity coupled with the difficulty in doing experiments, such as x-ray scattering or scanning tunneling microscopies, with nano-meter spatial resolution. Any one of these experiments in general yields insufficient information to give a clear picture of the situation. We are taking a two-pronged approach to mitigate this situation. First, instead of carrying out single or a few measurements, we seek to chart out an entire region of a phase diagram in detail with a single experimental probe. We are also seeking to combine experiments using different techniques to give complementary information.

One of the key concepts in complex materials is that competition between ground-states nearby in energy, in the presence of disorder, leads to a breakup of the system into nanoscale heterogeneous structures. This behavior is widespread and is not exotic, as we will demonstrate, leading to a rather generic phase diagram for complex materials in general. However, it is difficult to detect if measurements are made that are not sensitive to the relevant "order parameter" of the phase separation, or to features on the right length-scale. With this in mind we have revisited the phase diagram of two systems that exhibit metal-insulator transitions: the cubic manganite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0 < x < 0.5$ and $\text{Cu}(\text{Ir}_{1-x}\text{Co}_x)_2\text{S}_4$ for $0 < x < 0.6$ and will present these results here.

In the former, the competition is between a localized, polaronic, Jahn-Teller insulating phase and a delocalized ferrometallic metal. We use atomic pair distribution function (PDF) analysis of neutron and x-ray diffraction data on samples covering the full range of doping, collecting data over a wide range of temperatures from 10 K to 500 K. We show how the PDF is sensitive to the disordered Jahn-Teller distortion that accompanies the formation of localized polaronic charge state and chart this order parameter over a wide range of the phase diagram. The onset of polarons closely follows the electronic (insulator-metal) phase line except at $x=0.5$. Here we show that the polarons start to disappear on cooling, before recovering their concentration at the temperature where the remaining polarons order: the charge ordering temperature. We speculate that this is because the removal of a strain energy associated with having disordered polarons is removed, energetically stabilizing the localized state sufficiently to make it the ground-state rather than the delocalized metal. This shows the control that might be exerted on a system which has closely competing states, such that the presence or absence of a small lattice strain can determine the ground-state.

The $\text{Cu}(\text{Ir}_{1-x}\text{Cr}_x)_2\text{S}_4$ has many similarities. In the undoped state it has a metal insulator transition on cooling being a paramagnetic metal at high temperature but having a diamagnetic, charge-localized, insulating state at low temperature. In the low temperature state the (nominally) Ir^{4+} ions form into structural dimers, with a bond-shortening of 0.5 Å, which are assumed to be spin singlets due the loss of magnetic susceptibility accompanying this transition. The material has a macroscopic structural phase transition at the same temperature. It is unclear if the singlet state is driven by magnetic or charge/orbital degrees of freedom. By doping Cr onto the Ir sites, the Ir dimers can be diluted and the long-range ordered dimer state is quickly destroyed. However, the PDF is directly sensitive to *local* dimer formation (though not the singlet formation), regardless of whether the dimers are local or long-range ordered. To properly understand the competition giving rise to the metal-insulator transition it is important to know if, at the structural boundary, dimers lose their long-range order and melt, persisting locally, or whether they actually disappear and the charges delocalize. We show that in the undoped endmember, the latter case happens. This also happens with Cr doping: The dimer state is rather fragile with respect to transformation to a more delocalized metal.

However, a wider ranging survey of the full phase diagram up to $x=0.6$ indicated that local dimers are reentrant, they reappear on further Cr doping. This surprising result can be understood again because of the importance of lattice strain in the energy balance, as well as the ability of the system to use the degree of freedom of forming nanoscale heterogeneous states. The reentrant dimers forms a dome, not unlike the superconducting dome in the cuprates, centered at around $x=0.25$. We hypothesize that the presence of quenched lattice relaxation around the Cr defects produces a local strain that allows the dimers to form locally without paying the energy cost to form the strained region. In some sense they are parasitic on the Cr defects. Increasing the Cr doping introduces more strain-centers, but also weakens the energy of the localized dimer state by diluting the Ir^{4+} sublattice with non-dimer-active cobalt, reducing the number of dimers that can form. Again, a rather generic and recognizable phase diagram emerges from a system where very different states are competing in the presence of disorder that affects the energetics of one of the phases, resulting in this case in a disordered, broken *local*-symmetry, ground-state.

In the systems studied here the signal in our experimental probe was very sensitive to some aspect of one of the phases contributing to complex disordered ground-state: a Jahn-Teller polaronic distortion in the former case and an Ir-Ir dimer in the second case. We are now taking this generic approach to the high temperature cuprates and closely related nickelates. In this case the experimental signals in the PDF are much less robust and we are seeking ways to incorporate information from the spin and orbital (using resonant x-ray scattering) and electronic (using STM and EELS) degrees of freedom directly. This is a major challenge due to the nanoscale nature of the broken orders we are looking to characterize, but we have preliminary results that are encouraging. For example, we have demonstrated, albeit not with nanoscale resolution, direct imaging of micron-scale anti-ferroelectric domain formation, which unexpectedly breaks the crystallographic symmetry, in a bilayer manganite. These developments will be a focus of our next two years of work.

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Impact of Dynamic Instabilities and Inhomogeneities on Energy Materials

John Budai (budajd@ornl.gov), Olivier Delaire, Michael Manley, Eliot Specht and Gene Ice
Materials Science & Technology Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831

Planned Research Scope

Physical properties of materials such as thermal transport and phase stability are determined by nonlinear dynamic and static microstructural interactions at multiple length scales. We plan to investigate the impact of dynamic lattice instabilities and local microstructure on functional energy materials using a combination of elastic and inelastic x-ray and neutron scattering techniques. This research will initially focus on two interrelated materials systems: (1) Energy transport in thermoelectric materials and (2) The origin of dynamic instabilities and inhomogeneities in relaxor ferroelectrics. These two research thrusts focus on complementary materials systems that reflect interdependent facets underlying the impact of dynamic lattice instabilities and local microstructure.[1] In both cases, the emphasis will be on examining the role of strong lattice anharmonicity and microstructural inhomogeneities on multiple length scales to understand and enhance the useful physical properties. To perform these studies, we will make use of neutron and x-ray scattering facilities at the SNS, HFIR and APS facilities, as well as collaborate with synthesis, characterization and theory groups at ORNL. Scattering studies will enable us to separate and quantify the roles of lattice vibrations, chemical order and local defects in controlling energy transport and phase transitions.

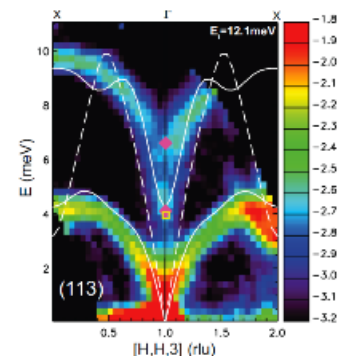


Fig. 1 Inelastic neutron scattering data showing the presence of a waterfall effect related to a lattice instability.

Energy transport and harvesting in thermoelectric materials

It is known that efficient thermoelectric properties can be achieved by decreasing thermal conductivity while increasing electrical conductivity.[2] However, these are often competing goals, and fundamental research is needed to understand how to control the microstructural mechanisms controlling energy transport involving both phonons and electrons. We will address this goal using inelastic neutron scattering to study the anharmonic phonon-phonon and electron-phonon interactions that can lead to phonon scattering and hence reduced thermal conductivity (e.g. Fig. 1). In particular, strong anharmonic phonon scattering often occurs near ferroelectric-like instabilities.[3] In parallel measurements, we will use elastic x-ray and neutron scattering studies of the same materials to characterize the effect of static microstructural defects on the thermal transport (e.g. Fig 2). Nanoscopic and mesoscopic lattice defects with a hierarchical architecture can effectively optimize phonon scattering.[4] X-ray studies will initially use diffuse scattering studies, and will expand to include spatially-resolved microdiffraction studies to identify the nature of local microstructural inhomogeneities. By combining the phonon scattering effects due to both lattice anharmonicity and lattice defects, predictive approaches for minimizing thermal transport can be developed.

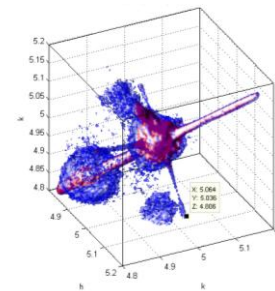


Fig. 2 Elastic diffuse x-ray scattering showing the presence of microstructural inhomogeneities.

Origin of dynamic instabilities and inhomogeneities in relaxor ferroelectrics

Efficient phonon scattering in thermoelectrics is often associated with a soft-mode, ferroelectric-like lattice instability.[3] In other functional materials such as ferroelectrics, a phase transition occurs when soft-mode phonon instabilities condense to change the lattice structure. Relaxor ferroelectrics represent a particularly interesting and useful class of ferroelectric materials in which mixed-ion alloys such as $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3)_{1-x}(\text{PbTiO}_3)_x$ exhibit a broad phase transition with strong dynamic, chemical and displacive disorder. These systems possess strong anharmonicity, and complex thermally-activated dynamic modes can emerge. Local ferroelectric fluctuations can condense into collective distortions called polar nanoregions (PNRs) associated with enhanced piezoelectric response. However, the microscopic origin of PNRs in terms of local dynamics, chemical order and lattice displacements remains unknown. Alternative hypotheses invoke local compositional fluctuations or intrinsic dynamic fluctuations. In recent theoretical work, the local fluctuations in relaxor ferroelectrics are hypothesized to be nonlinear discrete breather modes – a. k. a. intrinsic localized modes.[5] We will test the predictions of alternative hypotheses using a combination of inelastic neutron scattering to measure the temperature-dependent lattice dynamics, diffuse x-ray scattering to study static composition and strain fluctuations, and x-ray microdiffraction intensity fluctuation spectroscopy to measure long time-scale domain fluctuations.

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Inelastic X-ray Studies of Highly Correlated Systems – Polarization Analysis with RIXS

PI: Dr. Clement Burns
Dept. of Physics
1120 Everett Tower
Western Michigan University
Kalamazoo, MI 49008-5252
Ph: 269-387-4921
clement.burns@wmich.edu

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1.0 Future Plans

Our work involves studies of strongly correlated condensed matter systems using synchrotron x-ray sources. Much of the work involves using inelastic x-ray scattering (IXS) and Resonant Inelastic X-ray Scattering (RIXS) to study the electronic and vibrational excitations in these systems. Our current work primarily involves developing polarization analysis for the scattered photon. We designed and tested a toroidally bent graphite single crystal analyzer working at the copper K-edge, but the efficiency is low (1.5%). Currently, we are working on an analyzer for the Ir-edge using bent, thin, single crystal silicon.

1.1 Instrument Development Work

One problem with the current polarization analysis setup is that the size of the rotation stages for the polarization analyzer limit the energy loss which is achievable. We are correcting this with a small (but highly accurate) Attocube stage for analyzer crystal rotation. The main problem with the current graphite analyzer is its low efficiency (due to low reflectivity). To improve the efficiency we are moving to a bent single crystal silicon polarization analyzer. The higher reflectivity of Si should provide a factor of ~10-20 improvement in reflectivity. Currently the graphite analyzer increases the energy width from ~100 meV to 170 meV due to the thickness of the active layer of the graphite. To solve this we will use a higher Z material (Si) with a short absorption length for the analyzers.

We are currently working on methods to bend the Si to the correct shape. This work involves pulling Si against a created form. The Si is being characterized before and after bending with x-ray reflectivity measurements and optical profiling (to check the shape).

1.2 Planned measurements - 5-d transition metals – Ir compounds

Systems with strong electronic correlations have been one of the main areas of interest in condensed matter physics for the last several decades. 3-d transition metal oxides have many exotic interesting properties, such as high temperature superconductivity in the cuprates, and colossal magnetoresistance in the manganites. In the 5d systems there has also been interest in iridium based compounds such as Sr_2IrO_4 . Sr_2IrO_4 is a layered perovskite which has five electrons in t_{2g} orbitals which

are essentially triply degenerate. The wide bands in this material, along with a weak Coulomb repulsion energy, should make this system metallic, but it is insulating. Theory and experiment¹, have shown that the system is a novel type of Mott state due to the spin-orbit coupling in the material.

A Japanese group lead by Ishii has carried out low resolution (\sim eV) measurements of the electronic excitations in Sr_2IrO_4 at SPring-8.² The incident energy is set near the L_3 edge at ~ 11.2 keV. The RIXS process in this case is direct RIXS scattering, and is quite strong. At the peak, the scattering rate is about 3000 cps. This is a tremendous signal rate, more than two orders of magnitude larger than is typically seen for indirect RIXS scattering at the K -edge in cuprates. Three inelastic features were observed, at 0.5, 3.2, and 6 eV energy loss. The lowest energy peak is believed to correspond to excitation across the band gap, while the peaks at 3.2 and 6 eV are thought to be charge transfer excitations from the O $2p$ to the upper Hubbard, and the $3z^2-r^2$ bands respectively. The bands show little dispersion in momentum, although the spectral intensity varies substantially. More recently, high resolution RIXS measurements by Kim et al.³ resolved the excitation near 0.5 eV, and a lower energy magnon is visible. Typical count rates for the magnon were 300.

There are several interesting questions in this system where polarization analysis will be used. First, transverse and longitudinal magnons will have different outgoing polarizations. It therefore becomes simple to separate the contributions from the two different magnons using polarization analysis. Even with our current efficiency for the polarization analyzer we would still expect 4-5 cps from the magnon which is a quite strong signal. Improvements described above should easily give us another order of magnitude improvement in count rate.

First, we would study the electronic and magnon properties in Sr_2IrO_4 using polarization analysis. This work will allow a more definitive understanding of the electronic states and the dispersions of the magnons. Next of interest would be the bilayer systems $\text{Sr}_3\text{Ir}_2\text{O}_7$, which have two stacked IrO layers. Other Ir systems such as Ba_2IrO_4 would be studied next in a similar fashion, including the evolution the electronic state with doping.

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High Pressure study of lithium amidoborane: absence of dihydrogen bonding

PIs: Jiuhua Chen¹, Wendy Mao², Yusheng Zhao³, Chi-chang Kao⁴

Mailing address:

¹ Center for Study of Matter at Extreme Conditions, Department of Mechanical and Materials Engineering, Florida International University, VH-140, 11200 SW 8th Street, Miami, FL 33199

² Geological & Environmental Sciences Department, 450 Serra Mall, Braun Bldg #320, MC2115, Stanford University, Stanford, CA 94305-2115

³ High Pressure Science and Engineering Center, Department of Physics and Astronomy, University of Nevada, Las Vegas, 4505 S. Maryland Pkwy, Box 454002, Las Vegas, NV 89154-4002

⁴ 2575 Sand Hill Road, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

E-mails:

¹ chenj@fiu.edu; ² wmao@stanford.edu; ³ yusheng.zhao@unlv.edu; ⁴ ckao@slac.stanford.edu

Planned Research Scope: Pressure influence on ammonia borane derivatives, lithium amidoborane.

Future Plan: Pressure influence on rehydrogenation and new ammonia borane derivatives.

Abstract: Both in situ x-ray diffraction and Raman spectroscopy have been conducted at the high pressure facility of National Synchrotron Light Source (NSLS) and Raman system at FIU. High pressure x-ray diffraction of lithium amidoborane in a diamond anvil cell (DAC) up to 13 GPa indicates two pressure-induced phase transitions (Figure 1). This first high pressure phase appears at about 4 GPa, and is stable up to about 10 GPa. Corresponding changes in Raman spectroscopy are also observed in the same pressure range (Figure 2). The first phase transition is accompanied by remarkable change in the B-H stretching region (Figure 2a). The low frequency B-H stretching mode splits and the high frequency B-H stretching modes merge into singlet. Also notable change in optical image occurs at this phase transition. The sample is opaque to light before and it is transparent to light after phase transformation (Figure 3). The second phase transition is demonstrated by a merging of high frequency B-H stretching modes (Figure 2a) and a splitting of N-H stretching vibrational modes (Figure 2b).

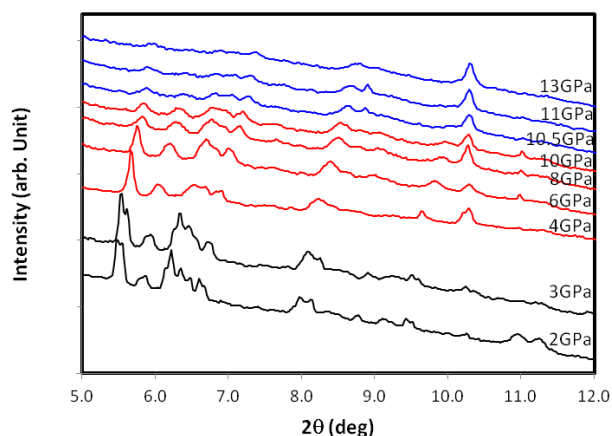


Figure 1. X-ray diffraction patterns of lithium amidoborane at high pressures.

At ambient pressure, both the N-H and B-N stretching modes of lithium amidoborane show blueshift to higher wavenumbers, whereas B-H stretching modes show redshift to lower wavenumbers compared to those of ammonia borane (Figure 4). This phenomenon indicates that lithium amidoborane has stronger N-H and B-N bonds and weaker B-H bond than its parent compound ammonia borane, which is consistent with the observation in the previous X-ray

studies regarding the B-H and B-N bond length. In addition, unlike the pressure dependence of dihydrogen bonding characteristic Raman modes (i.e. the N-H stretching modes) in its parent compound, these N-H stretching modes in lithium amidoborane shows a blueshift with increasing pressure (Figure 5). This indicates that the dihydrogen bonding is likely absent in the lithium amidoborane structure.

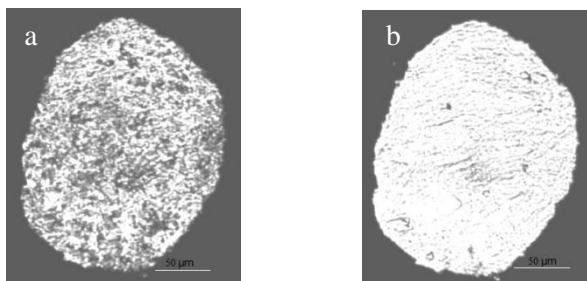


Figure 3. Micrographs of lithium amidoborane in the gasket hole: (a) at 2.4 GPa (before the first phase transition) and (b) at 3.9 GPa (after the first phase transition).

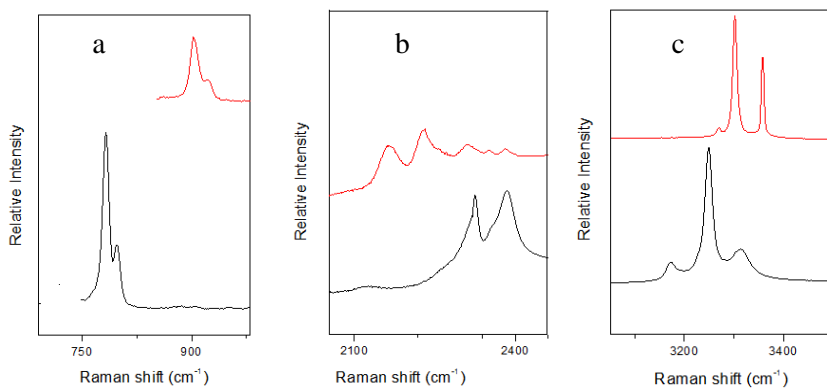


Figure 4. Comparison of the major Raman modes of ammonia borane (-) and lithium amidoborane (-): (a) B-N (b) B-H and (c) N-H stretching modes.

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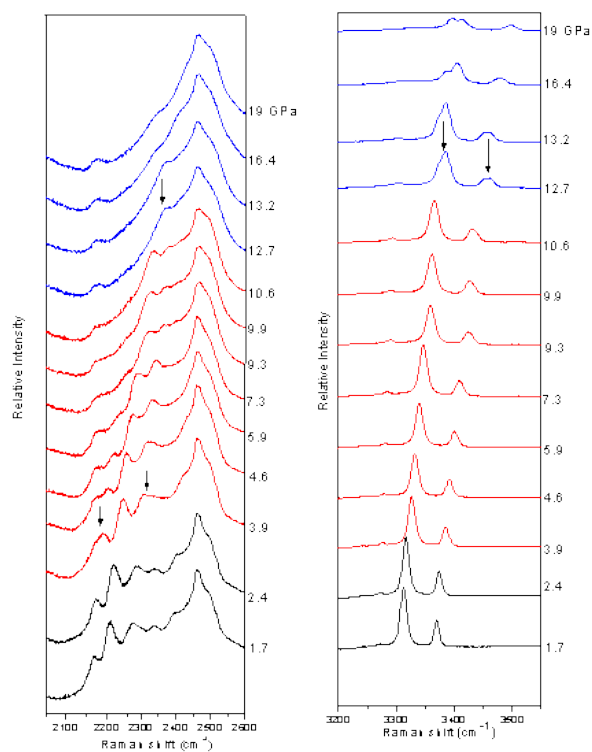


Figure 2. Raman spectra of lithium amidoborane at high pressures.

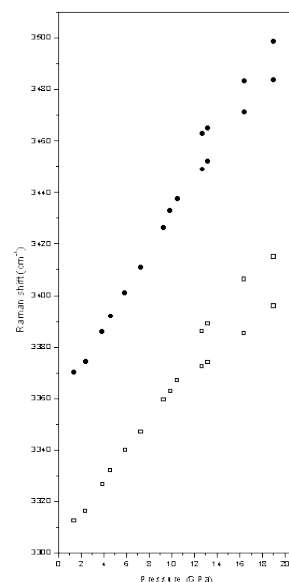


Figure 5. Pressure dependence of Raman shift of N-H stretching modes in lithium amidoborane.

Electrons, Spins, and Lattice Structures of Surface-Based Nanoscale Systems

Tai C. Chiang

Department of Physics, University of Illinois, 1110 West Green Street, Urbana, IL 61801

Email: tcchiang@illinois.edu

Planned Research Scope

Our research focuses on the physics of surfaces, interfaces, and tailored structures that are promising for a wide range of scientific and technological advances in the quantum, nano-, and meso-scale regimes. Measurements, modeling, and computation will be performed to determine and to understand the electronic, spintronic, and atomistic behavior of selected surface-based nanoscale systems prepared by deposition, artificial layering, self-assembly, and self-organization. Electrons confined in nanoscale systems form discrete states, or quantum well states, which are sensitive to the physical dimensions and boundary conditions. As a result, the electronic and spintronic properties of such systems including the wave functions, total energy, electronic charge distribution, spin distribution, and density of states can exhibit substantial quantum variations (or oscillations) as a function of system size and environment. The lattice structure of the system in turn responds to these changes as a result of electron-lattice coupling, possibly leading to distortions and new structures. These effects can be pronounced at the nanoscale because of quantum coherence, interference, and entanglement, and the resulting collective behavior can deviate far from the bulk limit. The underlying physics issues are of basic importance to *nanoscale and mesoscale science and technology*, a prevailing national research theme. Our planned research will be directed mainly at four areas: (1) ultrathin topological insulator films, their interactions with substrates, and their surface chemical reactions, (2) competition between electronic and lattice effects on the epitaxial growth of thin films, (3) dichroic effects associated with angle-resolved photoemission spectroscopy using circularly polarized light and the utility of this technique for surface spin texture mapping, and (4) temperature- and stress-induced phase transformations. The experimental work will include angle-resolved photoemission at the Synchrotron Radiation Center (SRC), x-ray diffraction and scattering at the Advanced Photon Source (APS), and related work at other domestic and international facilities. Modeling and first-principles calculations will be performed as needed. We are putting together a cryogenic high pressure system at APS for inelastic x-ray scattering (IXS) and thermal diffuse scattering (TDS) studies of (quantum) phase transitions under extreme conditions. Preliminary measurements are under way for the quantum paraelectric phase transition in SrTiO₃. We are interested in this material as a substrate for film growth, and in the consequences of its phase transitions on the overlayer behavior.

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16. P.J. Kowalczyk, O. Mahapatra, S.A. Brown, G. Bian, X. Wang, and T.-C. Chiang, "Electronic size effects in three-dimensional nanostructures," (submitted).
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Oxide Interfaces: emergent structure and dynamics

Roy Clarke

Department of Physics, University of Michigan,
Ann Arbor, MI 48109-1040
royc@umich.edu

Research Scope

The overall research direction of this program is focused on the behavior of epitaxial oxide heterostructures at atomic length scales (Ångstroms), and correspondingly short time-scales (fs -ns). The goal is a better basic understanding of structural and electronic correlations and how these can be exploited for technological applications, especially those of interest for the next generation of energy conversion and harvesting devices. Topics of interest include: probing the microscopic behavior of interfaces and buried layers; studies of materials and devices based on epitaxial interfaces; mapping the atomic structure of heterointerfaces using x-ray surface scattering; using ultrafast lasers to study the effects of transient strain in coherent manipulation of multi-ferroic order parameters; and investigating structural ordering and relaxation processes in real-time. Studies of such processes are well matched to the capabilities of accelerator-based x-ray sources such as the Advanced Photon Source (APS) at Argonne National Lab, and free-electron lasers such as the Linac Coherent Light Source (LCLS) at Stanford Linear Accelerator Center (SLAC). The overall broader goals of the proposed research are envisioned against the backdrop of the grand challenge of controlling matter and materials processes at the atomic scale.

Of particular interest for this project is the behavior of materials which exhibit both electric and magnetic polarization, so-called multiferroic materials. BiFeO_3 is an interesting example which has a large ordered spontaneous electric dipole moment and also antiferromagnetic ordering at ambient temperature. The interplay of these two types of ordering is of considerable interest in the context of correlated electron behavior as well as for potential device applications. Such behavior is well known in bulk ferroelectric and ferromagnetic materials, but the equivalent behavior in reduced dimensionality systems is only now being studied in some detail, for example in thin-film and heterostructure materials.

Another interesting example of a material exhibiting coupled magnetic and structural ordering is $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO). This system is of great interest for the fascinating variety of correlated-electron phenomena it exhibits: for example, LSMO undergoes a metal-insulator transition at about 370K and this coincides with a ferromagnetic-paramagnetic transition giving rise to so-called “colossal magnetoresistance” effects. The coupling between spin and orbital degrees of

freedom in this material also leads to interesting dynamical effects in which lattice and magnetic excitations can play off one another allowing for the possibility of transient strain manipulation of the magnetization and vice-versa. The behavior is therefore closely related to the multiferroic properties discussed above for BiFeO₃ except that here we are interested in lattice/magnetoelastic coupling induced by ultrafast laser pulses. In effect, we are utilizing time-domain pump-probe techniques to *separate* lattice and magnetic excitations in order to probe the fundamental question of how lattice distortions and magnetization are coupled and what is the time scale of their relaxation.

Recent Publications of DOE sponsored research under contract DE-FG02-06ER46273

1. The presence of a (1x1) oxygen overlayer on ZnO(0001) surfaces and at Schottky interfaces, **C.M. Schlepütz, Y. Yang**, N.S. Hussein, R. Heinhold, H.-S. Kim, M.W. Allen, S.M. Durbin and **R. Clarke**, *J. Phys.: Condens. Matter* **24**, 095007 (2012).
2. The limits of ultrahigh-resolution x-ray mapping: estimating uncertainties in thin-film and interface structure determination using phase retrieval methods, H. Zhou, R. Pindak, **R. Clarke**, D. Steinberg, and Y. Yacoby, *J. Phys. D* **45** 195302 (2012).
3. Surface x-ray scattering study of the O-polar face of ZnO, **Y. Yang**, M.W. Allen, **C.M. Schlepütz**, N.S. Hussein, R. Heinhold, M.W. Allen, S.M. Durbin and **R. Clarke**, *Surface Science* 2012 (in press).

PhD Theses

Naji Hussein, In-situ X-ray Synchrotron Phase Contrast Imaging; University of Michigan Ph.D., May, 2012.

Picosecond x-ray diagnostics for third and fourth generation synchrotron sources

PI: Matthew DeCamp
DOE Grant No: DE-FG02-11ER46816

Work in Progress and Future Plans

Currently we are working on several parallel tracks towards the development of ultrafast x-ray tools at the Advanced Photon Source. This includes designing a photolithographic mask for the acoustic phonon Bragg switch and construction of an x-ray delay line and pulsed x-ray source for x-ray pump/x-ray probe experiments. In addition, we are currently measuring the phonon generation in a variety of metallic thin films, paving a way to optimizing the Bragg switch.

Time-resolved x-ray diffraction of a photo-acoustic transducer

In an effort to better understand the dynamics of the generated acoustic pulses for use in the photo-acoustic Bragg switch, we are currently studying the acoustic phonon generation process from a series of transducer geometries. In particular, we are utilizing differing thickness gold films to generate acoustic phonons with a distinct spatio-temporal structure, as well as measuring the absolute efficiency of the process by directly measuring the dynamics generated by the metallic films.

To directly measure the gold film dynamics, we have grown a quasi-single crystal 200nm gold film on a Germanium substrate. A time-resolved x-ray diffraction experiment of the gold (111) peak demonstrates that the optical excitation increases the temperature of the film by 100 degrees in under 10ps (see figure 1). This rapid increase is consistent with the diffusion of the hot-electrons at speed at least 6 times that of the sound velocity in the gold film.

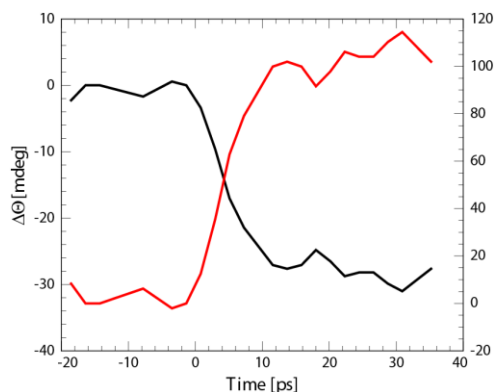


Figure 1: Time-resolved x-ray diffraction of a laser excited gold film. Angular x-ray diffraction shift (black) and temperature rise (red) of the gold as a function of time.

We have recently performed time-resolved x-ray experiments on the Germanium substrate with several different transducer thicknesses. By comparing the experimental results with numerical x-ray diffraction simulations, we have determined that the acoustic pulse shape is primarily determined by the film thickness, in particular, the generated wavevectors are directly proportional to the film thickness (see figure 2). When compared directly with a time-resolved x-ray diffraction of a bare Ge (111) substrate, the lattice dynamics are clearly different. In addition, it appears as though the electron dynamics in the gold film also play a role in the evolution time of the acoustic pulse.

We have recently had photolithographic time granted to us by the Center for Nanoscale Materials at Argonne National Lab to construct the prototype photoacoustic Bragg switch. The generated mask will allow us to generate a series of metallic gratings with differing wavevectors on a crystalline substrate,

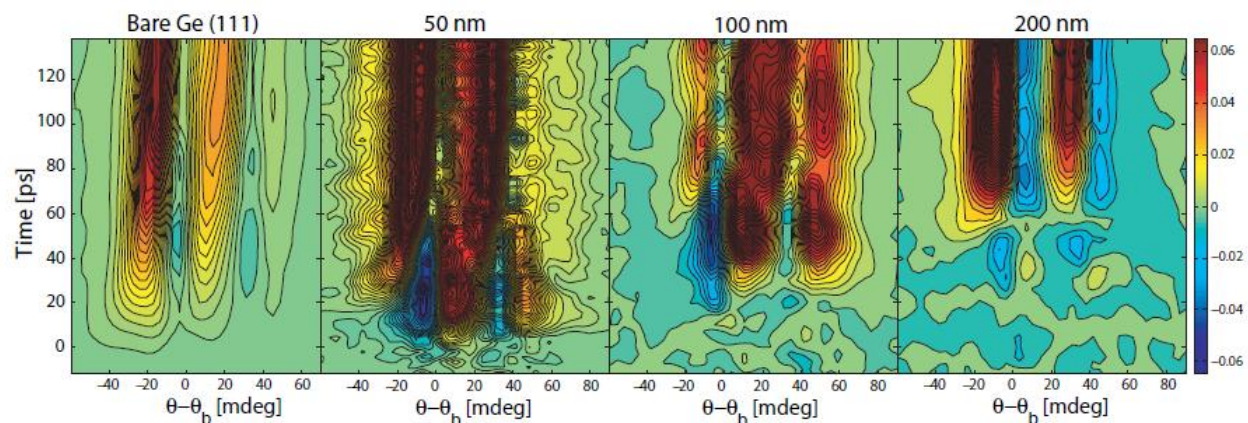


Figure 2: Time-resolved x-ray diffraction of ultrafast phonon generation from several different gold photo-acoustic transducers.

making it possible to have a tunable acoustic phonon switch. In addition, we anticipate that we will have beamtime at the APS within the next 6 months, providing a venue for testing the engineered acoustic phonon Bragg switch.

Construction of a pulsed x-ray source for Argonne National Labs

In addition to the construction of the x-ray Bragg switch, we are currently developing a series of pulsed x-ray tools for the APS for x-ray pump/x-ray probe spectroscopy. This includes the design and testing of a delay line for an x-ray pump-probe spectrometer and the construction of a laser-driven x-ray diode. The laser-driven diode is currently being constructed and tested at the University of Delaware. This diode will generate sufficient hard x-ray flux to have a viable x-ray probe of picosecond crystalline dynamics at the APS. When completed, we plan on installing this device at the APS for testing of an x-ray pump/x-ray probe experiment. In particular, the tunable x-ray pump pulse will be generated by the APS. Any x-ray dynamics will be probed using the picosecond x-ray diode and a conventional x-ray CCD camera.

Publications related to DOE funding

1. "Generation of acoustic pulses from a photo-acoustic transducer measured by time-resolved x-ray diffraction," Y. Gao and M.F. DeCamp *Applied Physics Letters* **100** 191903 (2012).
2. "Measurement of optical phonon dynamics in a bismuth thin film through a surface plasmon resonance" Z. Chen and M.F. DeCamp *Journal of Applied Physics* **112** 013527 (2012).

Time dynamics of oxides and related materials

T. P. Devereaux, W.-S. Lee, Y.-D. Chuang, Z.-X. Shen, Z. Hussain
Stanford Institute for Materials and Energy Sciences
SLAC National Accelerator Laboratory
2575 Sand Hill Rd.
Menlo Park, CA 94025
tpd@slac.stanford.edu

Research Scope:

The Time Dynamics of Oxides & Related Materials research area within the Stanford Institute for Materials and Energy Sciences (SIMES) at SLAC is largely a LCLS-focused effort using ultrafast and spectroscopy techniques, along with computational simulations, to address and probe electron dynamics in oxide and related materials that display a variety of relaxational behaviors across many timescales, reflecting the couplings of charge, spin, orbital, and lattice degrees of freedom so prevalent in transition metal oxide materials. The understanding of electron dynamic processes is related to a number of grand scientific challenges, as well as a number of use-inspired research focus areas.

The main project is to extend resonant x-ray scattering into the time domain using LCLS & multiscale simulations. This project has three specific goals: 1) to offer a direct probe of the time evolution of out-of-equilibrium charge transfer processes in correlated, quantum phases of materials; (2) to explore and probe charge and spin dynamics across thermal and quantum phase transitions; 3) to compliment quasi-particle evolution with time-resolved ARPES.

Recent Results:

We have recently completed a series of successful LCLS runs where the team members joined forces to make the first materials science LCLS run a highly successful one. We have performed time-resolved RXD measurements on various types of spin/charge/orbital orders in complex transition metal oxides, which have advanced our understanding of non-equilibrium properties of complex materials. First, we have discovered that the evolution of photo-excited charge (CO) and spin orders (SO) can exhibit a very different behavior than their thermal evolution, providing a new pathway to control novel nanoscale electronic orders. For example, in the nickelate, the correlation length and period of CO and SO remain unchanged during the photo-induced transient state, despite a large suppression of the order parameters, in sharp contrast to their thermal evolution. In addition, by separating the dynamics of order parameters' amplitude and phase, we found that CO and SO dynamics are locked together due to strong coupling between them. These results vividly demonstrate that the emergence of these orders are ultimately determined by their mutual coupling rather than the interaction within their individual degree of freedom.

In addition, a number of benchmarking experiments using resonant soft x-ray inelastic scattering (RIXS) have been performed under equilibrium conditions for the cuprate & pnictide superconductors, and under diamond anvil cells to explore high spin/low spin and metal-insulator transitions in correlated materials. A review article on RIXS in Rev. Mod. Phys. appeared that gave a snapshot of the current state-of-art experiments and theory.

Using state-of-the-art instrumentation at the soft x-ray ADRESS beamline at Swiss Light Source, we have, for the first time, resolved multi-phonon excitations via ultrahigh resolution RIXS at the oxygen *K*-edge. The multi-phonon excitations in 1D edge-shared cuprates, $\text{Ca}_{2+y}\text{Y}_{2-y}\text{Cu}_5\text{O}_{10}$, consist of harmonics of a 70 meV phonon. In collaboration between theory and experiment, we demonstrated that this phonon excitation reflects the doping evolution of the coupled electronic wavefunction, revealing a site-dependent e-ph coupling strength that exhibits an unexpected mode softening due to the magnetic phase transition.

This result paves the way for characterizing and controlling the e-ph coupling strength away from equilibrium, which is crucial for inducing new phases of matter.

Complementary progress has been achieved in calculating time-domain response functions for correlated electron systems using massively parallel multi-scale computing. We have developed a formalism for calculating pump-probe photoemission spectra in correlated systems using a combination of Keldysh and dynamical mean field theory techniques. We have shown how Bloch oscillations are damped with increasing interactions, and have investigated how the pumped system display spectra which are not simply characterized in terms of equilibrium spectra at elevated temperatures. In particular, we have shown that Mott gaps do not collapse when pumped.

Future Plans:

Multi-scale numerical simulations of time-domain spectroscopies: We are developing a complete tool set that combines the best aspects of many different computational techniques to provide the most complete picture of systems in- and out-of equilibrium. Our efforts include developing massively parallel codes & algorithms, usable on our local cluster, Tier 1 computing facilities at NERSC, and new GPU-based clusters, that combine crystal field/atomic multiplet, quantum cluster, density functional theory, and dynamical mean-field theory methods. In order to access time-domain spectroscopy, we will put a focus on formulating the time evolution of quantum states obtained via cluster diagonalizations.

Charge and spin dynamics of striped nickelates and other cuprates: In stripe ordered nickelates and cuprates, neutron scattering measurements have observed an anomalous softening of the phonon branch for bond-stretching modes near the charge-ordering wave-vector. It has been a long-standing question regarding the relation between the stripe phase and this phonon anomaly. To shed a new light to this problem, we will perform a mode-selective THz pump and resonant x-ray scattering probe experiments on stripe ordered nickelates and cuprates. We would like to manipulate the population of the bond-stretching phonons by pumping the system using a THz laser, and study the response of the stripes using resonant x-ray scattering (diffraction).

Study of interface heterostructures via resonant x-ray scattering: We intend to apply resonant x-ray scattering tools developed by our FWP team to explore the interface properties of oxide heterostructures. With its unique element specific and high scattering cross section of spin and orbital excitations, crucial spectroscopic information can be obtained to reveal detail microscopic mechanisms. Experiment will be done in close collaboration with the FWP led by Hwang. We expect more resonant x-ray scattering experiments, including both diffraction and inelastic scattering, will be designed and conducted on oxide heterostructures, also in connection with the theory development of this FWP.

Searching for an obscure CDW state in the cuprates: Increasing evidence suggests that CDW states away from $1/8^{\text{th}}$ filling are intertwined with high T_c superconductivity. In particular, a recent work has revealed a CDW-like signature in the ARPES spectrum in the single layer cuprate, $\text{Bi}_2\text{Ca}_2\text{CuO}_6$ (Bi2201) tied to the mysterious pseudogap phase. However, such a CDW state may be indiscernible by convention resonant X-ray diffraction experiment, since the signal may be very weak and buried under strong fluorescence. In this regard, RIXS may shed a new light on this problem as the spectrometer can separate elastic and inelastic channels of scattered light. Together with polarization analysis to further separate magnetic and charge scattering, a CDW state that tracks the pseudogap could be revealed.

Selected Publications (2011-2012):

1. W. S. Lee, Y. D. Chuang, R. Moore, L. Patthey, M. Trigo, D. Lu, P. S. Kirchmann, M. Yi, O. Krupin, M. Langner, N. Huse, J. Robinson, Y. Chen, Y. Zhu, S. Zhou, D. Reis, R. A. Kaindl, R. W. Sasagawa, T. P. Devereaux, D.-H. Lee, Z. X. Shen, and Z. Hussain. **Phase Fluctuations and the Absence of Topological Defects in a Photo-Excited Charge-Ordered Nickelate.** *Nature Communications* **3**, 838 (2012).
2. W. S. Lee, A. P. Sorini, M. Yi, Y. D. Chuang, B. Moritz, W. L. Yang, J.-H. Chu, H.H. Kuo, A.G. Cruz Gonzalez, I. R. Fisher, Z. Hussain, T. P. Devereaux, and Z. X. Shen. **Resonant Enhancement of Charge Density Wave Diffraction in the Rare-Earth Tri-Tellurides,** *Phys. Rev. B* **85**, 155142 (2012).
3. L.J.P. Ament, M. van Veenendaal, T.P. Devereaux, J.P. Hill, J. van den Brink. **Resonant inelastic x-ray scattering studies of elementary excitations.** *Reviews of Modern Physics* **83**, 705 (2011).
4. B. Moritz, T. P. Devereaux and J.K. Freericks, **Temporal response of nonequilibrium correlated electrons,** *Computer Physics Communications* **182**, 109 (2011).
5. O. Krupin, M. Trigo, W. F. Schlotter, M. Beye, F. Sorgenfrei, J. J. Turner, D. A. Reis, N. Gerken, S. Lee, W. S. Lee, G. Hays, Y. Acremann, B. Abbey, R. Coffee, M. Messerschmidt, S. P. Hau-Riege, G. Lapertot, J. Lüning, P. Heimann, R. Soufli, M. Fernández-Perea, M. Rowen, M. Holmes, S. L. Molodtsov, A. Föhlisch, W. Wurth. **Temporal Cross-correlation of x-ray free electron and optical lasers using soft x-ray pulse induced transient reflectivity.** *Optics Express* **20**, 11396 (2012).
6. W.F. Schlotter, J.J. Turner, M. Rowen, P. Heimann, M. Holmes, O. Krupin, M. Messerschmidt, S. Moeller, J. Krzywinski, R. Soufli, M. Fernández-Perea, N. Kelez, S. Lee, R. Coffee, G. Hays, M. Beye, N. Gerken, F. Sorgenfrei, S. Hau-Riege, L. Juha, J. Chalupsky, V. Hajkova, A.P. Mancuso, A. Singer, O. Yefanov, I. A. Vartanyants, G. Cadenazzi, B. Abbey, H. Sinn, J. Lüning, S. Schaffert, S. Eisebitt, W.-S. Lee, A. Scherz, A.R. Nilsson, and W. Wurth. **The Soft X-ray Instrument for Material Studies at the Linac Coherent Light Source X-ray Free-Electron Laser,** *Review of Scientific Instrum.* **83**, 043107 (2012).
7. S.L. Johnson, R.A. de Souza, U. Staub, P. Beaud, E. Mohr-Vorobeva, G. Ingold, A. Caviezel, V. Scagnoli, W.F. Schlotter, J.J. Turner, O. Krupin, W.S. Lee, Y.D. Chuang, L. Patthey, R.G. Moore, D. Lu, M. Yi, P.S. Kirchmann, M. Trigo, P. Denes, D. Doering, Z. Hussain, Z.X. Shen, D. Prabhakaran, and A.T. Boothroyd. **Femtosecond Dynamics of the Collinear-to-Spiral Antiferromagnetic Phase Transition in CuO.** *Phys. Rev. Lett.* **108**, 037203 (2012).
8. Y.J. Kim, A.P. Sorini, C. Stock, T.G. Perring, J. van den Brink, T.P. Devereaux. **Probing high-energy electronic excitations in NiO using inelastic neutron scattering,** *Phys. Rev. B* **84**, 085132 (2011).

Ultrafast Nanoscale Dynamics in Complex Oxide Electronic Materials

Paul G. Evans, *Department of Materials Science and Engineering, University of Wisconsin-Madison, 1509 University Ave., Madison, WI 53706*

evans@engr.wisc.edu

I. Introduction

Our research program probes the dynamics associated with the polarization and structural distortion of complex oxide electronic materials, taking advantage of the unique opportunity arising from the combination of nanofocused x-ray beams with ultrafast techniques. In 2011-2012 this work resulted in published works in nanodiffraction and the in dynamics of complex oxide superlattices,¹⁻⁴ as well as work that is either submitted or about to be submitted.^{5,6} Our future plans focus are: (i) to determine how applied electric fields can influence novel domain configurations in ferroelectric/dielectric superlattices, (ii) to combine optical pumping techniques with an x-ray nanoprobe in order to understand optically induced phenomena in these superlattices, and (iii) to probe the dynamics of striped domains in superlattices at the 10-100 nm scale via coherent scattering.

II. Planned Research

II.1 Electric-Field-Induced Structural Distortion in Ferroelectric-Dielectric Striped Domains

Ferroelectric-dielectric superlattices allow the relative importance of long-range electrostatic effects and the energy associated with domain walls to be straightforwardly varied. With the appropriate ratio of ferroelectric and dielectric atomic layers, the interaction between the electrical polarization of adjacent ferroelectric layers is very weak. Under these conditions, the ferroelectric polarization spontaneously forms a nanoscale striped domain pattern in order to reduce the polarization in the SrTiO₃ component. The atomic-scale structure of this domain pattern, the evolution of the polarization distribution in applied fields, and the structural distortion induced in the domain pattern by applied electric fields are all unknown. Recent theoretical studies predict that the domain structure will yield vortex domains and other unusual polarization distributions, and that these distributions will be particularly sensitive to applied fields. We are working now to address these issues. Our first results in this area are in Fig. 1, where we show that applied electric field leads to a large increase in the polarization of the SrTiO₃ component of a ferroelectric PbTiO₃/dielectric SrTiO₃ superlattice.⁵

II.2 Optically Induced Dynamics in Superlattices

It has recently been shown by Daranciang *et al.* (PRL **108**, 087601 2012) that the large carrier concentrations produced by intense fs-duration optical pulses can lead to significant structural distortion in ferroelectric thin films. In a subsequent experiment following their study, we have worked with an Advanced Photon Source/Center for Nanoscale Materials team in a combined, optical spectroscopy and x-ray diffraction experiment to show that the structural changes in a similarly pumped BiFeO₃ layer are associated with the dynamics of charge carriers.⁶ We are now developing the means to combine optical pumping with nanofocused x-ray beams in order to probe similar effects in ferroelectric/dielectric superlattices (Fig. 2). The nanofocused x-ray beam also leads to a novel experimental possibility to use the acoustic wave resulting from the optically induced distortion to excite the superlattice thin film heterostructure, as shown in Fig. 2(b). This has the potential to simplify the comparison of experiments

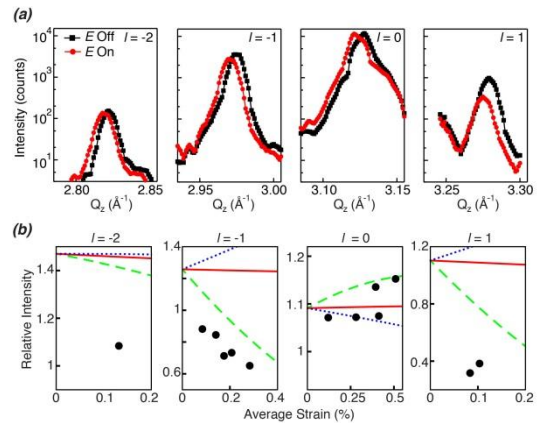


Figure 1 (a) Electric-field-driven evolution of the diffraction pattern of a PbTiO₃/SrTiO₃ superlattice. Note the large change in the relative intensities of reflections of different order l . (b) The intensity variation is best fit by a model in which the piezoelectric expansion occurs largely due to an increase in the polarization of the normally weakly polarized SrTiO₃ component (dashed line).

with theory because the stress imparted by the acoustic wave can easily be quantified. We are working with the Advanced Photon Source (APS) to include this excitation scheme in the experimental facilities accompanying the Short Pulse X-ray (SPX) facility of the APS upgrade.

II.3 Coherent X-ray Probes for Transition Mechanisms in Superlattice Domain Systems

We showed in 2011 that the transformation from the striped domain state to a uniform polarization configuration in a $\text{PbTiO}_3/\text{SrTiO}_3$ ferroelectric/dielectric superlattice occurs through the formation of large regions of uniform polarization and the subsequent expansion of these regions into the remaining stripes.³ Based on those experiments, however, we were not able to describe the arrangement of domains at the 10-200 nm length scale during the transition. The detailed mechanism of the transformation operates at this scale, just below the size of the focused beams of our experiments, and remains unknown. The coherence of the nanofocused x-ray beam provides opportunity to obtain spatial information about the structure and ferroelectric polarization at these scales. Preliminary results from October, 2012 show that the zone-plate x-ray beam is sufficiently coherent to observe coherent diffraction from the stripe domains and that the speckle pattern encodes spatial information at a length scale far smaller than the variation of the total intensity (Fig. 3). We are now working to acquire and analyze a series of these coherent scattering patterns during the field-driven transformation in order to image the transformation mechanism.

III. Publications in 2011-2012 Resulting from DOE-Sponsored Research

¹ P. Chen, J. Y. Jo, H. N. Lee, E. M. Dufresne, S. M. Nakhmanson, and P. G. Evans, “Domain- and symmetry-transition origins of reduced nanosecond piezoelectricity in ferroelectric/dielectric superlattices,” *New J. Phys.* **14**, 013034 (2012).

² P. G. Evans, D. E. Savage, C. B. Simmons, M. G. Lagally, S. N. Coppersmith, M. A. Eriksson, and T. U. Schulli, “Nanoscale Distortions of Si Quantum Wells in Si/SiGe Quantum-Electronic Heterostructures,” *Adv. Mater.* **24**, 5217 (2012).

³ J. Y. Jo, P. Chen, R. J. Sichel, S. J. Callori, J. Sinsheimer, E. M. Dufresne, M. Dawber, and P. G. Evans, “Nanosecond Dynamics of Ferroelectric/Dielectric Superlattices,” *Phys. Rev. Lett.* **107**, 055501 (2011).

⁴ J. Y. Jo, P. Chen, R. J. Sichel, S.-H. Baek, R. T. Smith, N. Balke, S. V. Kalinin, M. V. Holt, J. Maser, K. Evans-Lutterodt, Chang-Beom Eom, and Paul G. Evans, “Structural Consequences of Ferroelectric Nanolithography,” *Nano Lett.* **11**, 3080 (2011).

⁵ P. Chen, M. P. Cosgriff, S. J. Callori, B. W. Adams, E. M. Dufresne, M. Dawber, and P. G. Evans, “Field-Dependent Domain Distortion and Interlayer Polarization Distribution in $\text{PbTiO}_3/\text{SrTiO}_3$ Superlattices,” in preparation (2012).

⁶ H. Wen, P. Chen, M. P. Cosgriff, D. A. Walko, J. Hyuk Lee, C. Adamo, R. D. Schaller, J. F. Ihlefeld, E. M. Dufresne, D. G. Schlom, P. G. Evans, J. W. Freeland, and Y. Li, “Electronic origin of ultrafast photoinduced strain in BiFeO_3 ,” submitted (2012).

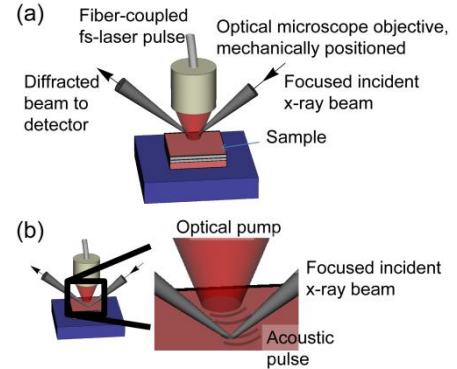


Figure 3 (a) Optical excitation with an x-ray nanoprobe. (b) Optically induced mechanical excitation.

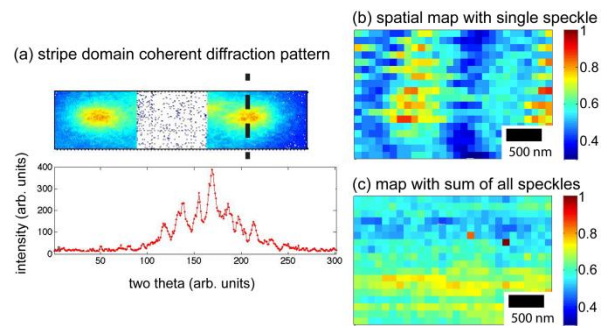


Figure 2 (a) Coherent x-ray diffraction pattern (above) and intensity profile (below) associated with the domain pattern of a $\text{PbTiO}_3/\text{SrTiO}_3$ superlattice, acquired with a 200-nm diameter focused incident x-ray beam. Intensity maps assembled from a single speckle (b) reveal the mesoscale distribution of the striped order, an effect which is not apparent in the map of the total diffuse intensity (c).

**PROBING THE ELECTRONIC AND MAGNETIC PROPERTIES
OF BULK MATERIALS, BURIED LAYERS AND
INTERFACES WITH STANDING-WAVE AND HARD-X-RAY PHOTOEMISSION**

C.S. Fadley

with P.J. Fischer, F. Hellman, J.B. Kortright

*Department of Physics, University of California Davis and
Magnetic Materials Program
Materials Sciences Division
Mailstop 2-100
Lawrence Berkeley National Laboratory
Berkeley, CA 94720
E-mail: fadley@lbl.gov*

I will present some recent highlights from the LBNL Magnetic Materials Program in soft x-ray photoemission (XPS, SXPS) and hard x-ray photoemission (HXPES, HAXPES) [1-14]. These involve combined SXPS and HXPES studies of buried layers and interfaces in magnetic and transition-metal oxide multilayers [4,5,7,9], hard x-ray photoemission studies of the bulk electronic structure of some spintronic materials [3,6,10,13]; including band-offset measurements in oxide multilayers[11]; the use of standing waves from multilayer mirrors to enhance depth resolution in photoemission [4,5,9], as well as in angle-resolved photoemission (ARPES) [1,14] and photoelectron microscopy [3]; and the prospects for carrying out bulk-sensitive hard x-ray ARPES (HARPES) [9,13]. Future projects will involve the application of these techniques to thin films of FeRh and similar materials exhibiting competing ferromagnetic and anti-ferromagnetic interactions; oxide multilayers of the following three systems: $\text{LaNiO}_3/\text{SrTiO}_3$, $\text{BiFeO}_3/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, and $\text{GdTlO}_3/\text{SrTiO}_3$ that show interesting interface electronic structure; multilayers of Co-doped ZnO and Al-doped ZnO that may provide a new type of magnetic semiconductor material, and the promising perpendicular anisotropy tunnel junction system of Ta/CoFeB/MgO

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Magnetic Soft X-ray Microscopy at LBNL

Peter Fischer

Center for X-ray Optics

Material Science Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720 U.S.A.

PJFischer@lbl.gov

<http://pifischer.lbl.gov>

Research in magnetism is motivated by the scientific curiosity to understand and control spins on multiple length, time and energy scales and thus to meet future challenges in terms of speed, size and energy efficiency of spin driven technologies. Imaging magnetic structures and their fast dynamics down to fundamental magnetic length and time scales with elemental sensitivity in emerging multi-element and nanostructured materials is highly desirable. Our research is part of the Magnetic Materials program at MSD/LBNL, which aims to develop a basic understanding of novel nano- and meso-scale magnetic structures and to explore new phenomena permitting the control of spins down to fundamental magnetic length and time scales.

Magnetic soft X-ray microscopy is a unique analytical technique combining X-ray magnetic circular dichroism (X-MCD) as element specific magnetic contrast mechanism with high spatial and temporal resolution [1]. Our approach is to use Fresnel zone plates as X-ray optical elements providing a spatial resolution down to currently 10nm [2] thus reaching out into fundamental magnetic length scales such as magnetic exchange lengths. The large field of view allows investigating both, the complexity and the stochasticity of magnetic processes, such as nucleation or reversal. Utilizing the inherent time structure of current synchrotron sources fast magnetization dynamics such as current induced wall and vortex dynamics in ferromagnetic elements can be performed with a stroboscopic pump-probe scheme with 70ps time resolution, limited by the lengths of the electron bunches.

In recent studies of magnetic vortex structures, we found a stochastic character in the nucleation process, which can be described within a symmetry breaking DM interaction [3]. With time resolved studies of dipolar coupled magnetic vortices, we found an efficient energy transfer mechanism, which can be used for novel magnetic logic elements [4].

We propose to build a next generation full-field soft X-ray microscope (XM-3) at a polarized undulator source to address important issues in materials, environmental and energy-related sciences [5]. At future high brilliant fsec X-ray sources snapshot images of nanoscale ultrafast spin dynamics become feasible with a spatial resolution approaching the <10nm regime.

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***In Situ* Synchrotron Studies of Reactivity at Polar Oxide Surfaces**

Dillon D. Fong, Hoydoo You, Paul H. Fuoss
Materials Science Division
Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439
(630) 252-3793, fong@anl.gov

Oxide materials display an amazingly diverse array of properties, from superconductivity to ferroelectricity, with applications ranging from inert thermal insulators to catalytically active electrodes. In the past decade, researchers have discovered the importance of surfaces and interfaces in these materials, as they can radically alter the innate behavior. This has given rise to the design of new oxide materials using surfaces and interfaces to deliberately improve function and enhance catalytic, conductive, and other properties [1, 2]. It is well-known, however, that the behavior of these materials depends strongly on their environmental conditions, as the oxide surface can interact closely with the gas phase, incorporating and losing oxygen and adsorbing and desorbing molecules, altering its local structure and properties during the process. This is exemplified by our results for ferroelectric heterostructures, where we find that the polarization can be manipulated by varying the partial pressure of oxygen in the environment rather than the usual applied voltage [3-5]. Our use of *in situ* hard x-ray synchrotron techniques allows atomic scale imaging of these heterostructures as they evolve in their elevated temperature, reactive environments.

In the next two years, we will focus on understanding the reactivity of these oxide heterostructures for a variety of chemical reactions. Of particular interest are oxidative reactions involving polar molecules and polar / non-polar surfaces. We will utilize the unique instrumentation we have recently developed to directly correlate the evolving structure and composition with surface reactivity as measured by gas chromatography / mass spectrometry. The use of atomically smooth, single-crystal surfaces will help to reduce the complexity of the reactions and allow direct comparison with theoretical investigations. Furthermore, such surfaces allow use of total reflection x-ray fluorescence and absorption spectroscopy to probe changes in surface composition and fine structure. Improved phase-retrieval techniques employing resonant scattering [6-8] will be developed and utilized to image adsorbate-induced changes throughout the heterostructure with sub-Ångstrom resolution. This level of resolution is crucial, as it can be used to indicate and characterize the appearance of local electric fields within the heterostructure. When combined with gas chromatography / mass spectrometry, these techniques will permit a unique *in situ* examination of how the surface structure and composition affects the catalytic turnover frequency, and, in turn, how the adsorption or desorption of different species can affect surface structure.

While some kinetic processes can be investigated with these techniques, coherent surface x-ray scattering (CSXS) methods are particularly well-suited to the study of surface dynamics [9, 10]. Surface morphology and roughness are known to play an integral part in reactivity [11], and polar surfaces in particular may be susceptible to structural changes before and after molecular adsorption or changes in oxygen partial pressure. For these materials, surfaces and interfaces typically act as sinks for point defects, making them regions of high mobility. In the near future, we will apply *in situ* CSXS techniques to understand the dynamics of oxide surfaces in reactive environments. In this presentation, I will discuss the present status of oxide reactivity studies and detail our plans for the upcoming years.

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Structure and Dynamics of Disordered and Heterogeneous Materials

Paul H. Fuoss, Dillon D. Fong, and Hoydoo You
Materials Science Division
Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439
(630) 252-3289; (630) 252-7777(Fax), fuoss@anl.gov

Furthering our understanding of the underlying mechanisms that govern the synthesis and fundamental properties of materials requires that local structure and dynamics in materials be resolved at nanometer length scales and sub-picosecond time scales. We are developing and using x-ray techniques to probe atomic-scale fluctuations, strain fields and structure in disordered and heterogeneous materials, and to understand the influence of these phenomena on materials properties and materials synthesis. Increases in the brightness of synchrotron x-ray sources have allowed observation of materials dynamics on ever-faster timescales, and our research has used, and will continue to use, this capability to explore basic mechanisms of materials synthesis and processing. The emergence of ultra-fast and coherent x-ray sources, both at the APS and LCLS, offer new opportunities to explore these fundamental processes by providing access to picosecond and femtosecond time scales with coherent fluxes that enable imaging on nanometer length scales. Taking full advantage of these properties to study the frontier of materials at state-of-the-art light sources requires the development of new techniques to uncover new science in materials.

During the next two years, our research will use the x-ray capabilities of the APS and the LCLS to probe materials structures and dynamics in two areas. The first research focus will be to build on our recent development of nano-focused Bragg Projection Ptychography (BPP), a coherent diffraction imaging technique, which we have successfully used to map crystalline strain distributions in the epitaxial stressor layer of a SiGe-on-SOI device prototype (Hruszkewycz, Nano Letters, 2012). We have demonstrated that BPP can be used to nondestructively reconstruct strain distribution maps in thin-film objects with better than 16 nm in-plane spatial and 2 pm out-of-plane resolution. We will also take advantage of the phase-sensitivity of BPP to image and follow the evolution of domains in ferroelectric thin films as a function of temperature and chemical environment. These studies will be facilitated by increasing the resolution and utility of BPP through improvements to the experimental configuration that will enable a broader Q range to be acquired, and by refining the reconstruction algorithms. High resolution images of strain distributions and local ferroelectricity in epitaxial thin films will be used to clarify the role of strain and strain relaxation in the materials synthesis, and is a natural extension of our long-term program of in situ x-ray studies of materials.

Second, the coherent, femtosecond hard x-ray pulses from LCLS provide unprecedented opportunities to observe the equilibrium dynamics of atomic motion in amorphous materials down to the atomic length scale and the corresponding femtosecond time scale. We have recently demonstrated that atomic resolution speckle can be observed from an atomic liquid using the LCLS, and that statistical properties of the liquid can be extracted from these patterns (Hruszkewycz, Phys. Rev. Lett, 2012). We plan to carry out XPCS measurements at high wave number (e.g. out to 3 \AA^{-1}) on time scales between 60 fs and 3 ns to observe the diffusive and vibrational dynamics in molecular glass-forming liquids. This time and length scale range will be ideal for observing the atomic-scale origin of the emergence of solid-like behavior from the liquid as the glass transition is approached. We will pioneer development of the proposed pulse-split-and-delay technique to allow femtosecond XPCS studies at LCLS by observing the change in contrast of a summed speckle pattern^{1,2}. These experiments will take advantage of the first x-ray pulse split-and-delay instrument³ that we are helping to commission at LCLS. The four-and-a-half orders of magnitude range of time scales made possible by this instrument will be used to separate the different predicted dynamical regimes⁴. Based on our recent results, we have chosen two glasses made of light elements, ortho-terphenyl ($\text{C}_{18}\text{H}_{14}$) and boron oxide (B_2O_3), which should provide optimum XPCS signal under conditions designed to reduce disturbance of the dynamics by pulsed beam heating at LCLS. These systems have also been the subject of complementary characterization through inelastic scattering^{5,6,7} and modeling⁴. As we vary temperature through the glass transition from liquid to solid, we will be able to directly see the separation of the diffusive modes from the vibrational modes. These measurements will provide new atomic resolution insight into dynamics at the glass transition, “one of the deepest and most important unsolved problems in condensed matter physics”⁸.

FY11-FY12 Publications of Paul H. Fuoss (• indicates lead role for SRS)

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Ultrafast Optical Manipulation and Detection of Emergent Phenomena in Topological Insulators

Nuh Gedik

Mailing Address: MIT, Department of Physics, 77 Massachusetts Avenue, 13-2114, Cambridge MA 02139

E-mail: gedik@mit.edu

Abstract:

The three-dimensional topological insulator (TI) is a new quantum phase of matter that exhibits quantum-Hall-like properties, even in the absence of an external magnetic field. These materials are insulators in the bulk but have a topologically protected conducting state at the surface. Charge carriers on these surface states behave like a two-dimensional gas of massless helical Dirac fermions for which the spin is ideally locked perpendicular to the momentum. The purpose of this project is to probe the unique collective electronic behaviors of topological insulators by developing and using advanced time resolved spectroscopic techniques with state-of-the-art temporal and spatial resolutions. Specifically, we will be focusing on three areas: 1) Imaging topological spin currents and topological quantum phase transitions using spin sensitive time-and angle resolved photoelectron spectroscopy; 2) Magneto-optical spectroscopy of topological insulators to study their anomalous magneto-electric quantization; and 3) Non-linear ultrafast optical responses of topological insulators to study interface physics between topological and non-topological materials. These experiments offer the unique possibility to observe the macroscopic manifestations of topological quantum order in topological insulators for the first time, which is a crucial first step to understanding how they can be used for future energy efficient electronics, spin based processing devices and fault-tolerant quantum computers.

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MECHANISMS OF ROUGHENING AND PATTERN FORMATION DURING THIN FILM DEPOSITION

Randall L. Headrick
rheadrick@uvm.edu
Department of Physics
Cook Physical Sciences Building
University of Vermont
Burlington, VT 05405

Planned Research Scope

Our planned research scope covers two main areas. One is the investigation of epitaxial thin film growth of complex oxide materials by off-axis sputter deposition. This work will utilize a recently commissioned in-situ x-ray diffraction system designed for this purpose. This work is in collaboration with Prof. Matt Dawber at Stony Brook U. We are interested in fundamental issues of roughening and pattern formation, as well as the possibility of creating strained epitaxial multilayers.

Second, we have constructed a nanoparticle source based on magnetron sputtering source. We will use the source to investigate mechanisms of cluster formation in sputter deposition, and studies of thin film formation from nanoparticles using in-situ x-ray scattering. Materials of interest range from simple metals to semiconductors and complex oxides.

In addition to these two main areas, we have forward-looking experiments on our agenda, including a preliminary investigation of coherent scattering in thin film growth and sputter erosion, in collaboration with Prof. Karl Ludwig (Boston U.)

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Using Spectroscopy for Designing New Types of Solar Cells

F. J. Himpsel, fhimpse@wisc.edu, Physics Department, University of Wisconsin
Madison, 1150 University Ave., Madison, WI 53706

Jinghua Guo, jguo@lbl.gov, Wanli Yang, WLYang@lbl.gov, Zahid Hussain,
ZHussain@lbl.gov, Advanced Light Source, LBNL, One Cyclotron Road,
Berkeley, CA 94720

Lionel Vayssieres, lvayssieres@lbl.gov, LBNL and Int. Res. Cent. for Renewable
Energy, State Key Laboratory of Multiphase Flow in Power Engineering, School of
Energy & Power Engineering, Xian Jiaotong University, Xian 710049, PR China

Spectroscopy with soft X-rays is used to assist the development of new materials and new designs for solar cells with better price/performance ratio. The starting point is the most general layout of a solar cell, which consists of a light absorber sandwiched between an electron donor and an electron acceptor. There are four relevant energy levels, which can be measured by a combination of X-ray absorption spectroscopy and photoelectron spectroscopy [1]. This allows much more variation than a standard semiconductor solar cell, where only the band gap is variable. Examples for the design process will be given, such as organic dyes as absorbers, p-doped diamond films as inert donors, and the combination of all three components in a single molecule (a d- π -a complex). In order to speed up the development of new solar cells, a feedback loop is currently being established between spectroscopy, theory, synthesis, and device fabrication. Initial results on the efficiency enhancement of photoanodes are reported [2].

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Novel Tools and Techniques of Today and Tomorrow: For studying Quantum Materials and Energy Problems

Zahid Hussain

Division Deputy for Scientific Support, Advanced Light Source,
Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
zhussain@lbl.gov

1. Momentum Resolved Soft X-rays Resonant Inelastic Scattering:

Scope and Motivation:

Electronic ordering of charge, orbital and spin at nanoscale are hallmarks of strongly correlated electron systems and quantum materials. The competing ground states associated with these ordered phases underlie the emergence of unique phenomena. The emergent properties evolve because of interplay of charge, orbital, spin, and lattice degrees of freedom interacting at different time, length and energy scale. The tool-of-choice for unraveling these phenomena is q-resolved soft x-ray resonant inelastic scattering (q-RIXS).

Plan:

As part of the collaboration with SIMES at SLAC, we are working together to develop a portable q-RIXS system utilizing advanced engineering and next generation of detector that will allow us to measure low energy excitations with complete control of q-resolution. This system will be ready for commissioning during middle of 2013. We plan to use this system at the ALS beamline 8.0 for static measurements and at LCLS-I for time domain studies. This system will allow us to develop the science case for higher resolution q-RIXS systems at QERLIN beamline at ALS, NGLS at LBNL and LCLS-II at SLAC. LCLS-II plan to have the added capabilities of two color soft x-rays allowing stimulated RIXS as well as pump-probe experiments. Coupling these advanced experimental tools with the existing computational and simulation capabilities as well as the proposed Theoretical Institute for Photon Sciences (TIPS) capabilities will provide a unique platform in tackling grand challenges and meeting the DOE mission needs.

2. Advanced Materials Beamline for Energy Research (AMBER):

Scope and Motivation:

The quest for renewable energy requires us to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels. The ever-increasing demand to diversify the energy portfolio and to minimize environmental impact while supplying global energy needs, has intensified the urgency for developing alternative energy sources and carriers. Significant

research efforts are under way and will continue in a broad range of fundamental science with the use of light sources such as synchrotron and free electron lasers. Energy-related materials research faces urgent challenges today. We need to go beyond the Edisonian hit and trial approach to more systematic research with the use of advanced tools applicable under realistic in-situ and operando conditions capable of exploring electronic and atomic structure of energy materials.

Plan:

How do we learn about the electronic and atomic characteristics of novel materials for efficient solar energy conversion (photovoltaics and water-splitting), energy storage (Li-ion batteries and multivalent-ion batteries), and efficient catalytic activity and selectivity in catalysis?

The *Intellectual Merit* of the soft x-ray research facility (AMBER) proposed at the ALS would allow scientists to address these questions with the use of in situ soft x-ray spectroscopy and nanospectroscopy tools that are fully optimized for energy science. AMBER will be based on some of the pioneering instrumental developments at the ALS:

- i) In-situ photon-in/electron-out spectroscopy with the use of an advanced ambient pressure x-ray photoelectron spectroscopy (APXPS) end-station that allows measuring electron binding energy and surface occupied electronic structure in the presence of reactant gases at a pressure up to 10 Torr with both elemental and chemical state selectivity. The end-station will use a newly developed system (ALS pioneered APXPS technique about ten years ago and received 2010 R&D100 Award) that has capability of both spatial resolution of 50-200 nm and very high throughput as well as flexibility of selecting broad range of depth sensitivity with the use of wide energy range undulator.
- ii) In-situ photon-in/photon-out soft x-ray spectroscopy (PIPOS) endstation that allows measuring the unoccupied and occupied electronic structure, and d-d excitations in transition metals and charge-transfer processes in energy conversion and storage in the presence of liquids or reactant gases at a pressure of above 1 bar with both elemental and chemical state selectivity. We will use unique high throughput and wide energy range, variable line spacing grating spectrograph developed by the ALS with over 100 times higher throughput than first-generation grating spectrographs.
- iii) In-situ scanning transmission x-ray microscopy (STXM) endstation allows measuring the unoccupied electronic structure with down to 10 nm special resolution in the presence of liquids or reactant gases at a pressure of above 1 bar with both elemental and chemical state selectivity. The ALS is the World leader with highest resolution soft x-ray STXM.

Ultrafast Dynamics of Low-Energy Excitations and Electronic Structure in Complex Materials

PI: Robert A. Kaindl, Co-PIs: Alessandra Lanzara, Robert W. Schoenlein
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
RAKaindl@lbl.gov, ALanzara@lbl.gov, RWSchoenlein@lbl.gov

The aim of our research is to apply advanced ultrafast tools, spanning from the THz to the X-ray regime, to shed new light on fundamental excitations and emergent phenomena in complex materials on the natural timescales that define their interactions. Measurements with femtosecond resolution can study quasiparticle dynamics, help separate correlated interactions between charge, spin, and lattice after perturbative excitation, or provide tailored excitation of low-energy excitations to investigate transient phases beyond thermally accessible regimes.

One component of our effort is focused on studies of low-energy excitations and many-body physics of correlated electron systems and nanoscale materials via femtosecond mid-IR and ultra-broadband THz spectroscopy.¹ Our previous studies of single-walled carbon nanotubes revealed a strong photoinduced mid-IR response, whose transition energy, oscillator strength, chirality enhancement, and dynamics manifests the observation of $1s$ - $2p$ intra-excitonic transitions.² While interband optics is limited by symmetry and momentum to a subset of excitons, *intra-excitonic* spectroscopy can detect excitons independent of these restrictions.³ We also studied few-layer epitaxial graphene, revealing an optical conductivity consistent with intra- and interband transitions of a dense Dirac electron plasma and ultrafast THz transmission changes that are dominated by excess hole carriers.⁴ Investigating strongly-correlated materials, we recently studied for the first time the ultrafast mid-IR response of nickelates.⁵ These materials are isostructural to cuprates, yet give access to intriguing “stripe” charge and spin order phases without superconductivity. We find a dramatic spectral weight transfer in the in-plane optical conductivity, indicating the opening of a mid-IR pseudogap already below a temperature $T^* \approx 250$ K far above stripe formation (≈ 105 K). Ultrafast excitation results in a sub-ps dynamics that reveals a femtosecond filling and re-emergence of the pseudogap (Fig. 1), thus tracking the development of fluctuating short-range charge order. The Ni-O stretching mode around 680 cm^{-1} indicates a non-thermal transient phase. The pseudogap reappears faster than the long-range stripe order measured in a collaboration with SLAC by time-resolved resonant X-ray scattering at LCLS.⁶ This further supports the prevalence of short-range charge correlations in the mid-IR pseudogap, whose dynamical breakup and reformation precedes the establishment of long-range stripe order.

In the future, we plan to apply ultrabroadband THz probes combined with tunable optical and mid-IR excitation to investigate phase transitions, vibrational symmetry breaking, and electron-boson coupling. Key vibrational modes in manganites, nickelates, or underdoped cuprates exhibit strong energy shifts and/or splittings below the ordering temperature, providing a window into the dynamics of symmetry breaking. After ultrafast stripe-order suppression, the bending mode spectrum of nickelates will reveal how fast the lattice reacts to a change of the electronic correlations. Conversely, coupling from the lattice *into* the electronic system can be studied by resonant vibrational excitation. The transient THz conductivity also provides access to the frequency-dependent carrier *transport*, to reveal how hole itineracy is affected by modulation of charge order. More insight into competing ground states will be obtained by applying THz probes to study photo-induced phase transitions. We plan to investigate the time-resolved THz conductivity of manganites (LCMO, LSMO) to investigate the low-energy electronic and lattice dynamics in the transient phase beyond the perturbative regime. Combined with time-resolved X-ray diffraction, this can help clarify a central issue – the relation between mesoscale charge/orbital order and charge transport. Beyond charge-order dynamics, we plan to expand our previous THz studies of quasiparticle and Cooper-pair dynamics in high- T_C

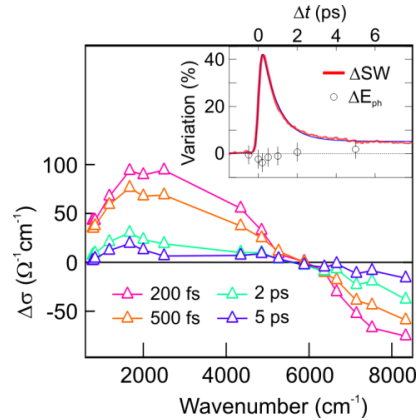


Fig. 1. Transient mid-IR conductivity spectra after ultrafast optical excitation of $\text{La}_{1.75}\text{Sr}_{0.25}\text{NiO}_4$, revealing a femtosecond filling and re-emergence of the pseudogap. Inset: dynamics of the mid-IR spectral weight transfer, compared to the center frequency of the Ni-O stretching mode.

cuprates to investigate the transient evolution of electron-boson coupling, to clarify the cause-effect relationship between phonons, the mid-IR spin resonance, and charge pairing.

The second part of this research is focused on applying ultrafast angle-resolved photoemission spectroscopy (ultrafast ARPES) to investigate

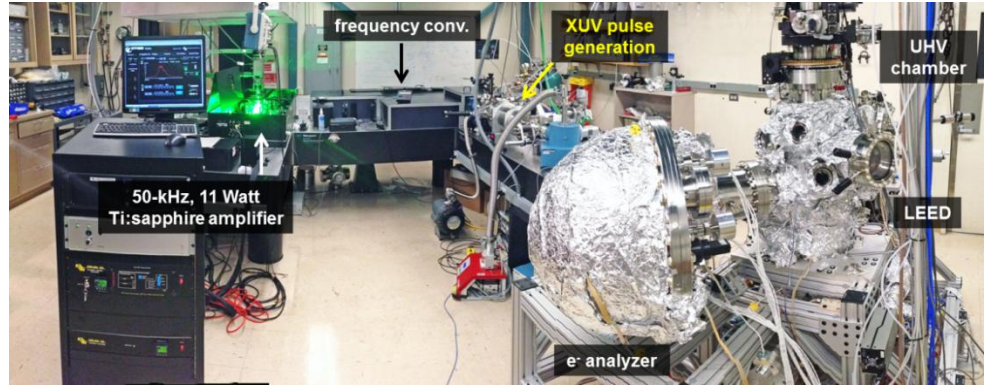


Fig. 2. New ultrafast ARPES laboratory, employing extreme ultraviolet (XUV) fs pulses.

the electronic band structure dynamics of complex materials across momentum space, with high energy and time resolution. For this, we have constructed a new laboratory for extreme ultraviolet (XUV) ultrafast ARPES, based on several key requirements: (i) an XUV source beyond ≈ 10 eV for access to the full Brillouin zone, (ii) high repetition rate, to avoid space charge broadening while maintaining high flux ($>10^{11}$ ph/s), (iii) a modern UHV chamber and photoelectron spectrometer, and (iv) sufficient laser pulse energy to generate tunable pump pulses in the mid-IR for resonant electronic or vibrational excitation. Our setup (Fig. 2) combines all these advantages. A state-of-the-art UHV chamber enables photoelectron spectroscopy, surface characterization, and sample preparation, along with tight focusing of pump pulses. Importantly, we have developed a powerful source of bright XUV harmonics at 50-kHz repetition rate. Half of the 11 W output of a cryo-cooled Ti:sapphire amplifier (KMLabs Wyvern) is frequency doubled in BBO and tightly focused into Kr gas. This results in near absorption-limited high-harmonic generation at 22.3 eV with very high efficiency ($\approx 5 \cdot 10^{-5}$) yielding $\approx 3 \cdot 10^{13}$ photons/s at the source. The UV driving pulses also ensure large spectral separation of the harmonics, enabling direct isolation of the 22.3 eV harmonic with metal filters. This high rep-rate source of bright femtosecond XUV pulses is ideally suited for ultrafast ARPES studies. During the startup, we also collaborated with the Quantum Materials program, using an oscillator-based 6-eV ARPES setup to explore nodal quasiparticle dynamics in cuprates.⁷

We plan to apply the new XUV ultrafast ARPES capability to a range of key experiments. First, we will study electronic band structure dynamics during photo-induced phase transitions in colossal magneto-resistance manganites and other transition metal oxides, for novel insight into metastable phases and the interactions underlying the correlated ground state. In LSMO, the linear Fermi surface topology is believed to result from stripe/CDW nesting – portending dramatic ultrafast renormalization of the electronic structure upon photo-induced melting of the ordered phase. Moreover, we can investigate electron-phonon coupling in the time-domain by studying transient modulation of the electronic band structure after excitation of coherent phonons. In high- T_C cuprates such as Bi-2212, we will employ XUV ultrafast ARPES to investigate the dynamics throughout all of momentum space to clarify the relationship between pseudogap and superconducting correlations. Ultrafast ARPES will provide novel insight into the dynamics of complex materials by resolving both non-equilibrium quasiparticles and the time evolution of the occupied electronic states directly in momentum and energy space.

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Nanoscale Dynamical Heterogeneity in Complex Magnetic Materials

Stephen D. Kevan, Principal Investigator

Professor of Physics
University of Oregon
Eugene, OR. 97403-1274
Office: 541-346-4742
FAX: 541-346-3422
e-mail: kevan@uoregon.edu

Award Number DE-SC0006905

A variety of nanostructured systems exhibit thermal- or field-driven intermittent behaviors that are a manifestation of nanoscale dynamical heterogeneity in a macroscopically homogeneous material. Ensemble dynamics of such systems often display complex and technologically important behaviors, e.g., two level tunneling centers impact a host of low temperature thermodynamic properties in most glasses, jamming in colloidal systems leads to stretched exponential kinetics and viscoelasticity, and superparamagnetic fluctuations in a granular magnetic film limit the density with which information can be stored. Thermally driven intermittency limits the utility of a nanoscale device or nanostructured material to store, process, or transmit information, to sense the environment, to harvest and convert energy, and a host of other applications. The desire to control and to use nano-objects and nanostructured materials will always compete with intermittency. The underlying hypothesis of our proposed research is that if we can probe, understand, and possibly control nanoscale intermittency, then we should be able to exercise some control over emergent material properties.

We apply resonant, coherent soft x-ray scattering techniques to probe nanoscale spatiotemporal correlations in magnetic films and transition metal oxides. Microscopic interactions in these systems support spontaneous domain structures on the scale of a few to a few hundred nanometers that produce unusual and useful macroscopic properties and offer excellent models to probe complex, intermittent behaviors. Operating at soft x-ray wavelength in resonance with various absorption edges, we can probe nanoscale orbital, magnetic, and charge correlations with simultaneous elemental selectivity.

Specific activities in the to be pursued in the coming year include

- 1) We will continue to probe magnetic domain rotational symmetries and to explore their relationship to field-driven Barkhausen cascades. An important experimental goal is to achieve the requisite sensitivity and stability to detect individual cascades with x-ray resonant magnetic scattering. We are also developing tools to measure statistical properties of the hidden domain symmetries.
- 2) We will expand recent studies of the thermally driven spin-reorientation transition in magnetic heterostructures, searching for magnetic analogs of liquid crystal phases and for the thermally driven analog of Barkhausen cascades. Recent improvements in the stability of our apparatus will allow us to probe a larger spatiotemporal dynamic range of domain wall fluctuations.

- 3) We will continue our effort to image orbital and spin domains in complex oxide materials using diffractive imaging in a Bragg geometry. This effort to date has focused on $\text{Pr}_x\text{Ca}_{1-x}\text{MnO}_3$ using fairly weak real-space source constraints. Recently, Stuart Wilkins at BNL has patterned oxides materials with an eye toward producing a stronger source constraint, and we have initiated a collaboration to bring his samples to BL12.0..2 at the ALS.

Our group collaborates closely with the Advanced Light Source at Lawrence Berkeley National Laboratory to lead ongoing improvements in coherent soft x-ray capabilities at the facility. New beamline instrumentation and experimental protocols as well as recent increases in source brightness provide major benefits to our program as well as to those of an expanding user community. We also are participating in detector projects that will be key features of future soft x-ray photon correlation spectroscopy experiments at the ALS and elsewhere. Our program will move to the COSMIC beamline at the ALS when it is commissioned in about 2 years, and we are actively involved in planning that new high priority project at the facility.

Ultra-broadband scalable THz generation, imaging and control

Task Leader: Ki-Yong Kim

*Institute for Research in Electronics and Applied Physics, University of Maryland, College Park,
MD 20742*

kykim@umd.edu

Future Plans

Measurement and imaging of ultrafast time-varying electric fields

We will study EFISH (electric field induced second harmonic) generation in femtosecond filamentation and potential application for broadband two-dimensional (2D) THz polarization characterization. We have studied the polarization of second harmonic produced in filamentation under a biased electric field. We find the second harmonic field produced along the laser polarization direction is linearly proportional to the biased field component along that direction. By sending laser probes with two orthogonal directions, we can fully characterize the magnitude and direction of the biased field. We will use this scheme to measure broadband THz waveforms with a full characterization of THz polarization. In addition, we will apply this scheme to map out ultrafast electric fields in laser-produced plasma filaments. This will show how the ultrafast electric fields evolve in time and space.

Full quantum calculation of two-color photoionization

We will develop a full quantum calculation of plasma currents in two-color photoionization and will compare it with our classical calculation. This will address the role of multiphoton and tunneling ionization in phase-sensitive plasma current generation, providing a better understanding of THz generation in two-color photoionization

Simultaneous THz/x-ray generation for spectroscopy

Lastly, we will develop a source for ultrafast THz/x-ray pump-probe spectroscopy. To this end, we will use two-color photoionization in a gas jet for simultaneous THz and high harmonic generation (HHG). Our recently developed high-power (0.5 TW), high-average-power (15 W) laser system is capable of providing 30 fs, 15 mJ, 800 nm pulses at a 1 kHz repetition rate and will be used for simultaneous THz and x-ray generation. Currently the laser can provide $>1 \mu\text{J}$, $>1 \text{ MV/m}$ THz pulses at 1 kHz and in principle can produce synchronous x-ray pulses in two-color laser fields by HHG. The emitted THz and x-ray pulses will be split by a metallic mirror with a hole and combined with an appropriate time delay-line. The excitation and probe energy level will be selected by choosing appropriate THz and x-ray filters. In addition, a cluster gas jet will be used and tested for efficient THz and x-ray generation. The source can be potentially used for table-top THz-pump and x-ray probe spectroscopy.

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- “Two-dimensional plasma current and optimized terahertz generation in two-color photoionization,”
T. I. Oh, Y. S. You, and K. Y. Kim,

Optics Express **20**, 19778 (2012).

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- “Measurement of ultrafast plasma currents in two-color laser-produced plasma,”
Y. You, T. I. Oh, and K. Y. Kim,
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- “Broadband THz radiation from two-color laser-produced plasma,”
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- “Two-dimensional photocurrent control in air plasma for optimized terahertz generation,”
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- “Scalable terahertz generation in two-color laser filamentation,”
Y. S. You, T. I. Oh, and K. Y. Kim,
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- “Modeling propagation effects on terahertz generation from ionizing two color laser pulses,”
L. Johnson, T. Antonsen, J. Palastro, and K. Y. Kim,
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Resonant soft x-ray scattering from molecular anisotropy

J. B. Kortright

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The first polarization-dependent resonant scattering study at the carbon K edge in an optically anisotropic polymer film demonstrated the ability to quantitatively analyze s - and p -polarized specular reflectivity $R(q)$ [1]. In the system chosen for study, rigid liquid crystalline side chains were known to orient with their long axis in the film plane near the surface, and modeling found that this in-plane orientation was independent of depth for 9 - 51 nm thick films exhibiting twist domains having different in-plane orientations. Pronounced anisotropy was observed near π^* lines of different side chain functional groups, and quantitative modeling of R_s and R_p yielded resonant optical constants δ and β along and perpendicular to the side chain axis that provide a more accurate description of the optical anisotropy than values obtained using absorption methods.

This study has several implications for further application of polarization-dependent resonant scattering in organic systems. One is that it should be possible to depth-resolve possible changes in laterally averaged orientation of specific polymer functional groups. Another is that orientational heterogeneity of optically anisotropic polymer domains such as in a polycrystalline film will yield resonant scattering, as recently observed in polycrystalline pentacene films [2]. These polarization dependent resonant scattering effects have analogs in visible light scattering from liquid crystals and polymers [3-7], where they are described in terms of form birefringence in which relatively large regions with uniform anisotropy scatter with different amplitude than adjacent, differently oriented regions. From a fundamental optical perspective, scattering at the carbon K edge is unique in combining strong resonant anisotropy in molecular polarizability of individual functional groups with wavelengths approaching (but not quite reaching) the dimensions between these structural units.

We are exploring the sensitivity of resonant scattering at these short length scales using atactic (disordered) polystyrene (PS) in which possible orientational correlations between phenyl groups at such short length scales are difficult to study experimentally. In PS films we are measuring carbon edge resonant scattering spectra at the highest q values accessible, corresponding to correlation lengths of only 3 nm. We find weak resonant elastic scattering (inconsistent with fluorescence) whose energy spectra are very different from those measured at low q values and whose q dependence is essentially flat. The scattering spectra depend somewhat the orientation of incident linear polarization, and show differences between as-cast and annealed films. In the same samples we are measuring forward scattered (transmitted) spectra across the carbon edge using a linear polarizer set parallel and crossed with respect to the incident linear polarization, and observe a weak resonant depolarization effect. These observations are being interpreted with the aid of theoretical formalisms developed in the context of dynamic and depolarized light

scattering from molecular systems [3,4], which suggest that this high-q diffuse scattering results from a combination of resonant orientational and both resonant and non-resonant density fluctuations of the different molecular entities within the polymer. The weak depolarization in the transmitted beam evidently results from resonant scattering out of the forward direction by these fluctuations. Thus it appears that resonant scattering can be beneficially extended from length scales of tens of nanometers and up, corresponding to phase-separated or polycrystalline grain structure, to the shortest accessible length scales where information about orientational correlations and chain conformation within polymers is of interest in many systems.

Other directions of our work with resonant scattering in soft condensed matter include application to polymers containing ionic species in the context of polymer electrolytes as part of the Soft Matter Electron Microscopy program at LBNL headed by N. Balsara [8], and application to study ordering of ionic liquids in confined geometries as part of a collaborative project between the Berkeley EFRC for Gas Separations Relevant to Clean Energy Applications and the National Energy Technology Laboratory. Interpretation of resonant scattering data in these studies will benefit from understanding gained in the fundamental study on randomly oriented anisotropies mentioned here.

We continue to apply resonant soft x-ray scattering to hard condensed matter, primarily magnetic materials, in the Magnetic Materials program at LBNL headed by P. Fischer. Here we have been focusing on developing new algorithms to self-consistently model the energy and q dependence of resonant scattering data [9,10], and applications of standing-wave enhanced photoemission to depth-resolve electronic structure across buried interfaces with C. Fadley [11-13].

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Publications from DOE sponsored research (2011 – 2012)

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Ultrafast phase transitions in materials probed by x-ray scattering and x-ray spectroscopy

Aaron M. Lindenberg, Stanford/SLAC

476 Lomita Mall, Stanford University
Stanford, CA 94305
aaronl@stanford.edu

Future research scope. This research program is a subtask that is part of the SIMES Field Work Proposal "Time-resolved soft x-ray materials science research at the LCLS and ALS." The general scope of this research program is to elucidate the origins of phase transitions and non-equilibrium behavior in strongly correlated electron systems, with the goal of understanding and controlling these phenomena on atomic length-scales and on femtosecond time-scales. Within this subtask the focus is divided between two main themes:

1) Studies of the femtosecond structural and electronic dynamics of ferroelectric and multiferroic thin film oxides. We are interested in disentangling the strongly correlated and coupled degrees of freedom exhibited by these materials, and exploring means for all-optically controlling them through direct interaction with relevant and specific degrees of freedom. Terahertz fields resonant with vibrational degrees of freedom and with field amplitudes of sufficient strength to drive well-defined atomic-scale displacements are used to directly modulate the ferroelectric polarization and explore the time-scales and atomic-scale rearrangements associated with these processes. Current studies indicate large-scale modulations of the ferroelectric polarization under THz excitation, and new capabilities for elucidating the coupled electronic and structural processes associated with the photovoltaic response of these materials.

2) Studies of the dynamics of solid-solid phase transitions in nanoscale materials under extremes of temperature, pressures, electric fields and electronic excitation. We are currently studying the dynamics of pressure-driven phase changes in semiconducting nanocrystalline materials, using femtosecond x-ray scattering to probe the atomic-scale pathways and structural intermediates associated with the emergence of new phases and their dependence on nanoscale size and shape. These studies serve to elucidate a fundamental but unresolved question concerning how the dynamics of nanoscale materials differ from the bulk, and explore opportunities for synthesizing new structural phases of matter. Other examples of related future work include: a) dynamics of phase-change materials in which x-rays can provide an atomic-scale snapshot of the microscopic mechanisms underlying the transformations and reverse transformations between crystalline and amorphous phases, and b) superionic materials, in which the first steps in ionic transport processes can be understood through direct measurements of the associated structural phase transitions.

DOE-sponsored Publications (2011-2012)

1. "Ultrafast photovoltaic response in ferroelectric nanolayers", Dan Daranciang,

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Real-Time X-ray Studies of Surface and Thin Film Processes

DE-FG02-03ER46037

Karl Ludwig

Dept. of Physics; Boston University; Boston, MA 02215

ludwig@bu.edu; (617) 353-9346

Research Scope:

Surface growth processes are at the core of many of our most widely used technologies today and increasing interest in the “digital design” of future materials for enhanced functionality can only come to fruition if we understand and learn how to control materials synthesis at surfaces and interfaces. The development of increasingly powerful x-ray sources and the new techniques they enable will have a major impact on our understanding and ability to control growth. To develop these opportunities we are utilizing a dedicated facility for real-time studies of surface and thin film processes at National Synchrotron Light Source (NSLS) beamline X21. We have been using the facility both to investigate fundamental growth issues in model systems and to examine kinetics in the technologically important cases of group III-nitride growth by molecular beam epitaxy and growth of dielectric and catalytic films by atomic layer deposition. In addition, using the high brilliance of the Advanced Photon Source (APS) and Linac Coherent Light Source (LCLS), we have begun laying the groundwork for coherent scattering studies that ultimately promise to elucidate the *dynamics*, rather than just the spatially-average kinetics, of surface growth processes.

Future Directions:

Coherent GISAXS studies now offer major new opportunities for the study of dynamical processes on growth surface. We plan to develop these in two directions. First, coherent scattering is crucial to better understanding dynamics of the important process of kinetic roughening. In later stages of film growth, typically a steady-state spectrum of surface fluctuations develops so that the conventional x-ray scattering pattern stops evolving. However the underlying dynamic processes of adsorption and relaxation continue, and it is these which determine the final film morphology on the nanometer and micron length scales. It is this underlying dynamics that can be accessed by coherent GISAXS speckle studies.

Second, with our experience identifying and quantifying dynamic discontinuities, we plan to use coherent GISAXS to investigate the dynamics of island formation, growth and coalescence. We expect that the coherent x-ray scattering will exhibit a smooth evolution until suddenly two or more islands impinge and rapidly coalesce. This sudden local rearrangement will cause a rapid change, or discontinuity, in the coherent speckle pattern, directly indicating the heterogeneous nature of the dynamics and revealing its fundamental time scales. To ensure that the discontinuities are well separated, we will use relatively high growth temperatures, giving high surface diffusivities so that islands/droplets are spaced relatively far apart.

Our experiments will utilize primarily APS beamline 8-ID and, when it becomes available, the NSLS-II Coherent Hard X-ray (CHX) beamline. The LCLS already has a time-averaged transverse coherent flux that is at least two orders of magnitude higher than that of current and planned synchrotrons. We also plan to perform experiments on the XCS station at LCLS to investigate dynamics on growth surfaces and have already submitted a proposal for LCLS Run 7. We well understand that the very limited beamtime available for any one research program at LCLS will limit the rate of progress. However, coherent GISAXS experiments are in some ways particularly well suited for the LCLS source characteristics at this point in its history. Tradeoff between scattered intensity and beam power density on the sample can be made by varying the incident angle near the angle of total external reflection and recent progress in implementing x-ray self-seeding will significantly increase longitudinal coherence. Our initial experiments would operate in

sequential mode, and thus not require split-and-delay speckle contrast techniques which are still being developed. While these first studies will explore island growth and coarsening dynamics and kinetic roughening dynamics on the time scale of seconds and longer, we also see them as a necessary first step toward the eventual exploration of faster surface growth dynamics using the pulsed nature of the source.

Publications 2011-2012:

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Phase transition dynamics in energy materials at extreme conditions

Wendy L. Mao

450 Serra Mall

Braun Bldg #320, MC2115

Stanford University

Stanford, CA 94305-2115

wmao@stanford.edu

One of the fundamental challenges in condensed matter physics is to understand the pathways that underlie structural and electronic phase transitions, e. g., how the atoms rearrange and, and how the electronic bonding and orbitals evolve during phase transitions. Ultrafast optical and X-ray pulses are powerful tools to study various dynamic processes with femtosecond and atomic-scale resolution. Furthermore, ultrafast dynamics measurements not only allow us to observe the existence of novel transient metastable states, but also could identify the relative roles that different degrees of freedom (charge, lattice, orbital and spin) play in strongly correlated materials since they typically have different characteristic time scales, leading to the further understanding of fundamental mechanisms of phase transitions and the formation of emergent states. We plan to expand our activities and start conducting time-resolved high pressure XRD on systems with structural transitions that can be probed on sub-ns timescales (e.g. phase change memory materials like GST), and also work to develop THz experiments in a diamond anvil cell (DAC). Initial tests for these experiments have utilized the considerable in-house laser facilities at SLAC to check feasibility and the required laser fluencies in preparation for high pressure LCLS experiments. We are also performing high-pressure ultrafast pump-probe differential reflectivity measurements where the generation and decay of coherent optical phonons are able to elucidate the mechanism of photon-driven insulator-metal transition in VO₂, with the hope of helping understand phase transition physics in other strongly correlated systems. To complement our dynamic studies we are also involved in activities looking at static high pressure behavior both to discover and understand new phases and phenomena and as complement for dynamic experiments and as a basis for understanding the nonequilibrium phases. We will continue to look at strongly correlated mixed valence compounds and have initiated a new project to look at high T_c superconductors like Hg cuprates. We will also continue to work closely with theory groups to interpret our high pressure synchrotron x-ray results.

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Advancing High-Pressure Research at HPCAT

P.I.: Ho-kwang (David) Mao, Russell J. Hemley, & Guoyin Shen

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington DC, 20015-1305

mao@gl.ciw.edu

The High Pressure Collaborative Access Team (HPCAT) beamline facility, located at Sector 16 of the Advanced Photon Source, is dedicated for high-pressure synchrotron x-radiation science and is supported by the X-Ray Scattering Program of BES. HPCAT has pioneered an arsenal of powerful *in-situ* x-ray diffraction and spectroscopy tools fully integrated with hydrostatic or uniaxial compression and simultaneous laser heating or cryogenic cooling, and has enabled high-pressure investigations of structural, vibrational, electronic, and magnetic properties that were impossible only a decade ago. The HPCAT program has led to myriad scientific breakthroughs in high-pressure physics, chemistry, materials, and Earth and planetary sciences as shown by the quality and quantity of its users community (Fig. 1) and publications (Fig. 2).

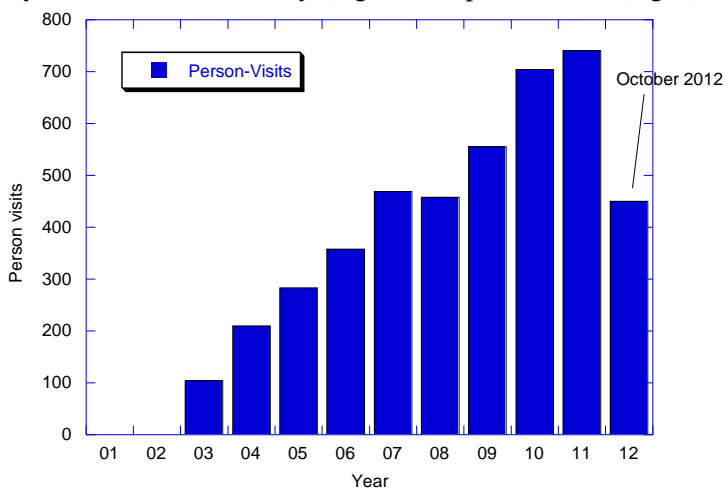


Fig. 1. The number of HPCAT user-visit shows a steady increase.

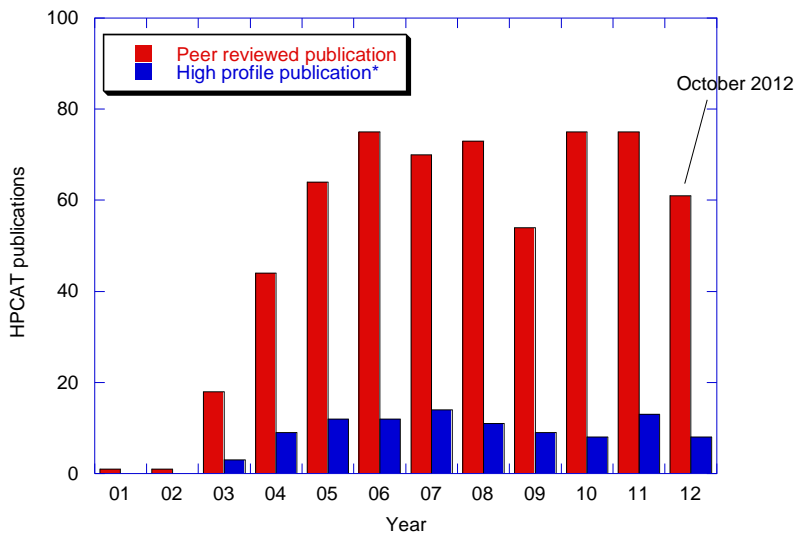


Fig. 2. The list of citations to publications of DOE sponsored research that have appeared in 2011-2012 can be found at <http://hpcat.gl.carnegiescience.edu/publications/hpcat>. HPCAT is a

world leader in high-pressure science and technology, as shown by its total number of publications (red bars), and publications with impact factors \geq PRL (blue bars).

Important progresses during 2011-2012

- We have successfully installed canted undulators in the fall of 2011. The immediate benefits from the canted operation include higher on-sample flux, flexibility in energy selection for specific experiments, and completely independent operations of each canted branch. The canted operation has enhanced our facility, allows for new capabilities to be developed, and increased the user activities.
- By using x-ray focusing optics (x-ray capillary), we have successfully minimized the unwanted signals from walls of high pressure device in high pressure inelastic x-ray scattering measurements. The depth resolution has been improved by an order of magnitude. This development will open a door for measuring the band-gap of hydrogen as a function of pressure, a grand-challenge in condensed matter physics.
- The in-line laser heating system has been significantly improved for studying matters under extreme conditions in a time resolved manner. Pulsed heating lasers are synchronized with synchrotron source, which allows for studying high pressure melting, phase transition, and behavior of materials under medium-strain dynamic compression.
- We have developed x-ray techniques for a comprehensive approach to study liquids at high pressures. Besides the traditional liquid structure determination, we have also developed x-ray radiography for liquid density and viscosity determination. Combining with the ultrasonic measurements, the sound velocities can be in situ measured together with structure and other macroscopic properties (density, viscosity).

Future plans

- In the coming year, we plan to upgrade the focusing optics for the x-ray spectroscopy beamline to enable Mbar x-ray spectroscopy experiments.
- We will continue to improve the depth-resolution in high pressure x-ray spectroscopy, a bottle neck in this area. In addition, we will use either multiple elements or large numeric aperture optics for increasing the solid angle in signal collection in x-ray emission and fluorescence spectroscopy.
- In high pressure x-ray diffraction, we have newly purchased a Pilatus detector which allows us to take meaningful x-ray diffraction at micro-sec and mili-sec time intervals. We plan to start several projects including (1) reaching the highest pressure by fast ramping techniques, (2) monitoring phase transitions (e.g., melting), (3) studying deformation mechanism under controlled strain rate.
- We have started the development of a high pressure white Laue technique in the past year. We will continue the development for studying materials defects and stress tensor. The promise of this technique lies in its fast measurement, thus allowing for time-resolved studies.
- We plan to install a high energy monochromator for the bending-magnet station 16-BMB operation. The energy range is 40-100 keV.

Dynamics of block copolymer nanocomposites

Simon Mochrie

Department of Physics, Sloane Physics Laboratory 68C, Yale University, New Haven, CT 06511

simon.mochrie@yale.edu

The overall objective of this project is to establish and investigate the basic physical principles underlying the structures and dynamics within block-copolymers and block copolymer-nanoparticle nanocomposites. The new understanding achieved will facilitate the design and creation of robust and stable nanocomposites with desirable properties. In addition, we will provide new insight into the dynamics of neat block copolymer materials. To carry out this program, we will rely on synchrotron-based small-angle x-ray scattering (SAXS), and transmission electron microscopy (TEM), to determine the nanocomposite structures. To investigate the dynamics of these systems, we will employ x-ray photon correlation spectroscopy (XPCS) experiments at beamline 8-ID-I at the Advanced Photon Source at Argonne National Laboratory and at the LCLS at the Stanford Linear Accelerator Center. The results achieved will guide and facilitate future efforts to create and process designer nanocomposites for specific applications, for example, in such energy-related areas as batteries and solar cells.

(1) Building on methods that we have established and refined for reliably creating CdS nanoparticles, decorated with PS-*b*-P2VP, we will create a library of model nanoparticles, that are decorated with PS-*b*-P2VP copolymers of different molecular weights and relative volume fractions. In this way we will be able to pick the size and composition of the decoration to achieve the desired material goal.

(2) Building on methods that we have established for preparing polymer blends, *etc.*, we will introduce the decorated nanoparticles created in (1) into block copolymer melts, blends and solutions, so as to create dispersions of these nanoparticles, that are macroscopically homogeneous, but which, on the nanoscale, are templated within the copolymer microstructure.

(3) In order to properly understand the parent copolymer structures and dynamics, we will carry out studies of the phase behavior and equilibrium dynamics of block copolymer blends involving blends of PS-*b*-P2VP and PS-*b*-PI. This system provides a rich variety of structures, whose dynamics we will seek to understand and characterize using x-ray photon correlation spectroscopy (XPCS) in preparation for using these materials to template decorated nanoparticles. Our recent experiments have revealed that XPCS studies of the dynamics of block copolymer melts and blends at the Advanced Photon Source are extremely challenging, because the signal rates are low. Therefore, we will carry out these experiments at the Linear Coherent Light Source (LCLS) at SLAC, by measuring the pulse-to-pulse correlations.

(4) Using examples of the materials created in (2) we will study the structure and dynamics of decorated nanoparticles in block-copolymer confined geometries, including in zero, one, and two-dimensional spaces. For nanocomposites built with decorated

nanoparticles with a size that is smaller than the characteristic size of the block copolymer morphology, and with a surface treatment that yields a strong preference for the interior of one of the blocks, we hypothesize that for low and moderate concentrations of nanoparticles, the block copolymer morphology will effectively constitute a template that, together with the overall concentration of nanoparticles, will define the nanoparticles' arrangement. In this fashion, it will be possible to study the temperature-dependent structure and dynamics of zero, one, and two dimensional systems of nanoparticles, *etc.*

(5) Building on the studies described in (4), we will exploit other examples of the decorated nanoparticles described in (1) and of the materials created in (2) to elucidate how the presence of these decorated nanoparticles feeds back onto the block-copolymer morphology. In particular, we will determine how the temperature-dependent morphology of a nanocomposite changes from that of the parent block copolymer morphology with the progressive addition of an increasing concentration of decorated nanoparticles. We hypothesize that in the case of nanocomposites built from PS-b-P2VP-decorated nanoparticles with a size that approaches or exceeds the characteristic size of the host PS-b-PI block copolymer morphology, the addition of such decorated nanoparticles will eventually give rise to novel nanocomposite morphologies, different from that of the host PS-b-PI copolymer system, but related to that of the PS-b-PI/PS-b-P2VP copolymer blend. We will investigate this hypothesis, and the resultant novel structures via SAXS, while their dynamics will be studied via XPCS.

Title: Ultrafast Magnetization Dynamics and Spin Transport Probed by Coherent Soft X-Rays

Principal Investigators:

Margaret Murnane and Henry C. Kapteyn, JILA and Department of Physics, University of Colorado, Boulder CO 80309-0440; Ph. (303) 210-0396; FAX (303) 492-5235; E-mail: murnane@jila.colorado.edu

Thomas J. Silva, Electromagnetics Division (m/s 818.03), NIST, 325 Broadway, Boulder, CO 80305, Ph. (303) 497-7826; FAX (303) 497-7364; E-mail: silva@boulder.nist.gov

Planned Research Scope:

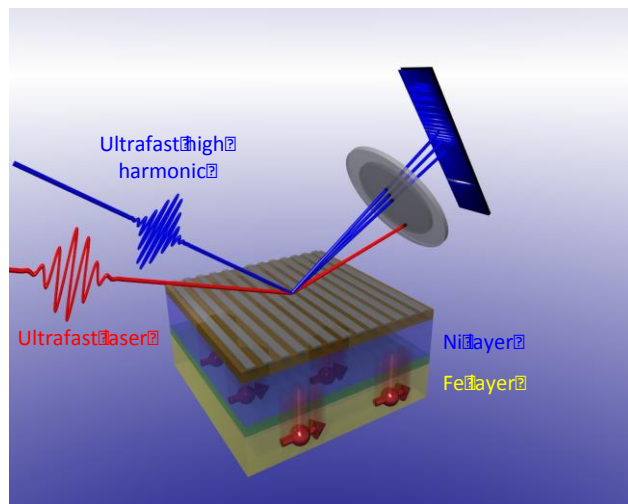
Magnetism has been the subject of scientific inquiry for more than 2000 years; however, it is still an incompletely understood phenomenon. The fundamental length and time scales for magnetic phenomena are nanometers (nm) and femtoseconds (fs). Furthermore, a detailed understanding of nanoscale magnetism has become much more critical in the 21st century with dramatic recent advances in magnetic data storage applications, as bits on a hard disk are already packed at scales of about 20nm. However, a comprehensive microscopic model of how spins, electrons, photons and phonons interact does not yet exist. This understanding is fundamentally constrained in large part by our current very-limited ability to directly observe magnetism on all relevant time and length scales. Further advances in storage capacity and energy efficiency depend critically on a detailed understanding of the limits of magnetic switching speed and density.

Until recently, measuring magnetic material dynamics used either ultrafast lasers and visible-wavelength light, or x-rays from large-scale electron storage facilities, such as synchrotrons and free electron lasers. Our recent work has shown that the fastest dynamics in magnetic materials can be captured using extreme ultraviolet (XUV) harmonics – with elemental resolution and at multiple atomic sites simultaneously. We first probed how fast the magnetic state can be destroyed in an Fe-Ni alloy, with elemental sensitivity for the first time [1]. We then addressed an important question: how do spins couple to the lattice such that the angular momentum is globally conserved during the demagnetization process. After exciting an Fe-Ni alloy with a fs laser pulse, the spin sublattices randomize on \ll ps timescales. Surprisingly, even in a strongly coupled ferromagnetic alloy, the demagnetization of Ni lags that of Fe by 10 fs [2]. Moreover, we were able to increase this time lag to 80 fs by diluting the alloy with Cu, which further reduced the exchange energy. After a 10 – 80fs time lag, which is characteristic of the exchange interaction energy, the Ni sublattice then demagnetizes at the same rate as Fe. This important fundamental topic has not been addressed either in theory or experiment to-date, and reveals both how the exchange interaction can mediate ultrafast magnetic dynamics in multispecies alloys, and how the intrinsic demagnetization process is indeed site-specific e.g. spins on one sublattice can interact more strongly with the optical field than spins on the other sublattice.

In our latest work, we uncovered evidence of so-called “superdiffusive”, laser-generated spin-currents in magnetic multilayers that are generated in the course of the laser-driven ultrafast demagnetization process [3]. We excited a magnetic multilayer (Fe/Ru/Ni) with a fs laser pulse, and separately, yet simultaneously, probed the magnetization response of the Ni and Fe layers. We found that optically induced demagnetization of the top Ni layer causes the buried Fe layer to undergo a surprising transient *enhancement* of the magnetization of up to 20%, when the two layers are aligned parallel with an applied magnetic field. This is due to an intense, pure majority spin-current that propagates into the buried Fe layer at ballistic velocities. Our findings shed light on a rich variety of new physics at play in femtosecond magnetization dynamics of technologically important magnetic alloys and multilayer systems.

Future Plans: We will probe and image ultrafast coupled charge-spin-phonon transport and dynamics in magnetic materials using the new tabletop spectroscopic and imaging techniques we have developed. We will further explore the excitation, detection, and imaging of laser-induced spin-current dynamics in layered magnetic/non-magnetic metallic structures. For example, we will study the propagation of superdiffusive spin currents in lateral spin-valve structures used for

spintronics applications, where we can correlate the optical detection of longitudinal spin current absorption (*i.e.* magnetization enhancement) with time-resolved, electrical detection of spin currents. We will also explore the nature of exchange interactions in other alloys. Finally, we will probe site-specific spin dynamics in complex materials at the $L_{2,3}$ edges at multiple atomic sites simultaneously using a new capability to generate bright beams in the soft x-ray region.



Caption – Extreme spin-currents in magnetic multilayers driven by ultrafast light pulses. After transient excitation of the electrons in the top Ni layer with a fs laser pulse, an extremely intense, pure majority spin-current propagates into the buried Fe layer at ballistic velocities. This giant, longitudinal spin-current is sufficiently large to transiently enhance the Fe magnetization by 20%. These new spin-dynamics in magnetic multilayers were unveiled for the first time by using high harmonic soft x-rays to capture magnetization dynamics in the Ni and Fe layers simultaneously with element-selectively at the $3p$ ($M_{2,3}$) absorption edges of Ni (66 eV) and Fe (52 eV), respectively. This new capability is leading to the discovery of many new physical processes that underpin spin-dynamics at the shortest time- and length-scales [3].

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X-ray Spectroscopy and Scattering Studies of Alloy Fuel Cell Catalysts

Anders Nilsson (Primary Contact), Michael Toney, Daniel Friebe and Hirohito Ogasawara
SIMES, SSRL and SUNCAT
SLAC National Accelerator Laboratory
Menlo Park, CA 94025
Phone: (650) 926-2233, Fax: (650) 926-4100, nilsson@slac.stanford.edu

The scientific goal of this research program is to develop new and use existing synchrotron radiation based x-ray diffraction and spectroscopy methods to address the material properties that control reactivity and stability of solid catalysts during electrocatalysis for energy utilization. The main objective is to fully understand reaction mechanisms and determine which parameters control the reactivity and stability of a catalyst surface during real operating conditions at the solid-liquid and solid-gas interfaces. We probe the electronic aspect of the chemical bond of various rate-determining intermediates under operando conditions. We determine what is adsorbed on the surface and the composition and structure of the catalyst itself under reaction conditions. One of the major challenges in catalysis is to understand the full reaction mechanisms where the most abundant surface intermediates are not always essential for the reaction rate since the important species may be formed only transiently with an ultra-short residence time. From interplay between theory and experiment there is the potential to derive a complete understanding of catalytic processes that eventually feeds into the design of new catalytic materials.

SLAC has a special combination of light source characteristics and new instruments that provides unique capabilities for *in situ* spectroscopy. The 3 GeV storage ring energy at SSRL brings excellent properties for the generation of intense both soft and hard x-rays and with the variation of the electron beam energy in the SLAC linear accelerator both soft and hard x-rays can be generated at LCLS. The combination of the 3 pillars of soft x-rays, hard x-rays, and ultrafast capabilities at one location provides for strong complementarity of various x-ray methods. Below is a summary of the various unique capabilities that will be used for studies in the 3 above indicated areas. Although the catalyst material, nature of the interface and reactants will be different, all experiments will be based on the same physical spectroscopic and scattering mechanisms.

- Through energy resolving the fluorescence detection in hard x-ray absorption spectroscopy (HERFD) with an x-ray spectrometer, the limitation given by the lifetime broadening for high Z-elements can be circumvented and more spectral details can be resolved. We have developed this method for solid-liquid interfaces under the current FWP with a focus on Pt L-edge spectroscopy to detect adsorbed species and Pt oxide formation. This technique will be further developed to other edges than Pt in the proposed program such Pd, Y and Ag .
- Using a novel design for an ambient pressure XPS system with a special in-situ PEMFC based electrochemical cell, we have demonstrated that it is possible to probe species on the surface during fuel cell operational conditions. This instrument will be further developed to also probe oxidation of hydrocarbons and alcohols in operating PEMFC devices and to probe solid-gas interfaces in solid-oxide fuel cells.
- We have in the past been most successful to use x-ray diffraction to determine the structure and in particular the lattice parameter of dealloyed catalysts during in-situ conditions. This technique will be further utilized for probing strain that often controls the catalytic activity.
- The ability to project the electronic structure in an atom-specific way of surface species through x-ray emission spectroscopy will together with theory provide for electronic structure design of catalysts. A new high transmission soft x-ray spectrometer system dedicated for

surface studies has open-up for a range of systems that previously have been most challenging. This will also be further developed for *in-operando* conditions to probe solid-liquid interfaces for both single-crystal surfaces and nanoparticles.

- A chemist's dream has been to follow chemical reactions on surfaces in real time. This can be accomplished with the new capabilities at LCLS. The above x-ray spectrometer system can also be used at LCLS providing the ability to probe the dynamics of the electronic structure changes in connection to bond making and breaking during catalytic reactions. We propose to use this approach to probe ultrafast process of elementary reaction steps that are essential in many electrocatalytic processes.

In PEMFC, regardless of which fuel is oxidized at the anode, a highly active and, at the same time, durable cathode catalyst for the ORR is necessary. Previous research has focused mostly on improving the ORR activity of Pt in various alloys, thereby taking advantage of ligand and strain effects on the adsorption energy of O/OH. Unfortunately, the most active bimetallic catalysts degrade over time, mostly due to dissolution of the less noble component. Moreover, even pure Pt nanoparticles undergo a significant loss of activity due to oxide formation, dissolution, Ostwald ripening and degradation of the carbon support. The team has previously demonstrated the ability of HERFD XAS to distinguish various Pt oxides and even chemisorbed O/OH on Pt-based model catalysts. Using two different model systems, Pt/Rh(111) and Pt/Au(111), a proof-of-principle was established that bimetallic interactions can drastically alter the competing pathways towards Pt oxide formation or Pt dissolution.

We plan to use in situ HERFD XAS to study Pt oxide formation in several well-defined bimetallic model catalysts based on single-crystals. This effort will be supported by DFT calculations in collaboration with SUNCAT. Our goal is to identify a "descriptor" that can be used to predict catalyst stability, and to determine if, or to which extent, catalyst stability and ORR activity could be limiting each other. One particularly promising ORR catalyst appears to be the Pt–Y system which is stable against dissolution while exhibiting up to 5 times higher ORR activity than pure Pt. Well-defined Pt–Y catalysts – size-selected clusters as well as single-crystal surface alloys – are prepared by collaborators at DTU (Chorkendorff group). We will employ in situ HERFD XAS and EXAFS at the Pt L_3 and Y K edges on size-selected clusters and single-crystals, as well as in situ grazing incidence x-ray diffraction (GIXD) on single-crystal samples to study the effect of electronic and geometric structure on catalyst stability and ORR activity.

The O chemisorption energy of Pt can be tuned via ligand and strain effects over a range of ~1 eV (e.g. Pt/Rh(111): +0.6 eV vs. Pt(111)). Since pure Ag(111) (+0.55 eV) and pure Pd(111) (-0.04 eV) are well within that range, one could envision completely avoiding the use of Pt and instead shifting the O adsorption strength of Ag or Pd closer towards that of Pt by using an appropriate bimetallic structure. In this case, however, due to the lower oxidation potentials of Ag and Pd, avoiding catalyst degradation becomes even more important than with Pt-based ORR catalysts. We will test similar design principles as for the Pt-based ORR catalysts and use in situ XAS and GIXD to probe metal oxide formation in situ, using well-defined Ag and Pd monolayers on single-crystal substrates. We will develop an experimental setup with thin-layer samples that allow for back-illumination in order to obtain $L_{2,3}$ absorption spectra in situ at medium x-ray energies (~3 keV).

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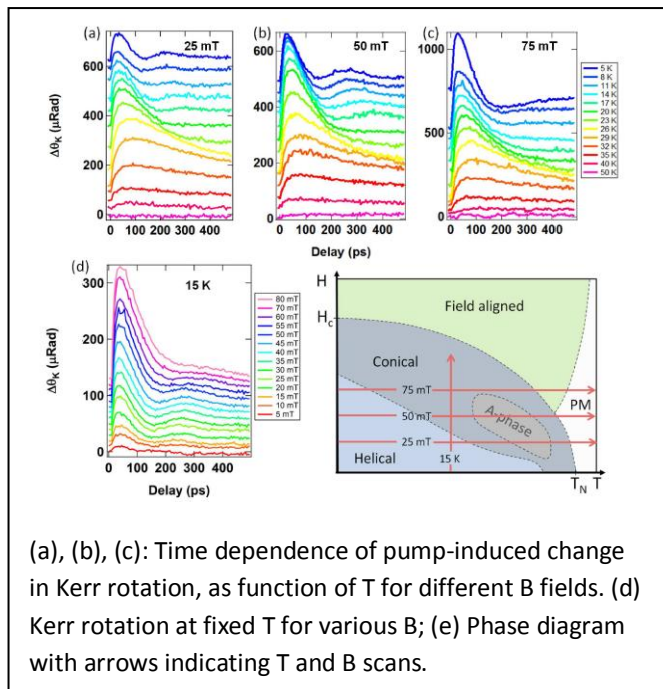
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Title: Time-resolved dynamics in itinerant helimagnets and Skyrmion dynamics

PI's: Joe Orenstein, Robert Schoenlein, Ramesh Ramamoorthy
jworenstein@lbl.gov, rwschoenlein@lbl.gov, ramesh@berkeley.edu

Background: Topological states of matter are attracting great attention in hopes that they will facilitate the next technological revolution. In strongly spin-orbit coupled crystals the chiral Dzyaloshinskii-Moriya interaction can impart a helical spin texture to the conduction electrons. Under certain conditions of temperature and applied magnetic field, the ground state of ordered spin-helices is replaced by a



topological Skyrmion lattice phase that is decoupled from the host crystal lattice. In collaboration with Christian Pfleiderer at University of Munich, we have teamed to study the sub-picosecond dynamics in one such system ($\text{Fe}_{1-x}\text{Co}_x\text{Si}$) [Koralek2012]. In this system excitation of the helical magnetic phase with femtosecond pulses of light is observed to generate coherent magnetization oscillations. From the dependence of the oscillation frequency on temperature and magnetic field (see figure left) the oscillations were identified as coherent helical spin excitations, called helimagnons. Probing in the time-domain

directly yields information on the underlying relaxation processes [Koralek2012].

Future plans: Skyrmions and helimagnetism in 3D and 2D crystals: Our experimental method is now being applied to a broader range of helimagnetic systems, including MnSi. The potential for discovery becomes even greater as we move from 3D systems such as FeCoSi and MnSi crystals to 2D systems. In thin films the Skyrmion lattice becomes stable over a much larger region of temperature-magnetic field phase space than in bulk crystals, and survives to near room temperature. Future plans include thin-film growth of MnSi in the **Ramesh** lab and a search for emergent interface phenomena; exploring how the dynamics of 2D Skyrmion lattices are affected by interfacial coupling to other forms of magnetic and ferroelectric order. Most exciting is the possibility that stable 2D Skyrmion lattices and their interfaces will allow us to create thin film structures in which control of topological matter enables entirely new functionality.

Many high value-added materials, including technical glasses, are manufactured via the liquid (molten) phase [1]. Increasingly industrial processes depend on the use of extreme conditions, supercritical solvents, such as water [2] and CO_2 [3], and nano-scale intermediates - all examples of disordered condensed matter. Our ability to follow the evolution of atomic arrangements in these materials *in situ* under simulated and real processing conditions is fundamental to manipulating physical properties. The utility of time-resolved high-energy x-ray diffraction (HE-XRD), and the complementary use of isotope-substitution neutron scattering, is particularly important for disordered materials where the scattering is predominantly diffuse. The nature of the sample environment and sample cells that allows us to study materials *in situ* at high pressure (p) [4], variable temperature (T) [1, 2] and electric field (E) [5] place severe constraints on data quality, limiting our ability to constrain structure models. Innovative data analysis [6] and modeling techniques [5], interfacing new sample cells with beamlines [7] will allow us to tackle the following problems:

Structural evolution of high temperature melts and liquids. The accuracy obtainable with modern day PDF derived from elastic scattering shows interesting, albeit subtle, behavior that is easier to interpret structurally. This will enable us to tackle problems such as structural inhomogeneity as the liquid passes through the glass transition temperature, T_g , [8] using time resolved HE-XRD and neutron scattering.

Aluminosilicate liquids span much of the range of the fragility scale, and are sometimes associated with density anomalies upon cooling. The structural origin of these anomalies, and their relationship to the features seen in scattering and PDFs of levitated melts in the supercooled regime will be the focus of new work over the next period. For example, pure silica is the archetypal strong liquid that easily forms glasses consisting of a continuous network of corner-shared SiO_4 tetrahedra. In contrast, liquid Al_2O_3 is one of the more fragile liquids. The stable liquid viscosity data show that it has a low activation energy of viscous flow. How do these two simple network forming melts i.e. $\text{SiO}_2 : \text{Al}_2\text{O}_3$ compare in their structural responses to cooling? How does their behavior compare with that of the aluminosilicate formed from them, especially the technologically important mullite composition, $3\text{Al}_2\text{O}_3:2\text{SiO}_2$?

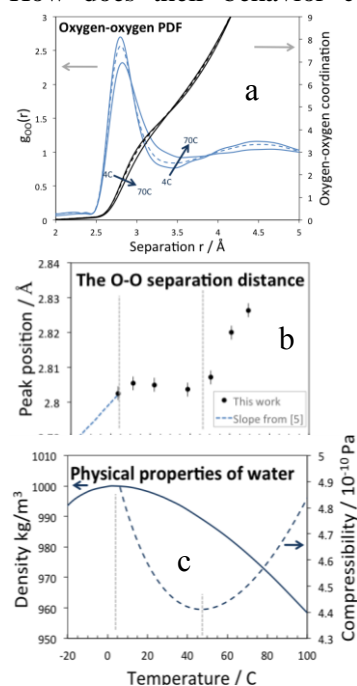


Fig. 1 (a) Oxygen-oxygen (O-O) PDF at 4, 22 and 70°C (blue lines); black lines are the coordination number (i.e. average number of oxygen neighbors) vs. separation distance. (b) T- dependence of O-O peak maximum position in the PDF matched to physical properties of water (b).

Water: The arrangement of neighboring molecules in liquid water is still vigorously debated. This is largely due to the difficulty in measuring the structure accurately. The most widely accepted model, the tetrahedral model is still questioned. Perspectives that at room temperature water is a heterogeneous fluid, are not supported by our data [2]. However careful analysis of the O...O separation (Fig. 1) shows a plateau in the oxygen separation roughly between the density maximum and isothermal compressibility minimum (Fig. 1 middle). The oxygen-oxygen coordination number at 3.4 \AA is 4.6(1) and temperature-independent. What are the origins of this temperature dependent behavior? The time resolved techniques developed here [6-8] are also well placed to provide continued insight in to the phenomenon of the "floating water bridge", a rope-like connection of pure water that forms between two beakers (Fig. 2) when a high potential difference, $\sim 10\text{kV}$ [5], is placed between them. We used HE-XRD to measure the pair distribution function within the water bridge. These were compared to normal liquid water and MD simulations [5] that suggest that surface tension, and not proposed anisotropy, is responsible for the stability of the bridge. The water bridge phenomenon is still not been adequately explained, although this unusual manipulation of matter has now been demonstrated in many organic liquids, including alcohols where surface tension is much less. We

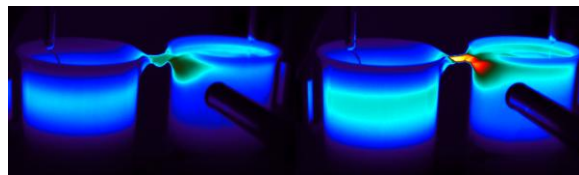


Fig. 2. Infrared thermal images of the floating water bridge setup at APS; color scale from 24°C (dark purple) to 50°C (bright yellow). The left image shows the bridge immediately before collapse, due to reduced voltage.

therefore propose to study this general phenomenon in several liquids using HE-XRD. For liquid water we plan to take advantage of the high flux at the SNS to investigate any anisotropic structure in the bridge. SAXS experiments will characterize or disprove the existence of nano-bubbles in the bridge, which have been suggested to explain the 7% density variation along the length of the bridge.

Fluids and glasses at high pressure. Mobile *hydrothermal* fluids are important determinants of reactivity but little is known about the structure of the prototypical system of most relevance, $\text{SiO}_2\text{-H}_2\text{O}$ fluids, with atomic arrangements that must differ substantially from amorphous SiO_2 and liquid water at room pT . Recent developments in sample cell environments allow us to examine these fluids and obtain reliable HE-XRD.

Chalcogenide glasses, like aluminosilicate glasses, are able to form networks but have the added feature of homopolar bonding (Fig. 3) and so they exhibit a rich compositional dependence.

In experiments on GeSe_4 glass up to pressures of 8.6 GPa [4] we observed a break-up of the intermediate range order in the glass and the average coordination number was found to remain constant in GeSe_4 glass, in contrast to the gradual increase found in GeSe_2 glass [9]. In Phase II we propose to compare the network in densified glassy Ge_2Se_3 with the liquid Al_2O_3 system studied previously. Key differences between the Ge_2Se_3 and Al_2O_3 structure factors are the sharpness of the principle peak and in the first sharp diffraction peak. These features are primarily associated with the extent of chemical ordering in real space and ring statistics respectively. Since Ge_2Se_3 is less densely packed than Al_2O_3 , and based on the changes in the structure factor for GeSe_4 spectra under p , it is expected that very similar scattering patterns and network structures would occur if liquid Al_2O_3 is compared to Ge_2Se_3 glass at p .

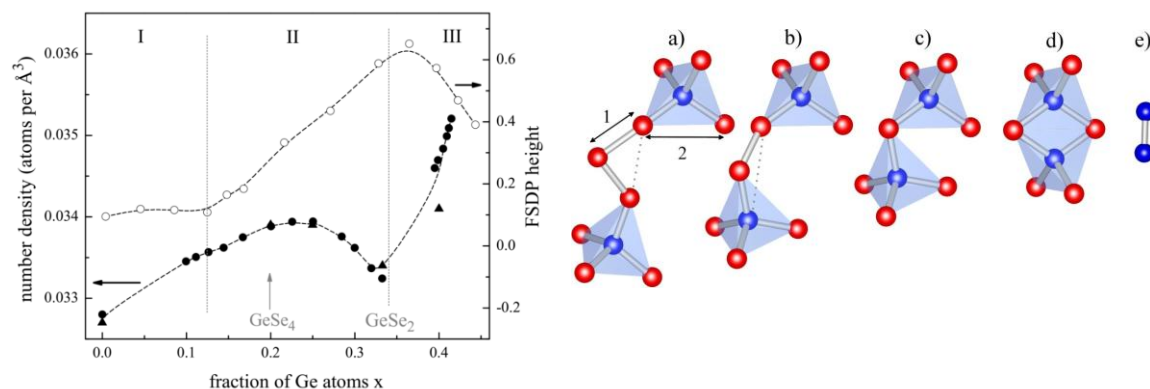


Fig. 3. Compositional dependence of density (filled circles/triangles) and First Sharp Diffraction Peak (open circles) in $\text{Ge}_x\text{Se}_{1-x}$ glasses at ambient pressure. The behavior shows three distinct regions. Region I - random distribution of Ge centered tetrahedra in Se matrix. Region II is where the tetrahedral network forms. Region III is a fully connected network with increasing concentration of defect edge sharing and homopolar Ge-Ge connections. Schematic diagrams of the connection types reported to occur in Ge-Se glasses are also shown. Right to left (e) represents Ge-Ge homopolar bonds, which is the shortest Ge-Ge separation, (d) is edge sharing tetrahedra, (c) is “normal” corner sharing, which produces only longer ($\sim 3.985\text{\AA}$) Se-Se separations (labeled 2) (b) is tetrahedra linked by a Se-Se homopolar bond, this creates a short Se-Se separation ($\sim 2.32\text{\AA}$, labeled 1). (a) tetrahedra separated by 2 Se atoms, this would produce different Ge-Se-Se and Se-Se-Se bond angles, and larger Ge-Ge separation.

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Element specific atomic arrangement of binary and ternary alloy nanosized catalysts in as prepared and active state (DESC-0006877)

Valeri Petkov
 Dow 203, Dept. Physics, Central Michigan University,
 Mt, Pleasant, MI 48859
Petkov@phy.cmich.edu

C.-J. Zhong
 Dept. Chemistry, SUNY Binghamton,
 Binghamton, NY 13902
cjzhong@binghamton.edu

- Research Goal:** The objective of this research project is to characterize the atomic-scale structure of nanosized (less than 10 nm in size) particle (NP) alloy catalysts in as prepared and active state under working conditions using element specific synchrotron radiation techniques such as high-energy resonant x-ray diffraction (XRD) coupled to differential atomic pair distribution functions analysis (PDF) and three-dimensional (3D) atomistic simulations.

2. Recent progress:

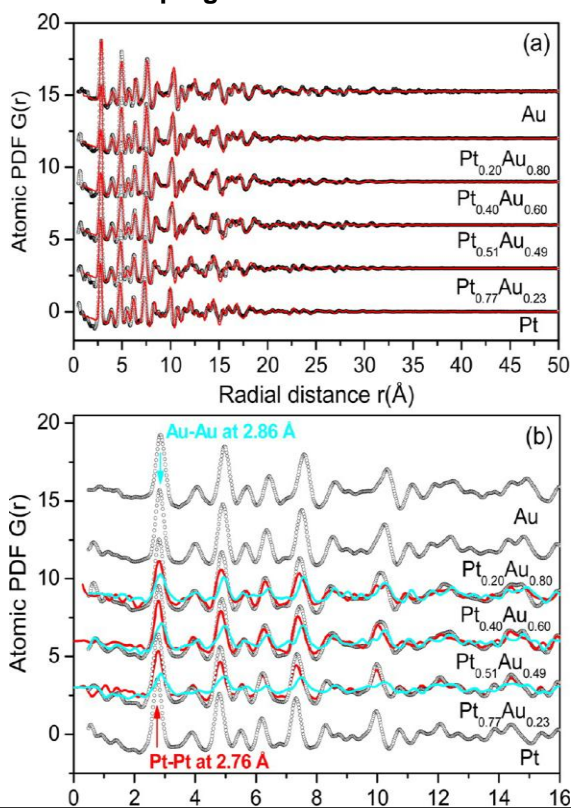


Fig 1: (a) Experimental (symbols) and model (line in red) atomic PDFs for 5.1(5) nm Au-Pt particles. The model PDFs are based on a fcc-type lattice. The respective goodness-of-fit factors are in the range of 18–20%. (b) Low r part of the experimental atomic PDFs for 5.1 nm Au-Pt particles (symbols). Experimental Pt differential PDFs (line in red) and Au-Au partial PDFs (line in cyan) are also shown. Arrows mark the positions of the Pt-Pt and Au-Au bond distances. The data sets are shifted by a constant factor for clarity.

We have studied the formation of nanosized alloys between a pair of elements, which are largely immiscible in bulk, in the archetypical case of Pt and Au by applying of resonant high-energy X-ray diffraction experiments coupled to atomic pair distribution functions analysis and computer simulations. Experimental total and Pt differential atomic PDFs are shown in Fig. 1a and 1b, respectively. The differential Pt PDFs were obtained by employing the so-called resonant XRD, which involves measuring two XRD data sets close to but below the absorption edge of Pt atomic species, taking the difference between these two data sets, and Fourier transforming it into a quantity called a Pt differential atomic PDF. Similarly to EXAFS experiments, the differential PDF reflects only correlations relative to the element whose absorption edge is probed. However, unlike EXAFS, it shows these correlations up to the longest interatomic distances to which they extend. By taking a difference between the total PDFs and Pt differential PDFs Au-Au partial PDFs were obtained. Partial Au-Au atomic PDFs are shown in Fig. 1b. As can be seen in Figure 1b, all three Pt differential PDFs have their first peak at a distance close to the position of the first peak in the PDF for pure Pt NPs. All three Au-Au partial PDFs have their first peak at exactly the same distance of 2.86 Å that is very close to the position of the first peak in the PDF for pure Au NPs. The result indicates that Au-Au and Pt-Pt bond lengths in 5.1(5) nm carbon supported Pt-Au NPs do not take some average values that scale with the Pt/Au relative content. Rather they remain very close to the respective

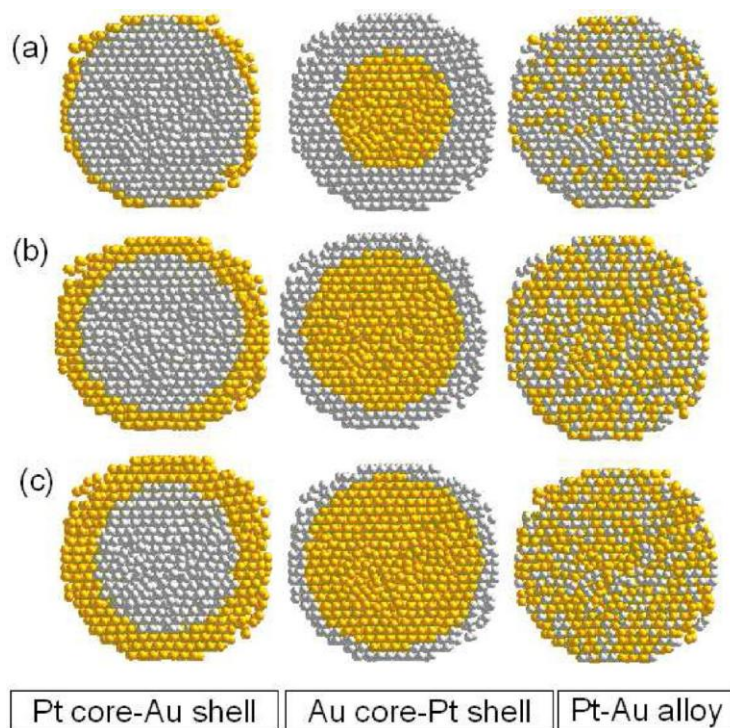
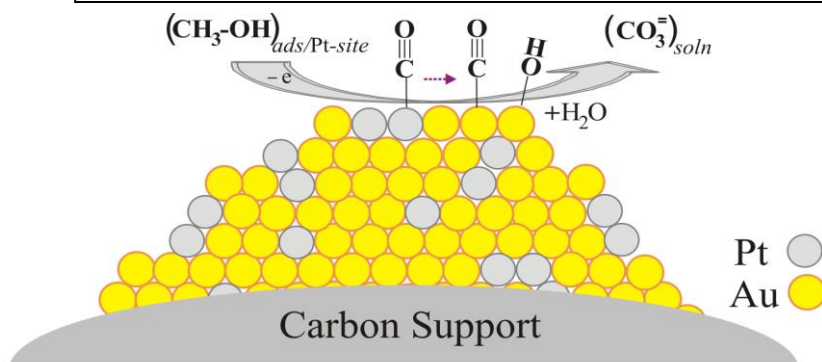


Fig. 2: Cross sections of 5.1 nm Pt-Au particles (about 5000 atoms) with a core-shell and random alloy structure: (a) $\text{Pt}_{0.77}\text{Au}_{0.23}$; (b) $\text{Pt}_{0.51}\text{Au}_{0.49}$; and (c) $\text{Pt}_{0.40}\text{Au}_{0.60}$. Pt atoms are in gray, Au in yellow. The ratio of Pt/Au atoms in the models exactly reflects the respective NP's chemical composition.



the carbonate (CO_3^{2-}) product in the oxidative reaction of methanol.

Fig. 3: Schematics of the catalytic oxidation of methanol on carbon supported PtAu alloy particles in terms of a surface adsorption and hydrogenation of methanol ($\text{CH}_3\text{-OH}_{\text{ads}}$) on Pt sites, an intermediate reaction step of C=O transfer (marked with an arrow) from Pt to neighboring Au sites, and the addition of hydroxyl (OH) and water (H_2O) from the latter sites to the C=O species resulting in the formation of the final carbonate product (CO_3^{\ominus})_{soln}.

atmosphere has a profound effect on their atomic-scale structure and catalytic properties. In particular, we found that the different gas atmospheres do not affect substantially the random alloy, face-centered-cubic structure type of the particles but do affect the way the metal atoms pack together. In an O_2

bond lengths of 2.76(1) and 2.86(1) Å in pure Pt and Au, respectively. To understand how do the size-different Pt (Pt diameter = 2.76 Å) and Au (Au diameter = 2.86 Å) atomic species arrange themselves across the 5.1(3) nm NPs we built structure models featuring NPs of real size (5.1 nm) and shape that are able to incorporate chemical order-disorder effects extending beyond a single unit cell of an fcc lattice. The models were built by reverse Monte Carlo simulations. Only structure models where Au and Pt atoms are well mixed together throughout the NPs produce Au-Au partials PDFs that are consistent with the experimental data. The result shows that the $\text{Pt}_x\text{Au}_{1-x}$ NPs studied here do not phase segregate contrary to their bulk counterparts and to what theory predicts. The findings allow explaining the catalytic activity of Pt-Au nanoparticles on the basis of an appropriate structure model as depicted in Fig. 3. It features Au-Pt nanoalloys. In particular, mixing of Pt and Au atoms at the atomic-scale may results in subtle Pt-to-Au net charge transfer as found in other studies. Such charge transfer may be expected to occur throughout the alloy $\text{Pt}_x\text{Au}_{1-x}$ NPs modifying the electron density distribution of all atoms and so affecting their catalytic activity. In particular, the decrease in the d-band vacancy at the Pt sites may facilitate the transfer of intermediate CO-like species toward the neighboring Au sites (see Fig 3) and, hence, facilitate the formation of

the carbonate (CO_3^{2-}) product in the oxidative reaction of methanol.

3. Future plans

We would like to concentrate on in situ studies of binary and ternary catalysts and also concentrate on the influence of the substrate on the catalytic properties. Recently we discovered that post-synthesis processing of nanosized catalysts in oxidizing (O_2 rich) and reducing (H_2)

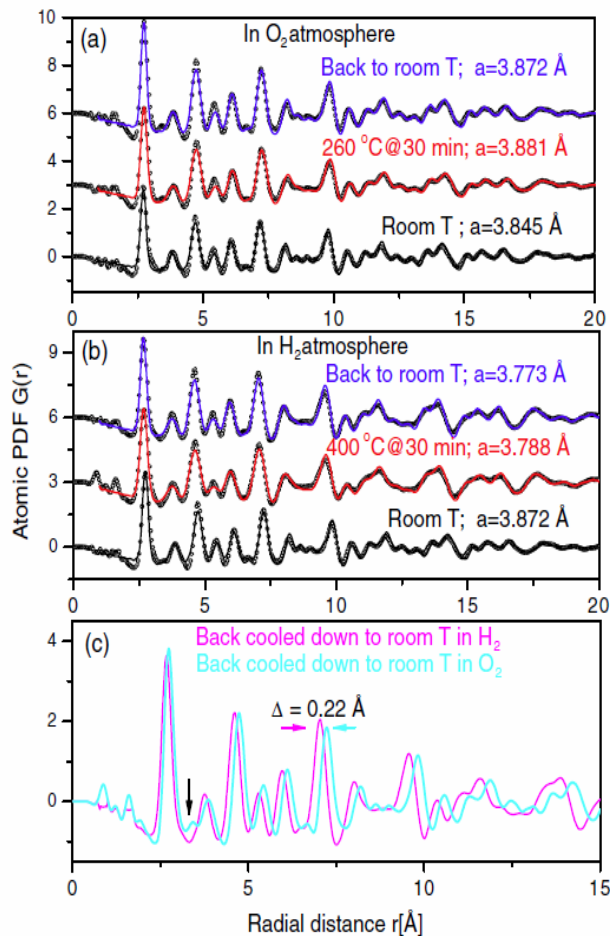


Fig. 4: Experimental (symbols) and model (solid line) atomic PDFs for Pt₂₅Ni₁₆Co₅₉ NPs. (a),(b) The refined fcc-lattice parameters are given by each data set. In (c), the experimental PDFs for samples treated in O₂ and H₂ atmospheres are compared to emphasize their different structural states.

atmosphere, atoms get extra separated from each other, whereas, in an H₂ atmosphere, they come closer together. The effect is substantial, amounting to 0.1 Å difference in the first neighbor atomic distances, and concurs with a dramatic change of the particle catalytic properties. In particular, the fact that NPs processed in an H₂ atmosphere are more compressed than those in the O₂ atmosphere processed NPs, has a dramatic effect on the catalytic activity for a CO oxidation reaction in the gas phase and an oxygen reduction reaction (ORR) in electrolytes. For example, with the H₂ treated Pt₂₅Ni₁₆Co₅₉ NPs, the gas phase CO conversion rate increases 10 times and the mass activity for electrocatalytic ORR increases 4 times. These results are fully in line with theoretical predictions that shrinking of the metal-metal distances lowers the energy level of the d-band electrons with respect to the Fermi level and so decreases the binding energy of the CO species to the NP surface, substantially improving the catalytic activity. In summary, reactive gasses, like condensed matter, can interact strongly with noble-TM particles less than 10 nm in size, resulting in a substantial modification of the way the metallic species pack together. When being treated in an oxidizing atmosphere, the atomic packing of the NPs loosens, whereas, in a reducing atmosphere, the atomic packing gets tighter, without changing its random alloy fcc-structure type character. We are planning on doing more in situ studies and study this effect in more details. Experiments are scheduled for December 2011. Resonant high-energy XRD studies are scheduled for

February 2013 aimed at studying the effect of support on the catalytic properties.

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Nonequilibrium Electron-Lattice Interactions: femtosecond x-ray diffuse scattering

David A. Reis*, Mariano Trigo,

SLAC National Accelerator Laboratory, 2575 Sand Hill Rd. Menlo Park, CA 94025

dreis@slac.stanford.edu

Our goal over the next three years is to perform the first measurements of time and momentum resolved non-equilibrium phonon dynamics of complex materials as a means to untangle the particularly strong interactions between the charge and lattice degrees of freedom. We have recently demonstrated the viability of time-domain inelastic x-ray scattering (TD-IXS) for measuring non-equilibrium lattice dynamics in photo-excited semiconductors using the femtosecond hard x-ray beam at LCLS. Here spectroscopic information is obtained by Fourier transforms of time- and momentum-resolved x-ray diffuse data. Ultimately this is a direct measurement of $S(\mathbf{q},t)$, and thus it has tremendous potential for developing a microscopic understanding of emergent phenomena in complex materials and as a probe of materials properties far from equilibrium. We will focus on: (a) the rare-earth tri-tellurides a prototypical CDW system and (b) the high- T_c cuprates in collaboration with PIs in the Time-dynamics of Oxides and Related Materials as well as the two quantum materials FWPs in SIMES.

The $R\text{Te}_3$ system has recently attracted attention as a system to investigate the role of Fermi surface (FS) nesting in CDW formation. Despite being prototypical CDW systems, the rare-earth tri-tellurides have long defied the standard CDW models. For example, an unsolved mystery is the fact that the CDW ordering wavevector does not match the FS nesting wavevector that should determine the ordering direction. One explanation for this is a large anisotropy in the elastic energy necessary to produce the concomitant lattice distortion. Thus, there is a unique opportunity for experiments at LCLS to shed light into this puzzle by disentangling the coupled degrees of freedom with an ultrafast pump-probe experiment. Here we will use hard x-rays at the LCLS to probe the diffuse scattering around the CDW Kohn anomaly as the electronic system is perturbed away from equilibrium. In this case, a short laser pulse impulsively melts the CDW state, kicking the lattice modes into a phase-coherent state, not just at the Fermi-nesting wavevector, but everywhere there is a finite electron-phonon interaction. The hard x-ray pulse then measures oscillations in the (non-thermal) diffuse scattering from these modes. Here TD-IXS can yield substantially new information about the formation of the CDW state and its coupling to low frequency modes near the Fermi-nesting wavevector. In this case the measurement of the low-frequency modes is limited only by decoherence due to anharmonic interactions, not by the measurement (which is limited only by the maximum time-delay).

In the high temperature superconductors (HTSC), the ability to map large areas of \mathbf{q} -space with femtosecond resolution will provide a way to pinpoint regions of reciprocal space where the electron-phonon coupling is particularly strong. We will bring to bear femtosecond diffuse x-ray scattering to this long outstanding problem in order to obtain the first ever mapping in three dimensional (t,ω,\mathbf{q}) -space –of the emission of phonons from hot electrons in a HTSC with extreme frequency and momentum resolution. We will use these experiments to identify relevant phonon modes related to the kinks observed in ARPES as well as attempt to unravel the mechanism for the newly discovered acoustic phonon anomalies at lower frequencies.

Our Approach: TD-IXS offers several advantages over conventional frequency-domain IXS for these measurements: **1.** Our approach yields exquisite resolution both in time (frequency) and momentum, without the need for high-resolution monochromators or analyzers, limited only by the pulse duration and synchronization. In contrast, current IXS is limited to few meV resolution with extremely low count rates; **2.** TD-IXS is sensitive to electron-phonon and phonon-phonon interactions because we measure *changes* in the phonon population **3.** Because it is a time-domain measurement, it is directly applicable to measuring non-equilibrium phenomena that are only transient. **4.** Finally, our energy resolution comes from a Fourier transform of the data, and thus we can use a 2D detector to capture large regions of \mathbf{q} space in parallel, while the frequency resolution is only limited by the maximum delay measured.

Pushing the limits: In addition to our scientific goals above, we intend to further develop time-resolved diffuse scattering methods to push both **time** and **momentum** resolution to the extreme. In fact the challenge of TD-IXS is in its high-frequency response, currently limited by the timing jitter between the pump and probe. We note that recent advances in time-resolution (via the hard x-ray timing tool), detector response, and in particular better x-ray energy resolution due to self seeding of the LCLS will allow even more detailed pictures to be taken, including of complex materials. Thus, part of this ambitious program will be to push the-state-of-the-art in ultrafast timing synchronization at the LCLS even further, to the sub-10fs limit, to reach the relevant high energy scale of the mysterious ARPES kink, ~ 70 meV. Our group has substantial expertise in ultrafast timing and short pulse generation and we will take advantage of close ties with the LCLS laser division to help solve this technical problem. In the optical regime we can generate sub-10 fs pulses with available Ti:Sapphire technology to reach these timescales in our optics labs.

Publications in 2011,2012:

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Collaborative and Partial Support:

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NANOPARTICLES AT LIQUID INTERFACES

*Thomas P. Russell**, *T. S. Emrick***

* Email: russell@mail.pse.umass.edu, **Email: tsemrick@mail.pse.umass.edu

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

Abstract

The temperature dependence of the dynamics of gold nanoparticles, functionalized with polystyrene (PS) dispersed in a PS matrix was investigated by x-ray photon correlation spectroscopy (XPCS). The molecular weight of the PS ligands relative to that of the PS matrix proved crucial. If the molecular weight of the PS ligands was small relative to that of the matrix, interpenetration of the host polymer into the ligands was limited and the dynamics of the NPs and the PS host were decoupled. Provided there was interpenetration, the dynamics of the NPs followed that of the PS host. These studies provided a basis on which to investigate the interfacial dynamics of the NPs. In order to increase the energy holding the NPs at a fluid/fluid or polymer/polymer interface, Janus NPs were prepared wherein the two hemispheres of the NPs favorably interact with one of the fluids or polymers. Gold-silica Janus particles were prepared by the hydrolysis of silica precursors on the surface of ≈ 40 nm gold nanoparticles. The gold seed particles are prepared via the standard citrate reduction method. The interfacial dynamics of the Janus NPs will be investigated by XPCS. The jamming of NPs at fluid interfaces is most easily accomplished by varying the interfacial area with a fixed number of adsorbed NPs. Studies were initiated to use an electric field to distort the shape of fluid droplets to which NPs were adsorbed, or to force the fusion of two droplets. In both cases a substantive change in the interfacial area could be affected that, in turn, led to a jamming of the NPs at the interface and a freezing-in of non-equilibrium shapes of the droplets. Results from these studies led to initial efforts on the generation of bicontinuous, jammed (bijel) systems using CdSe NPs with toluene and water.

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Title: Nanoparticles at Liquid Interfaces

Dynamic evolution of spin ordering across the insulator-metal transition in a correlated manganite

P.I.: Robert W. Schoenlein, Co-P.I.: Robert A. Kaindl

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

RWSchoenlein@lbl.gov, RAKaindl@lbl.gov

Background: Localized electronic ordering in transition metal oxides often plays an important role in the emergent properties of these materials. Examples include stripe phases in cuprates¹ and nickelates², CE-type charge/orbital/spin (CO/OO/SO) ordering in manganites^{3,4}, and charge ordering in multiferroics⁵. Localized electronic ordering is most prominent in colossal magnetoresistance (CMR) manganites where an insulator-metal transition (IMT) can be induced by an applied magnetic field (CMR effect).

Recent Results: Our previous static resonant soft X-ray scattering studies (Fig. 1) characterized the spin and orbital ordering in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ⁶. Here we focus on the dynamics of spin ordering in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ associated with the ultrafast IMT induced by an ultrashort laser pulse (~ 100 fs, 800 nm) using time-resolved resonant X ray scattering (trRXS) at ALS and LCLS beamlines (Fig. 8)^{6,7}. LCLS studies focus on the ultrafast destabilization of the spin and orbital order. ALS studies reveal the glass-like physics that mediate the dynamic ordering of spins in transient photo-excited $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, and indicate that the destabilization of electronic ordering via photo-excitation gives rise to the formation of small local ferromagnetic/metallic clusters.⁷⁻⁹ With increasing pump fluence, these microscopic clusters merge and form a meta-stable mesoscopic ferromagnetic/metallic phase.

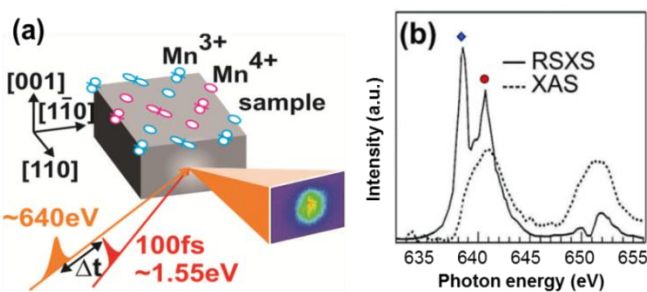


Fig. 1. (a) Schematic of trRXS with CE-type CO/OO/SO. (b) Energy profile of SO resonant diffraction peak (solid) and XAS spectrum (dotted).⁶

Our trRXS studies followed the evolution of spin order in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ over nearly 12 decades in time (70 ps to seconds) to reveal an unambiguous stretched-exponential behavior that is a hallmark of glass-like systems¹⁰. Moreover, the measurements show a dimensional crossover in the effective interaction from 1D at low pump fluence to 3D at high pump fluence (as shown in Fig. 2), suggesting that spin ordering and orbital ordering can be decoupled by transient photo-excitation.^{6,7}

The observed 1D recovery dynamics are consistent with a process by which the OO remains largely intact at low pump fluence, even while the SO is destabilized by photo-excitation. The intra-chain interaction along the quasi-1D OO path provides the restoring force for SO based on Goodenough-Kanamori rules¹¹. Above 4 mJ/cm^2 , both SO and OO are significantly destabilized. In this case, the intra-chain, inter-chain and c-axis couplings all become appreciable. The observed dimensional crossover suggests an interesting possibility that despite the intimate coupling of spin and orbital degrees in the ordered state, the SO and OO may be

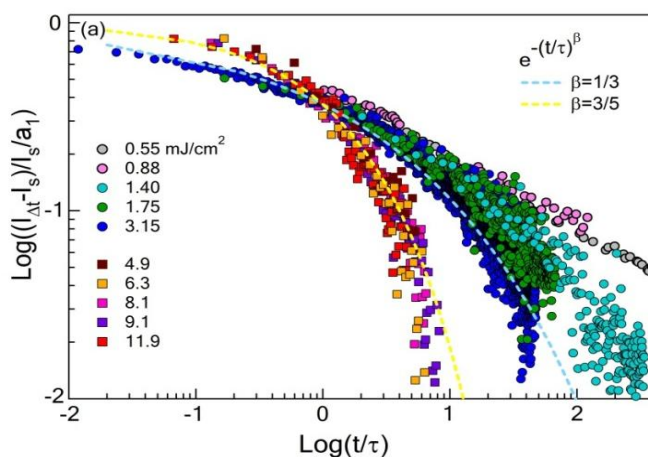


Fig. 2. (a) Log-Log plot of trRXS data with signal and time scale normalized by a_1 and β extracted from the fit with a stretched exponential. Dashed cyan ($\beta=1/3$) and yellow ($\beta=3/5$) lines are stretched-exponential functions: $\beta=d/(d+2)$ where d is the dimensionality of the system.^{7,10}

transiently decoupled in their response to ultrafast photo-excitation. Our work provides a new perspective for probing localized electronic order in other correlated materials, especially those where the fluctuating nature can play a critical role in the emergent properties.¹

Future Plans: We will apply trRXS techniques to manganites, nickelates, and multiferroics to investigate ordering dynamics and their role in emergent material properties. The bi-stripe phase in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ will be studied in collaboration with the Dessau group. Previous resonant X-ray¹² and ARPES¹³ studies confirmed the role of the bi-stripe phase in localizing the electronic states. The unique nature of the bi-stripe phase offers several possibilities to follow the transient *establishment* of bi-stripe order (and charge *localization*) via transient photo-doping, vibrational excitation, and transient nonequilibrium heating. In nickelates, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, we propose to investigate potential glassy dynamics associated with the spin stripes. These materials do not exhibit superconductivity, but are iso-structural with the high- T_C cuprates exhibiting similar spin stripes. In multiferroic LuFe_2O_4 we will apply trRXS to investigate frustrated charge ordering of Fe^{2+} and Fe^{3+} and its role in the novel ferroelectricity⁵.

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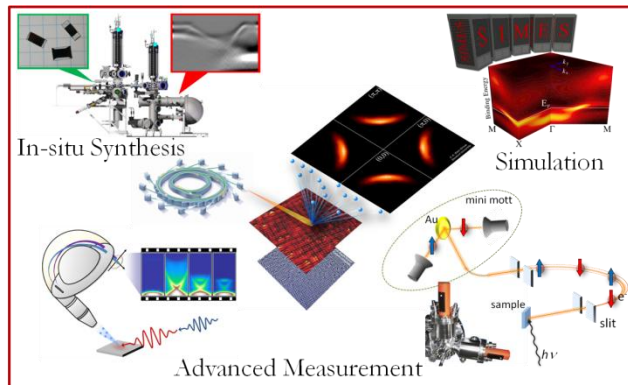
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Electronic and Magnetic Property of Quantum Materials

Z.-X. Shen, T. P. Devereaux, D.H. Lu, R. Moore, M. Hashimoto, P. Kirchmann
Stanford Institute for Materials and Energy Sciences
SLAC National Accelerator Laboratory
2575 Sand Hill Rd.
Menlo Park, CA 94025
zxshen@slac.stanford.edu
650-725-8254

Quantum materials research represents an exciting opportunity to advance our understanding of grand scientific challenges, and to impact future energy technologies. The multiple degrees of freedom from spin, charge, orbital and lattice often conspire to give rise to remarkable emerging properties. We undertake a comprehensive program to tackle this important but complex problem, through a "complete set" of ARPES experiments that includes energy, momentum, spin and time resolution, further complemented by in-situ materials synthesis and theoretical investigation. ARPES has grown to be one of the important techniques in the modern study of quantum materials and is now recognized as an essential contribution in the path towards a fundamental understanding of materials properties.



Recent ARPES results from 2011-2012 including new insights into the nature of pseudogap phase of high temperature superconductors, ultrafast dynamics of topological insulators and charge density wave systems, electronic structure of polaronic metal, hidden itinerant-spin phase revealed by a combined neutron and ARPES approach, symmetry breaking orbital anisotropy and Fermiology of pnictide superconductors, two dimensional electron gas at oxide surfaces.

Our planned program brings many new dimensions to existing ARPES experiments and theory of spectroscopy, thus elevating the expected level of impact. The new experimental capabilities include: a) new beamline with improved flux, resolution, polarization control and spectral range; b) pico-second laser based high (spectral) resolution ARPES system; c) femto-second laser based tr-ARPES system; d) sr-ARPES system; e) in-situ materials synthesis capability. At the same time, improvements in computational methods and architectures will highly accurate simulations of photon-based spectroscopies often able to connect quantitatively with measured spectra. We select four scientific areas to focus, including novel superconductivity, novel orbital, spin, and spin-orbit physics, quantum systems in low dimension, and non-equilibrium physics. This synergetic mixture of science drivers and experimental tools promises the best opportunity to attack the "problems of scale" presented by the complexity of quantum materials.

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Presentation Title: Coherent X-ray Diffractive Imaging of Magnetic Nanostructures

Principal Investigator: Oleg Shpyrko, University of California San Diego

Address: 9500 Gilman Drive, MC 0319
Department of Physics
University of California San Diego
La Jolla, CA 92093-0354

Email: oshpyrko@physics.ucsd.edu

We have successfully performed Coherent X-ray Diffractive Imaging (CXDI) of magnetic nanostructures. The approach of CXDI is a lens less alternative to lens-based techniques – the diffraction pattern formed by scattering a coherent x-ray beam from a sample is inverted numerically to form an image of the object. By removing the need for the optics, the spatial resolution achievable is no longer limited by the quality of the optical elements, but by the highest spatial frequencies measured in the x-ray diffraction pattern. We have also performed measurements of dynamics in several Charge Density Wave Compounds and antiferromagnetic systems using X-ray Photon Correlation Spectroscopy (XPCS) and x-ray micro- and nano-diffraction.

We plan to continue investigating the slow fluctuations, non-equilibrium, glassy relaxation, hysteresis and memory effects, as well as continuous vs. intermittent dynamics in Charge Density Wave (CDW) and antiferromagnetic systems. Domain wall fluctuations are believed to be the origin of $1/f$ noise in magnetic devices, so it is of interest to study these in real time. There have as yet been almost no studies of spin or CDW dynamics using coherent X-rays. Using coherent X-ray beams at the L- or M-edges of rare earth metals, such as Dy or Ho, which possess antiferromagnetic spiral structures at low temperatures and at accessible values of the wave vector transfer, we plan to carry out studies of the speckle structures around the magnetic satellite peaks in real time. We might find a similar type of slow glassy behavior in these helical magnets, to the dynamics we already observed in CDW systems, described above.

We are continuing our work on Coherent Diffractive Imaging of distribution of strain in isolated nanostructures, such as Ni and ZnO nanowires. We are also working on Bragg Ptychography measurements on extended objects – including imaging of ferroelectric domains in PZT films deposited on STO, complex magnetic phases (including helical antiferromagnets) and charge ordered oxides. We are also investigating nanoscale phase separation in correlated oxides, such as metal-insulator transition in VO_2 and V_2O_3 . Under some conditions we observe photoinduced persistent insulator-to-metal transition due to x-ray illumination, mechanisms of which are under investigation.

One of the more challenging problems we are working on involves deeper understanding of the nanoscale lattice distortions and ion diffusion processes that lead to degradation of energy storage materials (such ion battery electrodes) and their performance. In-situ Coherent X-ray Diffractive Imaging can provide unique insight into structural nanoscale properties of these materials under working conditions.

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Magnetic and Superconducting Materials at High Pressures

Viktor V. Struzhkin, R. J. Hemley, H.-K. Mao

*Geophysical laboratory, Carnegie Institution of Washington,
5251 Broad Branch Rd., N. W., Washington DC 20015
Email: vstruzhkin@gl.ciw.edu*

As a result of recent advances, experiments utilizing an unprecedented number of probes are now straightforward to perform over a wide range of pressures. This is especially important for testing theory; for example, a fundamental understanding of the mechanisms of superconductivity requires knowledge of crystal structure, electronic structure, and vibrational properties, including the interaction of the conduction electrons with lattice vibrations. Thus, our future studies will be centered around magnetic and transport measurements and complemented by a wide variety of high-pressure structural and spectroscopic methods involving laser and synchrotron radiation. The experimental challenges are listed below.

- Exploring new potential elemental superconductors (hydrogen) and already known superconductors (boron, sulfur, alkali metals, etc..) at the limit of static high pressure techniques.
- Investigating special classes of superconducting compounds (hydrides; high- T_c superconductors, cuprates and Fe-based superconductors; borides, polyaromatic hydrocarbon superconductors) that may provide new fundamental knowledge and may prove important for application as high-temperature/high-critical parameter superconductors.
- Investigating the pressure dependence of superconductivity and magnetic/phase transformations in 3d transition metal compounds including transitions from magnetic to nonmagnetic phases in a broad pressure-temperature range.
- Advancing transport and magnetic techniques for measurements on small samples at very high pressures in a wide temperature range, with the application of focused ion beam (FIB) technology tailored to the design of microcircuits down to a nanoscale size, thus expanding the horizon in the search for novel physical phenomena at ultrahigh pressures.

We will use the suite of transport techniques to measure the onset of superconducting T_c as a function of pressure in the multimegabar range, focusing on the superconductivity in hydrogen, and other simple elements at the limit of static high pressure techniques. The technique is based on a mutual induction principle involving micro-coils placed around the diamonds in a BeCu cell. This technique will be enhanced by the emerging microcircuit design aided by FIB or photolithography sample preparation, and will be extended with magnetic measurements by optically detected magnetic resonance from NV centers in diamond. We are implementing miniature diamond anvil cells suitable for superconductivity studies in various environments, including PPMS. Complimentary X-ray RIXS and other spectroscopic measurements of valence and core level excitations will be performed to probe the electronic structure and local spin state of 3d-metal ions. These new experiments have been made possible by the use of new Be gaskets and synchrotron x-ray methods. Raman scattering and synchrotron infrared techniques that we have developed will be used to study optical conductivity, magnon and phonon excitations, and phase transitions. A suite of x-ray diffraction techniques will be used for structural studies of single-crystal and polycrystalline samples.

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High Energy Diffraction Microscopy: Spatially Resolved Studies of Ductile Deformation at APS 1-ID

R. M. Suter (suter@cmu.edu) and A. D. Rollett (rollett@cmu.edu), Departments of Physics and Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213

Planned Research Scope

1. Publications

- a. We have submitted a paper (J. Appl. Crystallography) describing algorithms used in our microstructure reconstruction procedures. These algorithms have advanced significantly since our original presentation of the approach (Rev. Sci. Instru. **77**, 123905 (2006)).
- b. A paper describing the observation of twin nucleation and growth inside a bulk zirconium sample is in preparation. This work, in which twinning is observed with full knowledge of surrounding microstructure, is of great interest to the modeling community.
- c. A paper describing measurements of closely spaced strain steps in a single layer of copper is in preparation. Lattice rotation paths and path dispersion is explored near the onset of plastic deformation. Computational modeling, using initial structure based on the measurement, has been performed and will be directly compared to measured responses.

2. Analysis of existing data sets

- a. Large volume copper measurement: A volume containing several thousand grains has been tracked with HEDM and tomography as it undergoes tensile deformation. With the already reconstructed initial sample state, we will perform simulations using image based plasticity codes (developed by R. Lebensohn of LANL, parallelized at CMU, and translated into C++ by S.F. Li who has moved from CMU to LLNL).
- b. Zirconium: In addition to twinning, we observe the introduction of lattice orientation gradients and localized sub-structures, particularly those close to twins. These will be characterized statistically and compared to computational models. We will work with LANL scientists (Lebensohn and co-workers) to fully interpret these comparisons.

3. HEDM & Tomography Development: Taking advantage of APS Upgrade

- a. We are collaborating with AFRL (J. Schuren et al.), APS Sector 1 staff (J. Almer, et al.), and LLNL (S.F. Li and J. Bernier) on a project to combine far-field, grain averaged strain measurements, with our near-field intra-grain orientation mapping measurements. A Partner User Program (PUP-28256) allocation has been approved by APS management. The goal is to achieve spatially resolved strain and orientation information from samples under realistic thermo-mechanical conditions so as to enhance comparisons between measurements and models. The team has designed, built, and done first tests on a sophisticated loading system capable of tensile, compressive, and cyclic loading. A heating stage is under development. A set of dedicated nodes on an APS computer cluster have been installed for analysis during beamtimes. Integration of analysis software from the different approaches is underway. The resulting capability will be unique in the world.
- b. We are proposing a method that will allow full spatial resolution of strain states within grains that will use only near-field measurements. Thus, strains and lattice orientations will be measured simultaneously. The technique should be highly effective for identifying strain "hot spots" (in pre-plastic deformation sample states) that can be directly compared to those observed with computations. For routine use, this method will require the source brilliance characteristics associated with the APS Upgrade project. A proposal for a demonstration measurement is being readied (in collaboration with A. Beaudoin of UIUC) for the 2013-1 APS cycle. This capability will be unique in the world.

- c. We are working with Sector 1 staff to develop a high energy tomography capability with 100 nm spatial resolution. The goal is to enable examination of features such as cracks and inclusions in regions of interest identified by either coarser scale tomography or HEDM type measurements. A Partner User Program allocation at 1-ID (PUP-25240) is in place for this work. The technique uses compound refractive lenses placed downstream of the sample. The lenses create a weakly divergent beam that is imaged far downstream: at 1-ID, the sample is mounted in the B-hutch while imaging is performed 35 meters downstream in the end station E-hutch. In preliminary measurements, we have observed magnification by approximately 20X, which is consistent with expectations based on ray-tracing. A variety of interesting ray-optical and diffraction effects are also observed and are the subject of current analysis.
- d. We will extend orientation reconstructions to higher strain levels by using the map from each strain state as the starting point for the next strain state. We will test this approach using existing copper data where only dislocation slip occurs (i.e., reorientation is smooth, without jumps). We hope to extend the maximum indexable strain from about 15% to about 30%.

4. New Measurements

- a. We will perform detailed studies using combined orientation and elastic strain mapping to identify hot spots in the elastic regime and then to follow those regions as plasticity develops to elucidate the impact of hot spots on subsequent damage more completely than has previously been possible. The primary use of the data will be to compare against full-field computational models of materials response.
- b. In zirconium, we will apply the measurement of spatially resolved elastic strain, concentrating on individual, spatially resolved twinning events such as we have recently observed. We will strain a zirconium specimen, mapping the microstructure with near-field HEDM. Once a twin is observed, we will map the elastic strain state in that grain and in as many nearest neighbor grains as is feasible, using the far-field method. The primary use of the data will be to test hypotheses concerning twin formation in hexagonal metals. Once twins have been fully characterized, we will investigate the full orientation map and perform a survey of the orientations to pick out individual grains that should have large elastic strains because they are in unfavorable orientations for slip and/or twinning (i.e. high Taylor factor). We will repeat the far-field measurements on a few of these grains and compare their (elastic) strain state against full field simulations (elastic FFT, or finite element).
- c. We will repeat the development described above by continuing the tensile test with HEDM orientation mapping, using the solution from each strain step as the initial guess for the next step. The expected result is that we can extend the range of strain to a high enough level that void maps can be overlaid by orientation maps. Caré & Zaoui [*Acta mater.* (1996) **44** 1333] report finding voids at plastic strains less than 20%. Given that the forward modeling method is already able to index maps up to 15% only a modest extension will be required to achieve this goal (see 3.d above).
- d. Continuing with the tensile test, as soon as any voids are detected in the tomographic scans, we will commence scans at small strain intervals. This will permit us to resolve the growth of individual voids and their linking-up on the way to ductile failure. Such data is sorely needed by the computational community for testing new theoretical approaches to ductile failure [*Euro. J. Mech. A* **37** (2013) 35].

Publications: 2011 – 2012

R. Pokharel, S.F. Li, J. Lind, C.M. Hefferan, U. Lienert, R.A. Lebensohn, R.M. Suter, A.D. Rollett, "Quantifying damage accumulation using state-of-the-art FFT method," *Materials Science Forum* **702-703**, 515-518 (2012).

S.F. Li, J. Lind, C.M. Hefferan, R. Pokharel, U. Lienert, A.D. Rollett, R.M. Suter, "Three Dimensional Plastic Response in Polycrystalline Copper Via Near-Field High Energy X-ray Diffraction Microscopy," *J. Appl. Cryst.*, in press.

Title: Ultrafast Optical Spectroscopy: Investigating Dynamic Correlations in Complex Materials

PI: Stuart Trugman

Address: MS K771, MPA-CINT, Los Alamos National Laboratory, Los Alamos, NM 87545

Email: sat@lanl.gov

Future Plans:

Although we have been quite successful in using optical pump-probe spectroscopy to study quasiparticle dynamics in a variety of complex materials, we have also learned that in some materials, other ultrafast optical techniques will provide more direct access to the relevant order parameters. These techniques include time-resolved Kerr rotation (TRKR), time-resolved second harmonic generation (TR-SHG), and optical-pump, THz-probe (OPTP) spectroscopies. The TRKR signal measures magnetization dynamics, while TR-SHG is sensitive to both magnetic and FE order parameters under the appropriate conditions. OPTP spectroscopy generally measures complex conductivity dynamics, and is a particularly good probe of dynamics in superconductors (SC) since the real part of the conductivity is proportional to the quasiparticle fraction and the imaginary part to the fraction of Cooper pairs. We are currently extending our capabilities by building a system that will enable us to perform THz time-domain and OPTP spectroscopies in a high (8 T) magnetic field, which promises to provide much insight on the complex materials studied in this project. In addition, by modifying our existing setups, we can perform two-sided pump-probe experiments on appropriately fabricated oxide heterostructures, which will allow us to examine the influence of one order parameter on another. As described below, we have already begun performing some of these experiments on complex materials.

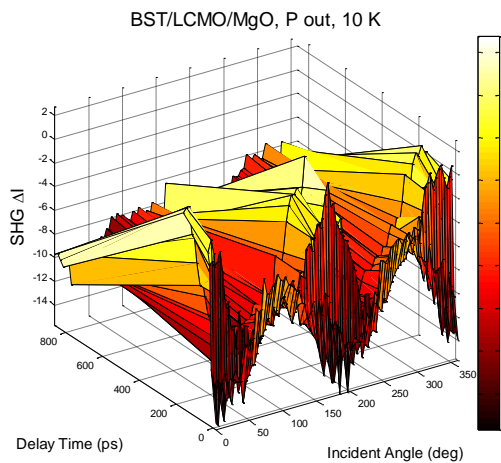


Figure 1. Time-resolved SHG taken at 10 K on a BST/LCMO heterostructure grown on a MgO substrate.

For example, second harmonic generation (SHG) has been previously demonstrated as an important tool for directly accessing the ferroelectric (FE) order parameter. Adding the dimension of time resolution to SHG can give insight into the changes in FE order after ultrafast excitation. We performed TR-SHG experiments on a sample composed of a layer of ferroelectric BST ($\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$) and a layer of ferromagnetic (FM) LCMO ($\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$) or LSMO ($\text{La}_{0.3}\text{Sr}_{0.7}\text{MnO}_3$). Static SHG reveals the potential coupling and enhancement of FE order through charge transfer from LCMO/LSMO. By using an ultrafast optical pulse to directly photoexcite the FM material (without directly

affecting the BST layer), we discovered a time-resolved change in the FE order that is linked to the photoinduced change in magnetization. Figure 1 depicts a 3D plot of the SHG pattern taken at 10 K at various laser time delays after photoexcitation. We are currently in the process of obtaining a more detailed understanding of these results.

In the next year, our efforts will continue to focus on using these advanced ultrafast optical techniques to directly probe SC, FM, AFM, and FE order parameters, as well as the time-dependent interactions between them. One planned experiment is TR-SHG on LuFe_2O_4 , which

will help us unravel the interactions between AFM and FE order parameters. We will also perform two-sided TRKR and optical pump-probe spectroscopy on YBCO/LSMO and BFO/LSMO heterostructures, which will enable us to examine the effects of destroying one order parameter on the other coexisting order. For example, if we photoexcite YBCO (breaking Cooper pairs) while monitoring the TRKR signal from LSMO, we will be able to directly measure the influence of the proximal SC order on magnetization dynamics in LSMO. In addition, we expect to receive novel single crystal samples, such as hexagonal manganites, through our long-standing collaboration with S. W. Cheong at Rutgers University, which we will study with a combination of the above-described techniques.

In actinide materials, the interplay of strong interactions between localized magnetic moments and mobile electrons (Kondo physics), as well as strong spin-orbit coupling, leads to an array of ground states that include magnetic order, superconductivity or metallic behavior with charge carriers whose mass can be hundreds of times the bare electron, i.e. heavy fermions. In this class of materials, small variations in the chemical composition lead to very different ground states, making an understanding of how this happens of fundamental importance. Uranium-based heavy-fermion compounds (such as $UMGa_5$ and UM_3 , $M=Rh, Co, Ni, Pd, Pt, Ga, Sn$) have been largely unexplored in their electronic properties while exhibiting all the characteristics mentioned above. This makes them an ideal playground for studying the dynamic response of heavy fermions in order to understand the origins of the ground state variation. We will investigate quasiparticle dynamics in a series of U-based heavy fermion compounds in which multiple f-electrons contribute to the ground state.

Phonons coupled to other degrees of freedom can result in phase transitions. Examples include (a) electron-phonon coupling that results in superconductivity, (b) the emergence of colossal magnetoresistance (CMR) from polaron dynamics in manganites and related compounds; and others. The effect of thermal energy in the phonon system on equilibrium properties is to some extent understood. It can be described by the temperature dependence of the order parameter, and a critical temperature above which the ordered phase disappears. How does this differ from the situation in which the phonons are excited coherently (non-thermally) by an ultrafast terahertz or IR pulse? Using the first principles techniques we have recently developed to calculate the fully quantum dynamics of coupled electron-phonon systems, we will study dilute Cooper pairs, essentially bipolarons (and the corresponding polarons), in the presence of driven optical phonons. A hypothetical scenario that we will investigate is that driving at the unperturbed optical phonon frequency excites distant phonons that may act somewhat like heat, and break apart the Cooper pairs. It is known, however, from previous calculations that phonons are locally softened and become nonlinear in the vicinity of polarons and bipolarons. We speculate that driving at a carefully chosen frequency somewhat below the bulk optical phonon frequency may selectively excite phonons only in the immediate vicinity of a bipolaron or Cooper pair, which can result in a new type of quasiparticle Q^* containing a bound (softened) phonon excitation. In the strong coupling regime, the Q^* particle can be much lighter than an ordinary bipolaron, suggesting the possibility of a higher T_c when they condense. We plan to investigate this and other scenarios both theoretically and experimentally.

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1. D. Golez, J. Bonca, L. Vidmar, and S. A. Trugman, "Relaxation dynamics of the Holstein polaron," submitted to Phys. Rev. Lett. (2012).

2. J. Lee, S. A. Trugman, C. D. Batista, C. L. Zhang, D. Talbayev, X. S. Xu, S. W. Cheong, D. A. Yarotski, A. J. Taylor, and R. P. Prasankumar, "Probing the interplay between quantum fluctuations and magnetic ordering in LuFe_2O_4 ", submitted to Nature Comm. (2012).
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12. D. Talbayev, S. A. Trugman, Seongsu Lee, Hee Taek Yi, S.-W. Cheong, and A. J. Taylor, "Long-wavelength magnetic and magnetoelectric excitations in the ferroelectric antiferromagnet BiFeO_3 ," Phys. Rev. B **83**, 094403 (2011).
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Photo-Electron Interactions in Dirac Quantum Materials

Xiaodong Xu, Assistant Professor
University of Washington
351560 UW physics C121, Seattle, WA 98195-1560
Phone: 206-543-8444, Email: xuxd@uw.edu

Operations of current electronic and photonic devices are based mainly on charge and spin internal degrees of freedom. However, a breakthrough in advanced energy technologies may emerge from a new family of devices, which will employ new materials that exploit principles and degrees of freedom other than charge and spin. There have been promising new materials emerging in the last few years, such as graphene, topological insulators, and, most recently, atomically-thin semiconductors. These new systems offer unique physical properties for possible unprecedented energy harvesting technologies. Here, we propose to apply the combination of optical spectroscopy with electrical transport measurements to investigate the physical properties of these new systems (Figure).

Graphene is a single sheet of carbon atoms arranged in a honeycomb lattice. The unique electronic properties of graphene set it apart from other two-dimensional (2D) electron systems. It has a linear electronic spectrum (Dirac cone), in which low energy electrons behave like relativistic particles and obey a massless-Dirac equation instead of the Schrödinger equation. Even though it is the thinnest material in the world, graphene has excellent electronic, optical, and mechanical properties. Such a rare combination of exceptional physical properties enables graphene to be a superior candidate for applications in ultrafast, broadband, and energy efficient optoelectronics. Recent theoretical and experimental progresses (including ours) have shown possible carrier multiplication in graphene. Our plan is to comprehensively investigate this effect using high quality graphene FETs by spatial and temporal resolved photocurrent measurements, which may lead to new photovoltaics.

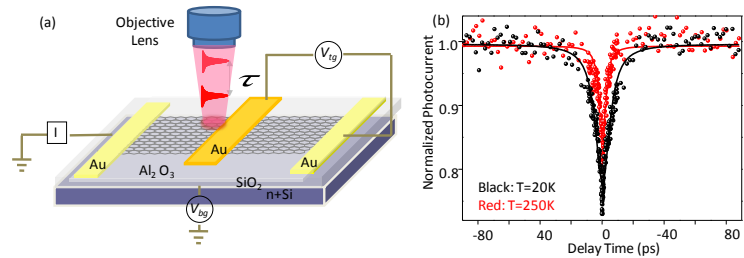


Figure. (a) Schematic of ultrafast pump-probe photocurrent measurements of a graphene p-n junction. (b) Measured photocurrent dynamics at 250 K (black) and 20 K (red).

Bi_2Se_3 is a well-known 3D topological insulator, which is insulating in the bulk but has gapless surface states protected by bulk-topology. Exotic optoelectronic response has been theoretically predicted in this new system, originating from the spin-momentum locked surface states. In our lab, we have also shown interesting chiral edge photocurrent from Bi_2Se_3 nanoribbons, which is ascribed to the strong Rashba spin-orbital coupling induced surface states. Our plan is to further investigate the optoelectronic response and its dynamics in topologically protected surface states.

Atomically-thin semiconductors have been recently found in the group VI transition metal dichalcogenides MX_2 , where M is either W or Mo, and X represents S or Se. In monolayer MX_2 , M and X form hexagonal lattice structure in a prismatic coordination, with energy degenerate valleys located at the corners of the Brillouin zone. Due to the broken inversion symmetry, we have predicted that these valleys can be distinguished by physical quantities such as valley magnetic moments and valley polarizations. For example, there are circularly-polarized optical selection rules associated with the valley indexes. Recent experiments (including ours) demonstrated optical generation of valley polarization by optical pumping. We have further demonstrated the electrical control of valley polarization in bilayer MoS_2 . The next experiment is to apply ultrafast optical techniques to investigate valley dynamics.

Imaging, Dynamics, and Reactivity of Interfaces Important to the Sciences of Energy Conversion and Storage

H. You, D. Fong, P. H. Fuoss
Materials Science Division
Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439
(630) 252-3429; (630) 252-7777(Fax), hyou@anl.gov

Knowledge of the structure and dynamics of interfaces is often critical to our understanding of catalytic and chemical processes directly relevant to energy conversion and storage. Such processes occur under highly active, often complex or extreme environments. One of the best ways to study the processes in such environments is to use hard x-rays that can penetrate chamber walls and gas ambients. We have shown in previous years that the dynamics and reactivity of interfaces in real operating conditions can be measured with coherent x-rays and x-ray photon correlation measurements. These interface-sensitive coherent x-ray techniques will be further developed for, and applied to, interfaces important and relevant to the sciences of energy conversion and storage devices.

In the coming two years, we will focus on real-space imaging of the interfaces using coherent x-ray diffraction techniques. We will develop lensless imaging techniques suitable for the examining interfaces in surface-scattering reflection geometry. There has been remarkable progress in use of x-rays for imaging non-periodic objects, after realizing that the phase problem can be overcome iteratively when “oversampling” the diffraction intensities in reciprocal space.^{1,2} In particular, ptychography³ has gained considerable interest due not only to its applicability to non-periodic extended objects but also to its remarkable robustness and rapid convergence in obtaining unique images. A particularly useful lensless imaging technique measures outgoing x-rays in the far field, one meter or farther away from the sample, allowing operation with a chamber where the sample can be placed in an environment at least 20 cm from any optical elements such as lenses, slits, or detectors. This enables investigations of samples and processes in real environments in real time completely free from the lenses or optical elements. Thus, x-ray ptychography provides a pathway to *in-situ* imaging of the interfaces during active reactions.

The first step in our plan to develop these new capabilities is imaging surfaces and interfaces as topographic height distributions. An example of a common height distribution is the step structures of the surfaces or interfaces of simple semiconductor and metals. In our preliminary study, we found that a height distribution in a reflection scattering geometry can be projected to an extended, non-periodic phase object in a forward small-angle scattering geometry. This projection allows us to use the ptychography techniques previously developed for imaging objects in small angle scattering to image the surface height distributions in a reflection surface scattering geometry, but with a considerably higher spatial resolution due to the large momentum transfers of the reflection geometry. The project will, in principle, allow us to image monoatomic step structures with lateral resolutions of tens of nanometers. In coming years, we will implement this projection approach and further develop the lensless microscopy for in situ investigations of materials important for energy storage and conversion devices. In this talk and poster, we will present an outline of the projection scheme and present recent simulation studies that guide our future development.

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Title: Ultrafast Spectroscopy of Gap Formation and Dynamics in Correlated Electronic Systems

Subtask contact: Jianxin Zhu

Address: MS B262, T-4, Los Alamos National Laboratory, Los Alamos, NM 87545

Email: jxzhou@lanl.gov

PI: Stuart Trugman

Address: MS K771, MPA-CINT, Los Alamos National Laboratory, Los Alamos, NM 87545

Email: sat@lanl.gov

Future Plans:

We propose to develop a suite of new theoretical approaches to understand the physics of quasiparticle excitations and gap formation in strongly correlated materials, with an emphasis on *f*-electron systems. These new approaches will be built on LANL-unique achievements in modeling the ultrafast response in correlated electron systems. The exact diagonalization of a simple but self-consistent model will form the basis for exact treatment of quasiparticle formation and dynamics and the evolution of self-energy. Additionally, a novel mean-field approach will be developed. It includes a full microscopic effective field theory to treat the interactions between electronic and/or lattice degrees of freedom in the presence of a laser pump field in the microscopic Hamiltonian with interactions.

Although it is well accepted that in *f*-electron systems, the interplay between the Coulomb repulsion of localized *f*-electrons and their hybridization to extended conduction electrons is responsible for most of their exotic properties including magnetism, heavy fermionic behavior, and unconventional superconductivity as well as quantum criticality, a full understanding of the underlying microscopic processes remains a scientific challenge. We will focus on understanding ultrafast dynamics in *f*-electron systems to untangle these competing degrees of freedom by addressing the unresolved issues of momentum-dependent *f*-electron hybridization, multiple gapping, exotic ordering, and the coexistence and interplay of competing phases. We will start with a periodic Anderson lattice model in the presence of a time-dependent field, and calculate the time-resolved optical conductivity and spectral function in a heavy fermion system with the existence of a hybridization gap. By tuning the strength of the time-dependent field, we will be able to selectively study the quasiparticle and gap dynamics. The theoretical approach will be verified by comparing the obtained results with ultrafast optical/mid-IR spectroscopy and time/angle-resolved photoemission spectroscopy measurements on UPd₂Al₃, a heavy fermion system known to have a single hybridization gap. With a full energy-, momentum-, and time-resolved picture of electronic self-energy, we will differentiate the timescales unique to quasiparticle dynamics and hybridization gap recovery, driving our insights into the heavy fermion behavior in *f*-electron systems to an even deeper level.

As appropriate, the theoretical approach will be generalized to study the role of electron-phonon coupling in the heavy fermion systems, and the situation with competing ordered phases.

Relevant Publications:

1. J. Tao, R. P. Prasankumar, E. E. M. Chia, A. J. Taylor, and J.-X. Zhu, "Theory of ultrafast carrier dynamics in high-temperature superconductors: Pump fluence dependence," *Phys. Rev. B* **85**, 144302 (2012).
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Participant List

Participant List

Name	Organization	E-Mail
Abbamonte, Peter	University of Illinois at Urbana-Champaign	abbamonte@mrl.illinois.edu
Averitt, Richard	Boston University	raveritt@bu.edu
Billinge, Simon	BNL / Columbia University	billinge@bnl.gov
Bozin, Emil	BNL / Columbia University	bozin@bnl.gov
Brock, Joel	Cornell University	joel.brock@cornell.edu
Budai, John	Oak Ridge National Laboratory	budaijd@ornl.gov
Burns, Clement	Western Michigan University	clement.burns@wmich.edu
Cahill, David	University of Illinois at Urbana-Champaign	d-cahill@illinois.edu
Campuzano, Juan Carlos	Argonne National Laboratory	campuzano@anl.gov
Chen, Jihua	Florida International University	chenj@fiu.edu
Chiang, Tai C.	University of Illinois at Urbana-Champaign	tcchiang@illinois.edu
Clarke, Roy	University of Michigan	royc@umich.edu
Cornelius, Andrew	University of Nevada, Las Vegas	alcornel@unlv.nevada.edu
Crockett, Teresa	U.S. Department of Energy	teresa.crockett@science.doe.gov
DeCamp, Matthew	University of Delaware	mdecamp@udel.edu
Devereaux, Thomas	SLAC / Stanford University	tpd@slac.stanford.edu
Dürr, Hermann	SLAC National Accelerator Laboratory	hdurr@slac.stanford.edu
Evans, Paul	University of Wisconsin-Madison	evans@engr.wisc.edu
Fadley, Charles	Lawrence Berkeley National Laboratory	Fadley@lbl.gov
Fischer, Peter	Lawrence Berkeley National Laboratory	PJFischer@lbl.gov
Fong, Dillon	Argonne National Laboratory	fong@anl.gov
Fuoss, Paul	Argonne National Laboratory	fuoss@anl.gov
Gedik, Nuh	Massachusetts Institute of Technology	gedik@mit.edu
Hasan, M. Zahid	Princeton University	mzhasan@princeton.edu

Headrick, Randall	University of Vermont	rheadrick@uvm.edu
Hill, John	Brookhaven National Laboratory	hill@bnl.gov
Himpsel, Franz	University of Wisconsin-Madison	fhimpsel@wisc.edu
Horton, Linda	U.S. Department of Energy	linda.horton@science.doe.gov
Hussain, Zahid	Lawrence Berkeley National Laboratory	Zhussain@lbl.gov
Johnson, Erik	Brookhaven National Laboratory	erik@bnl.gov
Kaindl, Robert	Lawrence Berkeley National Laboratory	RAKaindl@lbl.gov
Kapteyn, Henry	JILA/University of Colorado	henry.kapteyn@colorado.edu
Kerch, Helen	U.S. Department of Energy	helen.kerch@science.doe.gov
Kevan, Steve	University of Oregon	kevan@uoregon.edu
Kim, Ki-Yong	University of Maryland	kykim@umd.edu
Kirchmann, Patrick	SLAC / Stanford University	kirchman@slac.stanford.edu
Kiser, Lee-Ann	Oak Ridge Institute for Science and Education	Lee-Ann.Kiser@orise.orau.gov
Kortright, Jeffrey	Lawrence Berkeley National Laboratory	jbkortright@lbl.gov
Lee, Wei-Sheng	SLAC / Stanford University	leews@stanford.edu
Lindenberg, Aaron	SLAC / Stanford University	aaronl@stanford.edu
Ludwig, Karl	Boston University	ludwig@bu.edu
Mao, Hokwang (Dave)	Carnegie Institution of Washington	mao@gl.ciw.edu
Mao, Wendy	SLAC / Stanford University	wmao@stanford.edu
Mochrie, Simon	Yale University	simon.mochrie@yale.edu
Moore, Robert	SLAC / Stanford University	rgmoore@slac.stanford.edu
Murnane, Margaret	JILA/University of Colorado	murnane@jila.colorado.edu
Nilsson, Anders	SLAC National Accelerator Laboratory	nilsson@slac.stanford.edu
Orenstein, Joseph	LBNL / University of California, Berkeley	jworenstein@lbl.gov
Parise, John	Stony Brook University	john.parise@stonybrook.edu
Petkov, Valeri	Central Michigan University	petkov@phy.cmich.edu
Prasankumar, Rohit	Los Alamos National Laboratory	rpprasan@lanl.gov

Prendergast, David	Lawrence Berkeley National Laboratory	dgprendergast@lbl.gov
Reis, David	SLAC National Accelerator Laboratory	dreis@slac.stanford.edu
Rollett, Anthony	Carnegie Mellon University	rollett@andrew.cmu.edu
Russell, Thomas	University of Massachusetts Amherst	russell@mail.pse.umass.edu
Schoenlein, Robert	Lawrence Berkeley National Laboratory	rwschoenlein@lbl.gov
Shen, Guoyin	Carnegie Institution of Washington	gshen@ciw.edu
Shen, Zhi-Xun	SLAC National Accelerator Laboratory	zxshen@stanford.edu
Shpyrko, Oleg	University of California, San Diego	oleg.shpyrko@gmail.com
Silva, Tom	NIST, Boulder	silva@boulder.nist.gov
Stephenson, Brian	Argonne National Laboratory	aps-director@aps.anl.gov
Stohr, Joachim	SLAC National Accelerator Laboratory	stohr@slac.stanford.edu
Struzhkin, Viktor	Carnegie Institution of Washington	vstruzhkin@gl.ciw.edu
Suter, Robert	Carnegie Mellon University	suter@cmu.edu
Toney, Michael	SLAC / Stanford University	mftoney@slac.stanford.edu
Wilkins, Stuart	Brookhaven National Laboratory	swilkins@bnl.gov
Wilson, Lane	U.S. Department of Energy	lane.wilson@science.doe.gov
Xu, Xiaodong	University of Washington	xuxd@uw.edu
You, Hoydoo	Argonne National Laboratory	hyou@anl.gov
Zhu, Jian-Xin	Los Alamos National Laboratory	jxzhu@lanl.gov