X-ray Scattering
Principal Investigators' Meeting

Hilton Washington DC North/Gaithersburg
Gaithersburg, Maryland
November 5–7, 2014

This document was produced under contract number DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

The research grants and contracts described in this document are supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division.

Foreword

This book of abstracts summarizes the scientific content of the 2014 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 5-7, 2014, at the Hilton Washington DC North/Gaithersburg in Gaithersburg, Maryland, is the fourth 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. 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 X-ray Scattering Principal Investigators' Meeting
Hilton Washington DC North/Gaithersburg, Gaithersburg, Maryland
November 5–7, 2014

Wednesday, November 5

8:10	Introduction and BES Program Overview, *Helen Kerch* (BES)	
8:30	Overview talk – *Oleg Shpyrko* (University of California, San Diego)	(Poster A1)
8:55	(8 minute talks, followed by a poster)	
	Karl Ludwig (Boston University)	(Poster A2)
	Steve Kevan (University of Oregon)	(Poster A3)
	Roy Clarke (University of Michigan)	(Poster A4)
	John Freeland (Argonne National Lab)	(Poster A5)
	Paul Evans (University of Wisconsin)	(Poster A6)
9:35	Poster session and break	
10:30	Overview talk – *Stephan Hruszkewycz* (Argonne National Lab)	(Poster B1)
10:55	(8 minute talks, followed by a poster)	
	Brian Stephenson (Argonne National Lab)	(Poster B2)
	Dillon Fong (Argonne National Lab)	(Poster B3)
	Hoydoo You (Argonne National Lab)	(Poster B4)
	Randy Headrick (University of Vermont)	(Poster B5)
	Franz Himpsel (University of Wisconsin)	(Poster B6)
11:35	Poster session and break	
12:30	Working lunch – (Lunch discussion topic TBD)	
2:00	Overview talk – *Xiaodong Xu* (University of Washington)	(Poster C1)
2:25	(8 minute talks, followed by a poster)	
	Di Xiao (Carnegie Mellon University)	(Poster C2)
	Tony Heinz (SLAC National Accelerator Lab)	(Poster C3)
	Denis Karaiskaj (University of South Florida)	(Poster C4)
	David Hilton (University of Alabama – Birmingham)	(Poster C5)
	Jie Shan (Penn State University)	(Poster C6)
3:05	Poster session and break	
4:00	Overview talk – *Rick Averitt* (University of California, San Diego)	(Poster D1)

4:25 (8 minute talks, followed by a poster)

Dimitri Basov (University of California, San Diego)	(Poster D2)
Venkat Gopalan (Penn State University)	(Poster D3)
Roman Engel-Herbert (Penn State University)	(Poster D4)
Haidan Wen (Argonne National Lab)	(Poster D5)
Youngduck Kim (Columbia University)	(Poster D6)
Michael Fogler (University of California, San Diego)	(Poster D7)

5:05 Poster session and break

6:00 Adjourn for the day, Dinner, Informal evening activities and discussions

Thursday, November 6

8:20 Introduction for the day, general discussion, *Lane Wilson* (BES)

8:30 Overview talk – *Mark Dean* (Brookhaven National Lab) (Poster E1)

8:55 (8 minute talks, followed by a poster)

Clem Burns (Western Michigan University)	(Poster E2)
John Hill (Brookhaven National Lab)	(Poster E3)
Emil Bozin (Brookhaven National Lab)	(Poster E4)
Peter Abbamonte (University of Illinois – UC)	(Poster E5)
Tai Chiang (University of Illinois – UC)	(Poster E6)

9:35 Poster session and break

10:30 Overview talk – *Tom Devereaux* (SLAC National Accelerator Lab) (Poster F1)

10:55 (8 minute talks, followed by a poster)

Wei-Sheng Lee (SLAC National Accelerator Lab)	(Poster F2)
Aaron Lindenberg (SLAC National Accelerator Lab)	(Poster F3)
Wendy Mao (SLAC National Accelerator Lab)	(Poster F4)
David Reis (SLAC National Accelerator Lab)	(Poster F5)
Mariano Trigo (SLAC National Accelerator Lab)	(Poster F6)

11:35 Poster session and break

12:30 Working lunch – (Lunch discussion topic, TBD)

2:00 Overview talk – *Margaret Murnane* (University of Colorado) (Poster G1)

2:25 (8 minute talks, followed by a poster)

Mike Schneider (NIST – Colorado)	(Poster G2)
Henry Kapteyn (University of Colorado, KMLabs)	(Poster G3)

	Hermann Dürr (SLAC National Accelerator Lab)	(Poster G4)
	Jo Stöhr (SLAC National Accelerator Lab)	(Poster G5)
	Alexander Reid (SLAC National Accelerator Lab)	(Poster G6)
3:05	Poster session and break	
4:00	Overview talk – *Andrew Millis* (Columbia University)	(Poster H1)
4:25	(8 minute talks, followed by a poster)	
	James Rondinelli (Northwestern University)	(Poster H2)
	Zahid Hasan (Princeton University)	(Poster H3)
	Alessandra Lanzara (Lawrence Berkeley National Lab)	(Poster H4)
	Robert Kaindl (Lawrence Berkeley National Lab)	(Poster H5)
	Nuh Gedik (Massachusetts Institute of Technology)	(Poster H6)
5:05	Poster session and break	
6:00	Adjourn for the day, Dinner, Informal evening activities and discussions	

Friday, November 7

8:00	(8 minute talks, followed by a poster)	
	Guoyin Shen (Carnegie Institution for Science)	(Poster I1)
	David Mao (Carnegie Institution for Science)	(Poster I2)
	Viktor Struzhkin (Carnegie Institution for Science)	(Poster I3)
	John Parise (SUNY – Stonybrook)	(Poster I4)
	Valeri Petkov (Central Michigan University)	(Poster I5)
	Simon Billinge (Brookhaven National Lab)	(Poster I6)
	Ki-Yong Kim (University of Maryland)	(Poster I7)
	Uwe Bergmann (SLAC National Accelerator Lab)	(Poster I8)
9:04	Poster session and break	
10:00	Overview talk – *Z. X. Shen* (SLAC National Accelerator Lab)	(Poster J1)
10:25	(8 minute talks, followed by a poster)	
	Donghui Lu (SLAC National Accelerator Lab)	(Poster J2)
	Robert Moore (SLAC National Accelerator Lab)	(Poster J3)
	Brian Moritz (SLAC National Accelerator Lab)	(Poster J4)
	Patrick Kirchmann (SLAC National Accelerator Lab)	(Poster J5)
	Jonathan Sobota (SLAC National Accelerator Lab)	(Poster J6)
11:05	Poster session and break	
12:00	Brief parting remarks and discussion, Adjourn	

Table of Contents

Table of Contents

Abstracts

Resonant Soft X-Ray Scattering Studies of Spontaneous and Engineered Electronic Order in Transition Metal Oxides

Peter Abbamonte
abbamonte@mrl.illinois.edu
Department of Physics and Seitz Materials Research Laboratory
University of Illinois, Urbana, IL, 61801

Program Scope

The goal of this project is to understand the interplay between engineered nanoscale order, created artificially by nanofabrication techniques, and the innate electronic instabilities in transition metal oxides. By "instability" we refer here to spontaneous electronic order such as stripe phases, charge or spin density waves, orbital order, or intrinsic electronic inhomogeneity due to proximity to a quantum critical point. The long-term goal is to understand what role inhomogeneous phases play in the fundamental properties of interacting electron systems, and how such inhomogeneity could interact with artificial structures to create new phenomena.

An integral part of this activity the development of new x-ray scattering techniques and their application to targeted problems in interacting electron systems.

Recent Progress: *Discovery of charge density wave domain walls in the vicinity of the superconducting dome in 1T-$TiSe_2$*

Unconventional superconductivity is nearly always found in the vicinity of another ordered state, such as antiferromagnetism, charge density wave (CDW), or stripe order. This suggests a fundamental connection between superconductivity and fluctuations in some other order parameter.

To gain a deeper insight into this phenomenon, we used high-pressure x-ray scattering to study the CDW order in the layered dichalcogenide $TiSe_2$, which is known to exhibit superconductivity when the CDW is suppressed by pressure [1] or Cu intercalation [2]. These experiments use a new setup in which x-ray scattering can be carried out in a diamond anvil cell at low temperatures.

We succeeded in suppressing the CDW in $TiSe_2$ fully to zero temperature, establishing for the first time the existence of a quantum critical point (QCP) at $P_c = 5.1 \pm 0.2$ GPa, which is more than 1 GPa beyond the end of the SC region (Fig. 1). Unexpectedly, at P = 3 GPa we

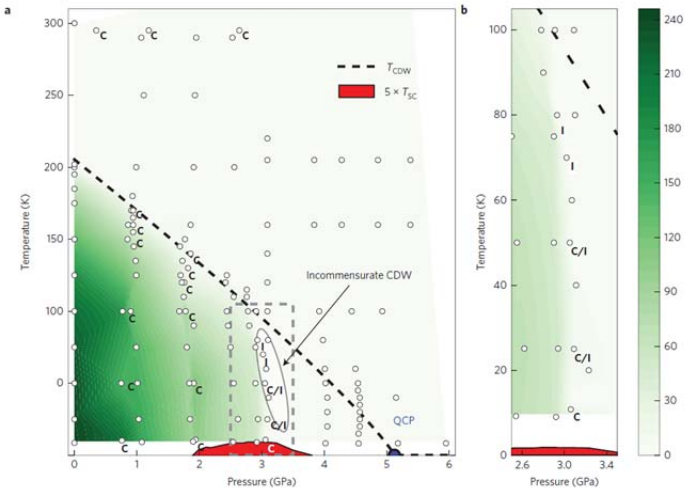


Figure 1 Pressure-temperature phase diagram of 1T-$TiSe_2$, showing the existence of an incommensurate phase, indicating the presence of domain wall fluctuations in the vicinity of the superconducting dome.

observed a reentrant, weakly first order, incommensurate phase, indicating the presence of a Lifshitz tricritical point somewhere above the superconducting dome. Our study suggests that superconductivity in $TiSe_2$ may not be connected to the amplitude QCP itself, but to the dynamics of CDW domain walls. This study was recently published in Nature Physics [3].

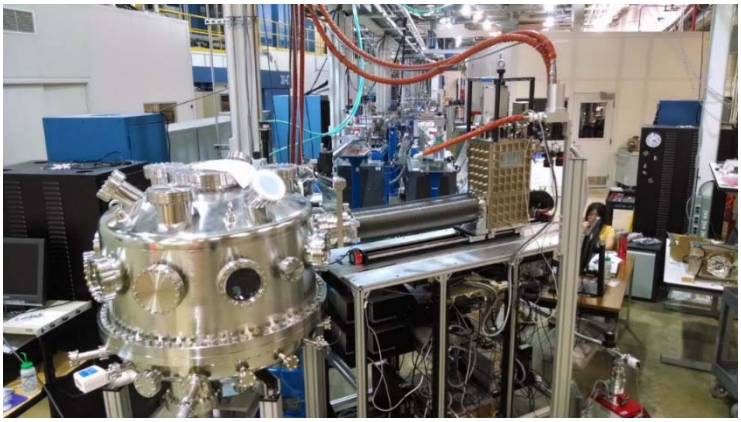


Figure 2 New RSXS endstation at the IEX-CDT beam line at the Advanced Photon Source, showing the 240 pixel TES array detector installed last summer. TES detectors were previously used study the cosmic microwave background, e.g., at the BICEP2 facility at the South Pole Telescope. IEX-CDT will be the first facility to use these detectors for scattering experiments.

Future Plans: *Scattering with superconducting TES detectors at the Advanced Photon Source*

After many years of effort, our new IEX-CDT soft x-ray beam line at the Advanced Photon Source is running and has entered the commissioning stage (Fig. 2). First light was achieved in February and photons were admitted into the scattering endstation in June. This facility will transform the way resonant soft x-ray scattering (RSXS) experiments are done, and will—for the first time—allow studies of fluctuating or glassy charge and spin order in correlated materials.

They key innovation at IEX-CDT will be the first ever use of transition edge sensor (TES) detectors (built at NIST in Boulder, CO) to perform scattering experiments at a synchrotron (Fig. 2). A TES is a microcalorimeter that detects individual x-ray photons through the temperature change of a micron-sized, superconducting island. These detectors exhibit unit quantum efficiency and intrinsic energy resolution of 1 eV. Previously, such detectors have mainly been used for cosmic microwave background experiments, notably at the BICEP2 experiment at the South Pole Telescope. These detectors will solve the vexing fluorescence problem in RSXS, i.e., the presence of fluorescence that swamps the elastic and quasi-elastic scattering of interest. This will allow studies of disordered phenomena such as glassy charge or spin order, which is believed, for example, to be relevant to the mechanism of superconductivity in many unconventional superconductors.

References

1. A. F. Kusmartseva, et al., Pressure Induced Superconductivity in Pristine 1T-$TiSe_2$, Phys. Rev. Lett. 103, 236401 (2009)
2. E. Morosan, et al., Superconductivity in Cu_xTiSe_2, Nature Phys. **2**, 544 (2006)
3. Y. I. Joe, et al., Emergence of charge density wave domain walls above the superconducting dome in 1T-$TiSe_2$, Nature Phys. **10**, 421 (2014)
4. P. Abbamonte, et al., Spatially modulated Mottness in $La_{2-x}Ba_xCuO_4$, Nature Phys. **1**, 155 (2005)

Publications (Oct. 2012 – present | this activity only)

1. L. K. Wagner, P. Abbamonte, Effect of electron correlation on the electronic structure and spin-lattice coupling of high-T_c cuprates: Quantum Monte Carlo calculations, Phys. Rev. B **90**, 125129 (2014)
2. A. Kogar, S. Vig, Y. Gan, P. Abbamonte, Temperature-resolution anomalies in the reconstruction of time dynamics from energy-loss experiments, J. Phys. B, Invited Issue on Ultrafast Electron and Molecular Dynamics **47**, 12 (2014)
3. J. C. T. Lee, A. R. Damodaran, R. Ramesh, L. W. Martin, P. Abbamonte, X-ray diffraction studies of stripelike ferroelectric domains in thin films of $BiFeO_3$, Phys. Rev. B **89**, 214104 (2014)
4. Y. I. Joe, X. M. Chen, P. Ghaemi, K. D. Finkelstein, G. A. de la Peña, Y. Gan, J. C. T. Lee, S. Yuan, J. Geck, G. J. MacDougall, T. C. Chiang, S. L. Cooper, E. Fradkin, P. Abbamonte, Emergence of charge density wave domain walls above the superconducting dome in $TiSe_2$, Nature Physics **10**, 421 (2014)
5. J. L. McChesney, R. Reininger, M. Ramanathan, C. Benson, G. Srajer, P. Abbamonte, J. C. Campuzano, N. Inst. Methods A **746**, 98 (2014)
6. C.-C. Lee, X. M. Chen, Y. Gan, C.-L. Yeh, H. C. Hsueh, P. Abbamonte, W. Ku, First-Principles Method of Propagation of Tightly Bound Excitons: Verifying the Exciton Band Structure of LiF with Inelastic x-Ray Scattering, Phys. Rev. Lett. **111**, 157401 (2013)
7. D. Benjamin, D. Abanin, P. Abbamonte, E. Demler, Microscopic theory of resonant soft x-ray scattering in systems with charge order: The Example of Charge Stripes in High-Temperature Cuprate Superconductors, Phys. Rev. Lett. **110**, 137002 (2013)
8. S. Smadici, B. B. Nelson-Cheeseman, A. Bhattacharya, P. Abbamonte, Interface ferromagnetism in a $SrMnO_3/LaMnO_3$ superlattice, Phys. Rev. B **86**, 174427 (2012)

See also (Listing of funding info not permitted by journal):

9. P. Abbamonte, Picking up fine vibrations, Nature Physics **9**, 759 (2013)
10. P. Abbamonte, Resonant Inelastic X-Ray Scattering, Synchrotron Radiation News **25**, 2 (2012)

Multifunctional Materials Research Using Ultrafast Optical Spectroscopy
DE-FG02-09ER46643

R. D. Averitt, UC San Diego and Boston University, Department of Physics

Program Scope

A major challenge in condensed matter physics is photoactive control of quantum phases. Correlated transition metal oxides are particularly sensitive to external control because of energy degeneracy in a complex degree-of-freedom landscape. Photoexcitation provides a route to dynamically explore this landscape, initiating reconfiguration of the microscopic electronic and structural properties, resulting in the enhancement or emergence of novel phases. It is increasingly possible to precisely tune the local environment in complex materials providing the means to control macroscopic functionality and offering a glimpse into how microscopic interactions conspire towards emergent behavior. Dynamic tuning with pulsed electromagnetic fields can reduce or overcome energetic barriers enabling access to transient or metastable states [1-4]. Transition metal oxides (TMOs) are of considerable interest with regards to dynamic tuning because of strong structure-function coupling arising, predominantly, from octahedral rotations and distortions [5]. In this program, these ideas are being experimentally explored in the vanadates, manganites, and nickelates with a primary emphasis on exploring the insulator-to-metal (IMT) transition using terahertz time domain spectroscopy, which includes optical-pump terahertz-probe spectroscopy (OPTP) and terahertz-pump terahertz-probe spectroscopy (TPTP).

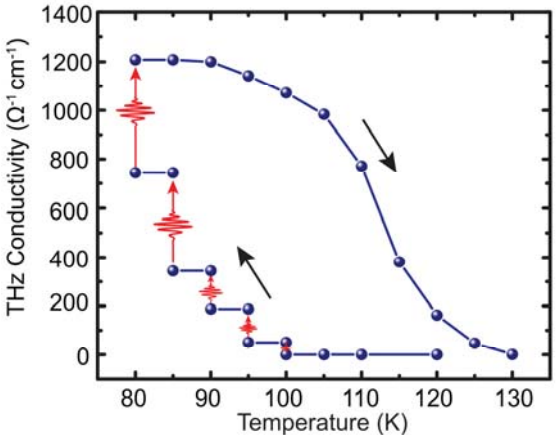


Photo-induced IMT in LCMO thin film. With decreasing temperature, two measurements of the THz conductivity are taken at each temperature. The first is in the absence of photoexcitation. The second measurement is following photoexcitation with sub-50fs 1.5eV pulses. At 100K and below, photoexcitation results in an increase in the conductivity. The conductivity at a given temperature reaches a final state that is robust, yielding a step-like progression as the temperature is decreased. Further, the value of the conductivity is maintained upon removal of the photoexcitation. With increasing temperature (in the absence of photoexcitation) the conductivity decreases with a return to the insulating phase at 130K.

Recent Progress

Results have been obtained on strained $La_{2/3}Ca_{1/3}MnO_3$ (LCMO), V_2O_3, and $NdNiO_3$ (NNO) thin films. For LCMO, we have observed a metastable photoinduced IMT that does not require external stimuli to be maintained. In particular, below 100K, photoexcitation (with 1.55 eV pulses) recovers a strain-hidden ferromagnetic metallic phase, similar to what can be achieved with applied static magnetic fields (Fig. 1) [6]. In addition, single shot measurements reveal that the transition is not a cumulative effect, but rather arises from a cooperative process requiring a critical absorbed photon density. Analysis reveals a step-wise transition with a distinct threshold with magnetoelastic coupling playing a primary role in stabilizing the photoinduced metallic phase.

For V_2O_3, we have investigated (using OPTP) the dynamics of the IMT. We have identified a scaling of the conductivity dynamics upon renormalizing the time axis with a simple power law that depends solely on the experimentally determined temperatures. The dynamics arise from nucleation and growth of the metallic phase, which can be described by the Avrami model. This shows that the temporal scaling arises from spatial scaling of the growth of the metallic volume fraction, highlighting the self-similar nature of the dynamics [7].

Our studies of NNO films also utilize OPTP to investigate the IMT. The dynamics are in stark contrast to V_2O_3, exhibiting a larger and faster conductivity increase with no evidence of nucleation and growth. It appears that the conductivity dynamics closely follow the magnetization dynamics [8,9]. These results are currently being written up for publication.

Future Plans

During the next year of this program, we are pursuing terahertz-induced dynamics in V_2O_3 and NNO, and LCMO to compare with our previous work on VO_2 with a goal of determining the energy density thresholds of THz electric field induced IMT. This will utilize our expertise in sculpting the spatio-temporal profiles of THz pulses using metamaterials. In addition, the metastable nature of the transition in strained LCMO will be investigated focusing on micro-to-meso scale aspects of the IMT. This will include nano-probe x-ray studies at the Advanced Photon Source and ultrafast scattering at the Linac Coherent Light Source in collaboration with H. Wen and J. Freeland, and near-field studies in collaboration with D. Basov at UCSD. These new experiments are funded under the program "Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures", DE-SC0012375 (V. Gopalan, PI). The expertise in OPTP and TPTP developed in this single-PI program will also be utilized to investigate photoinduced superconductivity under the program "Ultrafast infrared nano-spectroscopy and nano-imaging of unconventional superconductivity in cuprate and pnictide high-T_c systems", DE-SC0012592 (D. Basov, PI).

References

[1] J. Orenstein, "Ultrafast spectroscopy of quantum materials," Phys. Today 65, 44–50 (2012).
[2] J. Zhang, R. D. Averitt, "Dynamics and Control in Complex Transition Metal Oxides," Ann. Rev. Mat. Res. **44**, 19 (2014).
[3] D. Fausti et al., "Light-induced superconductivity in a stripe-ordered cuprate," Science (New York, N.Y.) **331**, 189–91 (2011).
[4] L. Stojchevska et al., "Ultrafast Switching to a Stable Hidden Quantum State in an Electronic Crystal," Science **344**, 177–180 (2014).
[5] J. M. Rondinelli, S. J. May, J. W. Freeland, "Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery," MRS Bulletin **37**, 261–270 (2012).
[6] J. Zhang, et al, "Cooperative photoinduced metastable phase control in strained manganite films," submitted.
[7] E. Abreu, et al , "Dynamic conductivity scaling in photoexcited V_2O_3 thin films," submitted.
[8] E. Abreu, et al, "Coupled conductivity and magnetization dynamics during the photoinduced insulator-metal transition in ultrathin $NdNiO_3$," in preparation.
[9] A. D. Caviglia, et al, "Photoinduced melting of magnetic order in the correlated electron insulator $NdNiO_3$," Phys. Rev. B **88**, 220401(R) (2013).

Publications

[1] J. Zhang, R. D. Averitt, “Dynamics and Control in Complex Transition Metal Oxides,” Ann. Rev. Mat. Res. 44, 19 (2014).
[2] M. Liu, M. Wagner, J. Zhang, A. McLeod, S. Kittiwatanakul, Z. Fei, E. Abreu, M. Goldflam, A. J. Sternbach, S. Dai, K. G. West, J. Liu, S. A. Wolf, R. D. Averitt, D. N. Basov, “Symmetry breaking and geometric confinement in VO_2: Results from three-dimensional infrared nano-imaging,” Appl. Phys. Lett. **104**, 121905 (2014).
[3] M. K. Liu, M. Wagner, E. Abreu, S. Kittiwatanakul, A. McLeod, Z. Fei, M. Goldflam, S. Dai, M. M. Fogler, J. Lu, S. A. Wolf, R. D. Averitt, D. N. Basov, “Anisotropic Electronic State via Spontaneous Phase Separation in Strained Vanadium Oxide Films,” Phys. Rev. Lett. **111**, 096602 (2013).
[4] J. Zhang, X. Tan, M. Liu, S. W. Teitelbaum, K. A. Nelson, D. N. Basov, W. Wu, R.D. Averitt, “Cooperative photoinduced metastable phase control in strained manganite films”, submitted.
[5] E. Abreu, S. Wang, G. Ramirez, M. Liu, J. Zhang, K. Geng, I. K. Schuller, R. D. Averitt, “Dynamic conductivity scaling in photoexcited V_2O_3 thin films,” submitted.
[6] E. Abreu, D. Meyers, K. Geng, J. Zhang, J. Chakhalian, R. D. Averitt, “Coupled conductivity and magnetization dynamics during the photoinduced insulator-metal transition in ultrathin $NdNiO_3$,” in preparation.

Ultrafast infrared nano-spectroscopy and nano-imaging of unconventional superconductivity in high-Tc systems

D.N.Basov (UCSD), R. Averitt (UCSD), M. Fogler (UCSD), J.Hone (Columbia University), A.J. Millis (Columbia University)

Program Scope

High-Tc superconductivity is surpassed by few, if any, other unsolved problems in contemporary physics in terms of its richness, complexity, impact on other fields, and potential technological importance. This multi-PI effort is focused at the investigation of the intrinsic spatio-temporal electromagnetic response of unconventional high-Tc superconductors including copper oxides and iron pnictides. One goal of the proposed work is to carry out pump-probe infrared (IR) spectroscopy and imaging studies with 10-nm spatial resolution and a sub pico second temporal resolution using fundamentally novel instrumentation developed by the team. Ultrafast nano-IR measurements augmented with more conventional diffraction-limited pump-probe experiments will allow our team to study several ongoing problems central to the mysteries of unconventional superconductivity. We will critically examine the hypothesis of local superconductivity at temperatures above the bulk Tc and investigate the possibility for enhancing superconductivity through intense illumination at infrared and THz frequencies. This program will enable an entire suite of experiments previously either impossible or technically implausible, and deliver critically important insights not only for unconventional superconductivity but across the entire field of correlated electron systems.

Recent Progress

We designed and modeled hybrid metamaterial-cuprate structures for the exploration of photo-induced effects in high-Tc superconductors. The initial experiments will be performed using a series of $La_{2-x}Sr_xCuO_4$ (LaSr214) and $La_{2-x}Ba_xCuO_4$ (LaBa214) single crystals revealing interesting interplay between spin/charge ordering and superconductivity. Earlier static infrared data obtained by co-PIs set the stage for modeling. We have chosen to utilize split ring resonator (SRR) implementation of metamaterials for our hybrid structures.

Future Plans

We will investigate photo-induced effects in hybrid SRR-LaSr214 and SRR-LaBa214 structures. We will use a combination of far-field and near field nano-IR methods applied to the same structures.

Towards understanding and control of nano-scale fluctuations in strongly correlated electron systems

S. J. L. Billinge, E. S. Bozin, J. P. Hill and J. M. Tranquada
Condensed Matter Physics & Materials Science Department, Brookhaven National Laboratory

Program Scope

Our goal is to understand the role, ubiquity and importance of nanoscale fluctuations in determining the properties of complex electronic materials. To do this we develop novel nano-sensitive probes and apply them to three scientific objectives: understanding the relationship between nanoscale broken symmetry states and the pseudogap phenomenon in cuprates and charge density wave (CDW) materials, understanding the relationship between nanoscale fluctuations and emergent properties such as superconductivity in cuprates and CDW materials, and understanding the nature and origin of emphanisis, the emergence of local fluctuating distortions on warming, in high performance thermoelectric materials.

Recent Progress

Local symmetry breaking in the pseudogap regime: The focus here is to determine *local* phase diagrams of these systems that exhibit, metal-insulator transitions, emergent behavior and pseudogap phenomena. Using powder diffraction and atomic pair distribution function (PDF) methods, we have discovered evidence for local, fluctuating broken symmetry states well above long-range charge ordered states in $La_{1.67}Sr_{0.33}NiO_4$ and $La_{2-x}Ba_xCuO_4$. We are beginning the process of mapping these out as a function of temperature and doping, and relating them to spectroscopic measures of the pseudogap. These are described in references [1,2]. In addition manuscripts are submitted, or close to submission, showing local dynamic C_2 symmetry breaking in $La_{2-x}Ba_xCuO_4$ over a wide range of temperature and doping, and the first observation of an intraunitcell nematic CDW state in $BaTi_2(As,Sb)_2O$, which is a compound that is intermediate in structure and properties between the cuprate- and iron-based superconductors.

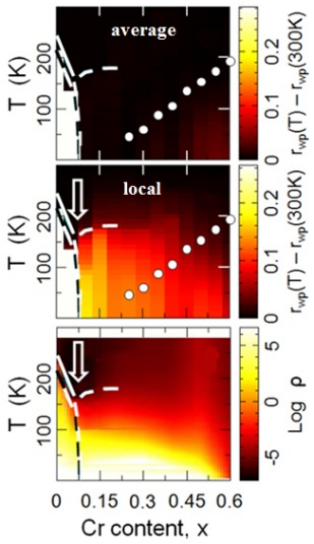


Fig. 1 $Cu(Ir_{1-x}Cr_x)_2S_4$ Average vs local phase diagrams of long range (top) and short range (middle) dimer order. Evolution of charge transport (bottom) [3].

Metal-insulator transitions in spinels: These are model systems for studying the importance and ubiquity of competition and nanoscale heterogeneities in complex electronic materials. They illustrate how the study of local structure and local phase diagrams is essential for understanding the physics of complex materials [3,4]. A comparison of the local and long-range average phase diagrams of $Cu(Ir_{1-x}Cr_x)_2S_4$ is shown in Fig. 1 (top two panels, respectively) and the resistivity of the material (bottom panel) which follows the local phase diagram and not the average one. We believe similar principles operate in the strongly correlated electron systems.

Origin and ubiquity of emphanisis: Following our discovery of emphanisis (defined in the scope) in 2010, we have worked to establish and further characterize the effect. From inelastic neutron scattering study we found evidence of dynamic local fluctuations in incipient ferroelectric PbTe [5], and further found similar effects in the related SnTe system, the first non-lead containing

system to show the effect [6], which also suggested that the ferroelectric and emphanitic responses are of different origin, an issue that needs further exploration. The emphanisis in SnTe is illustrated in Fig. 2 where the PDF peaks become highly non-Gaussian and multi-valued at high temperature.

Technique development: This period saw a number of important developments to the PDF technique for studying local structure, all supported by BES. Notably, we combined PDF with computed tomography (ctPDF) allowing for spatially resolved (with resolution on the 10-100 μm scale) studies of local structure [7]. This is illustrated in Fig. 3. We also demonstrated that it is possible to get semi-quantitative PDFs from electron diffraction data (ePDF) [8].

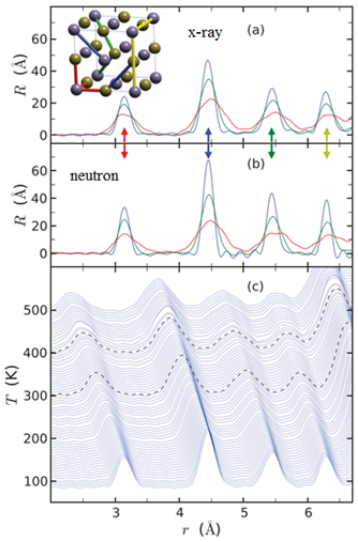


Fig. 2 Local off-centering symmetry breaking in the high temperature regime of SnTe from x-ray PDF and neutron PDF measurements [6].

Future Plans

Local symmetry breaking in the pseudogap regime: We will concentrate next on the important $YBa_2Cu_3O_{6+d}$ compound which was recently shown to have robust charge order competing with superconductivity in the underdoped regime. We are interested to know whether, as we showed in the nickelate and LBCO systems, local fluctuating charge/orbital orders persist over a wider range of temperature and doping using PDF and powder diffraction approaches that were successful in those other systems, and determine its character.

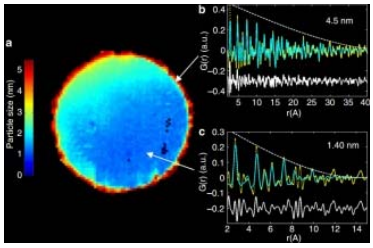


Fig. 3 Distribution of Pd nanoparticle size within the 3mm Φ catalyst body from ctPDF [7].

Symmetry breaking in CDW systems: A similar competition between charge order (in this case a "conventional" charge density wave) and superconductivity has been observed in a number of CDW systems. We will concentrate on two families of such CDW systems initially, 2H-$Ta(Se_{1-x}S_x)_2$ and $Zr(Te_{1-x}Se_x)_3$, in an attempt to find one with a sufficiently robust structural response that we can see the local symmetry broken state in PDF. 2H-$TaSe_2$ and $ZrTe_3$ end-members will be assessed first. In both doping destabilizes long range CDW order and superconductivity emerges, with possible CDW fluctuations persisting.

Origing of Emphanisis: We are now trying to further understand the relationship of emphanisis to ferrolectricity by studying doped PbTe that shows both ferroelectricity and emphanisis. The doping can happen on the metal site (Ge in $Pb_{1-x}Ge_xTe$) or the chalcogen site (S,Se in $PbTe_{1-x}S_x$). In both cases, a few percent of dopants induce ferroelectricity.

References

[1] M. Abeykoon *et al.*, *Phys. Rev. Lett.* **111**, 096404 (2013).
[2] M. Garcia-Fernandez *et al.*, *Phys. Rev. B* **88**, 075134 (2013).
[3] E.S. Bozin *et al.*, *Sci. Rep.* **4**, 4081 (2014).
[4] K.R. Knox *et al.*, *Phys. Rev. B* **88**, 174114 (2013).
[5] K.M.O. Jensen *et al.*, *Phys. Rev. B* **86**, 085313 (2012).
[6] K.R. Knox *et al.*, *Phys. Rev. B* **89**, 014102 (2014).
[7] S.D. M. Jacques et al., *Nat. Commun.* **4**, 2536 (2013).
[8] M. Abeykoon *et al.*, *Z. Kristallogr.* **227**, 248 (2012).

Publications

1. Hefei Hu, Yimei Zhu, Xiaoya Shi, Qiang Li, Ruidan Zhong, John A. Schneeloch, Genda Gu, John M. Tranquada and Simon J. L. Billinge, **Nanoscale coherent intergrowth-like defects in a crystal of $La_{1.9}Ca_{1.1}Cu_2O_{6+\delta}$ made superconducting by high-pressure oxygen annealing**, *Phys. Rev. B*, accepted for publication (2014).
2. H. Chi, H. Kim, J. C. Thomas, G. Shi, K. Sun, M. Abeykoon, E. S. Bozin, X. Shi, Q. Li, X. Shi, E. Kioupakis, A. Van der Ven, M. Kaviany and C. Uher, **Low-temperature structural and transport anomalies in Cu_2Se**, *Phys. Rev. B* **89**, 195209 (2014).
3. N. Lazarevic, E. S. Bozin, M. Scepanovic, M. Opacic, Hechang Lei, C. Petrovic and Z. V. Popovic, **Probing $IrTe_2$ crystal symmetry by polarized Raman scattering**, *Phys. Rev. B* **89**, 224301 (2014).
4. E. S. Božin, K.R. Knox, P. Juhás, Y. S. Hor, J. F. Mitchell and S. J. L. Billinge, **$Cu(Ir_{1-x}Cr_x)_2S_4$: a model system for studying nanoscale phase coexistence at the metal-insulator transition**, *Sci. Rep.* **4**, 4081 (2014).
5. K. R. Knox, E. S. Bozin, C. D. Malliakas, M. G. Kanatzidis and S. J. L. Billinge, **Local off-centering symmetry breaking in the high temperature regime of SnTe**, *Phys. Rev. B* **89**, 014102 (2014).
6. Lei Hechang, Abeykoon Milinda, Wang Kefeng, Bozin Emil S., Ryu Hyejin, Graf D., Warren J. B. and Petrovic C., **Physical properties of $K_xNi_{2-y}Se_2$ single crystals**, *J. Phys: Condens. Mat.* **26**, 015701 (2014).
7. K. R. Knox, A. M. M. Abeykoon, H. Zheng, W.-G. Yin, A. M. Tsvelik, J. F. Mitchell, S. J. L. Billinge and E. S. Bozin, **Local structural evidence for strong electronic correlations in spinel $LiRh_2O_4$**, *Phys. Rev. B* **88**, 174114 (2013).
8. Simon D. M. Jacques, Marco Di Michiel, Simon A. J. Kimber, Xiaohao Yang, Robert J. Cernik, Andrew M. Beale and Simon J. L. Billinge, **Pair distribution function computed tomography**, *Nat. Commun.* **4**, 2536 (2013).
9. Milinda Abeykoon, Emil S. Bozin, Genda Gu, John Hill, John Tranquada and Simon J. L. Billinge, **Evidence for short-range-ordered charge stripes far above the charge-ordering transition in $La_{1.67}Sr_{0.33}NiO_4$**, *Phys. Rev. Lett.* **111**, 096404 (2013).
10. Garcia-Fernandez M., Wilkins S., Lu M., Li Q., Gray K., Zheng H., Mitchell J. and Khomskii D., **Antiferromagnetic domain structure in bilayer manganite**, *Phys. Rev. B* **88**, 075134 (2013).
11. M. P. M. Dean, G. Dellea, R. S. Springell, F. Yakhou-Harris, K. Kummer, N. B. Brookes, X. Liu, Y.-J. Sun, J. Strle, T. Schmitt, L. Braicovich, G. Ghiringhelli, I. Bozovic and J. P. Hill, **Persistence of magnetic excitations in $La_{2-x}Sr_xCuO_4$ from the undoped insulator to the heavily overdoped non-superconducting metal**, *Nat. Mater.* **12**, 1019–1023 (2013).
12. X. Shi, D. Popović, C. Panagopoulos, G. Logvenov, A. T. Bollinger and I. Bozovic, **Emergence of superconductivity from the dynamically heterogeneous insulating state in $La_{2-x}Sr_xCuO_4$**, *Nat. Mater.* **12**, 47-51 (2013).
13. D. H. Torchinsky, F. Mahmood, A. T. Bollinger, I. Božović and N. Gedik, **Fluctuating charge density waves in a cuprate superconductor**, *Nat. Mater.* **12**, 387-391 (2013).
14. Hechang Lei, Kefeng Wang, Milinda Abeykoon, Emil S. Bozin and Cedomir Petrovic, **New layered fluorosulfide $SrFBiS_2$**, *Inorg. Chem.* **52**, 10685−10689 (2013).

15. M. Vucinic-Vasic, E. S. Bozin, L. Bessais, G. Stojanovic, U. Kozmidis-Luburic, M. Abeykoon, B. Jancar, A. Meden, A. Kremenovic and B. Antic, **Thermal evolution of cation distribution/crystallite size and their correlation with the magnetic state of Yb-substituted zinc ferrite nanoparticles**, *J. Phys. Chem. C* **117**, 12358-12365 (2013).
16. V. Thampy, S. Blanco-Canosa, M. Garcia-Fernandez, M. P. M. Dean, G. D. Gu, M. Först, T. Loew, B. Keimer, M. Le Tacon, S. B. Wilkins and J. P. Hill , **Comparison of charge modulations in $La_{1.875}Ba_{0.125}CuO_4$ and $YBa_2Cu_3O_{6.6}$**, *Phys. Rev. B* **88**, (2013).
17. S. J. L. Billinge, **Pair distribution function technique: principles and methods**, In **Uniting Electron Crystallography and Powder Diffraction**, (Springer Science \& Business Media, Dordrecht, 2013), U. Kolb and W. I. F. David and K. Shankland, Eds., of *NATO Science for Peace and Security Series B: Physics and Biophysics*, pp. 179 - 190.
18. S. I. Sanchez, M. W. Small, E. S. Bozin, J.-G. Wen, J.-M. Zuo and R. G. Nuzzo, **Metastability and Structural Polymorphism in Noble Metals: The Role of Composition and Metal Atom Coordination in Mono- and Bimetallic Nanoclusters**, *ACS Nano* **7**, 1542 (2013).
19. B. Antic, M. Perovic, A. Kremenovic, J. Blanusa, V. Spasojevic, P. Vulic, L. Bessais and E. S. Bozin, **An integrated study of thermal treatment effects on the microstructure and magnetic properties of Zn ferrite nanoparticles**, *J. Phys: Condens. Mat.* **25**, 086001 (2013).
20. H. Gretarsson, J. P. Clancy, X. Liu, J. P. Hill, E. S. Bozin, Y. Singh, S. Manni, P. Gegenwart, J. H. Kim, A. H. Said, D. Casa, T. Gog, M. H. Upton, H.-S. Kim, J. Yu, V. M. Katukuri, L. Hozoi, J. van den Brink and Y.-J. Kim, **Crystal-Field Splitting and Correlation Effect on the Electronic Structure of A_2IrO_3**, *Phys. Rev. Lett.* **110**, 076402 (2013).
21. Emil S. Bozin, Pavol Juhás and Simon J. L. Billinge, **Local structure of bulk and nanocrystalline semiconductors using total scattering methods**, In **Characterization of semiconductor heterostructures and nanostructures**, (Elsevier, Amsterdam, 2013), Giovanni Agostini and Carlo Lamberti, Eds., pp. 229-257.
22. T. Egami and S. J. L. Billinge, **Underneath the Bragg peaks: structural analysis of complex materials**, 2nd Ed.,Elsevier, Amsterdam, 2012.
23. S. J. L. Billinge, P. Juhas and E. S. Božin, **Fundamentals of pair distribution function analysis**, In **Crystallography for Health and Biosciences**, (Insubria University Press, Insubria Como Italy, 2012), A. Guagliardi and Norberto Masciocchi, Eds., pp. 163-176.
24. H. C. Lei, K. F. Wang, R. W. Hu, H. J. Ryu, M. Abeykoon, E. S. Bozin and C. Petrovic, **Iron chalcogenide superconductors at high magnetic fields**, *Sci. Technol. Adv. Mater.* **13**, 054305 (2012).
25. Q. Jie, R. W. Hu, E. S. Bozin, A. Llobet, I. Zaliznyak, C. Petrovic and Q. Li, **Electronic thermoelectric power factor and Metal - Insulator transition in $FeSb_2$**, *Phys. Rev. B* **86**, 115121 (2012).
26. H. C. Lei, E. S. Bozin, A. Llobet, V. Ivanovski, V. Koteski, J. Belosevic-Cavor, B. Cekic and C. Petrovic, **Frustrated magnetism in $La_2O_3(Fe_{1-x}Mn_x)_2Se_2$ tuned by Fe/Mn ratio**, *Phys. Rev. B* **86**, 125122 (2012).
27. Emil S. Božin, T. Chatterji and Simon J. L. Billinge, **Local structure of ReO_3 at ambient pressure from neutron total scattering study**, *Phys. Rev. B* **86**, 094110 (2012).

28. Kirsten M. O. Jensen, Emil S. Bozin, Christos D. Malliakas, Matthew B. Stone, Mark D. Lumsden, Mercouri G. Kanatzidis, Stephen M. Shapiro and Simon J. L. Billinge, **Lattice dynamics reveals a local symmetry breaking in the emergent dipole phase of PbTe**, *Phys. Rev. B* **86**, 085313 Selected as PRB Editor's Suggestion paper (2012).
29. N. Lazarevic, M. Abeykoon, P. W. Stephens, H. C. Lei, E. S. Bozin, C. Petrovic and Z. V. Popovic, **Vacancy-induced nanoscale phase separation in $K_xFe_{2-y}Se_2$ single crystals evidenced by Raman scattering and powder x-ray diffraction**, *Phys. Rev. B* **86**, 054503 (2012).
30. I Sochnikov, Y Shokef, G Logvenov, I Božović, A Shaulov and Y Yeshurun, **Fluxoid quantization effects in high-T_c superconducting double networks**, *J. Phys. Chem. Solids* **400**, 022109 (2012).
31. V Gasparov and I. Bozovic, **Magnetic field and temperature dependence of complex conductance of ultrathin $La_{1.65}Sr_{0.45}CuO_4/La_2CuO_4$ films**, *Phys. Rev. B* **86**, 094523 (2012).
32. Milinda Abeykoon, Christos D. Malliakas, Pavol Juhás, Emil S. Bozin, Mercouri G. Kanatzidis and Simon J. L. Billinge, **Quantitative nanostructure characterization using atomic pair distribution functions obtained from laboratory electron microscopes**, *Z. Kristallogr.* **227**, 248-256 Highlighted on the journal cover (2012).

Inelastic X-ray Studies of Highly Correlated Systems

PI: Clement Burns, Western Michigan University

Program Scope

Our work involves studies of strongly correlated 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 electronic and vibrational excitations.

A goal of our current work is to measure polarization of the scattered x-ray during RIXS. Scattering can change the energy, wavevector, and polarization of the x-ray. Currently, only the first two are measured. This is unfortunate, since polarization carries valuable information about the states involved in the scattering, including symmetry information. Specifically, we wish to develop polarization analysis for materials with strong spin-orbit coupling such as the iridates. We have previously developed a curved graphite polarization analyzer for measurements at the copper *K*-edge[1], but polarization effects are likely to be more interesting at the *L*- and *M*- edges.

Some Recent Progress

We have been creating and characterizing bent single crystal Si polarization analyzers for the iridium L_3-edge. Recently, we have bending very thin Si single crystal wafers to limit the strain. The Si is bent in a double toroidal shape which is a good approximation to the logarithmic spiral which is the exact shape required to have the curved surface meet the Bragg condition. The advantage of using a good crystal is that it keeps the good energy resolution of the main analyzer. So far, we have been able to achieve resolutions of about 140 meV but only with an efficiency of about 0.5%.

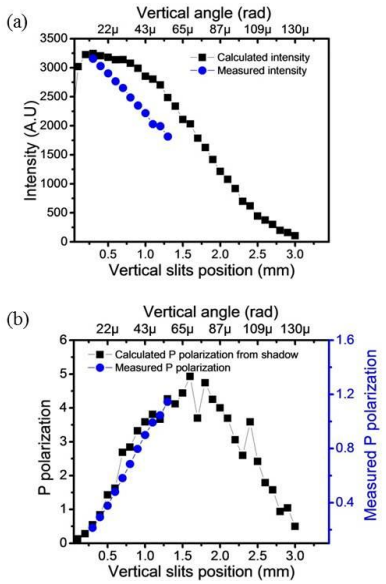


Fig. 1. Polarization measurements and simulations for radiation out of the plane of the synchrotron.

We have also carried out measurements and simulations to study the polarization of the incident x-ray synchrotron beam above the plane of the electron beam. We find good agreement with standard models of synchrotron radiation as shown in Fig. 1. Characterizing the beam polarization is necessary in order to know the ratio of the initial polarization components, and may also be useful for aligning the polarization analyzer in the polarization flipped channel.

Sector 30 of the APS has been devoted to inelastic x-ray scattering since its inception, with both medium (~100 meV) and high (1 meV) resolution endstations. Recently, the APS has decided to split the inelastic scattering program with the medium resolution instrument moving to its own beam line at Sector 27. Polarization analysis capabilities for medium resolution will be available for all users on the new sector. The polarization setup on the beam line will initially use flat graphite, which is suitable for studies that do not require good energy resolution. The flat graphite has an efficiency of a few percent.

We have also carried out studies of the magnetic excitations in $BaIrO_3$. $BaIrO_3$ is an interesting 5-*d* transition metal system. It contains Ir atoms in both quasi 1-*d* zigzag chains and 2-*d* planes. It has a combined ferromagnetic and charge density wave (CDW) transition[2] at 180 K, and the system displays unusual non-linear voltage characteristics that may or may not be

related to the CDW[3]. In addition to the transition at 180 K, there is a second magnetic transition at 26 K, which leads to a different ferromagnetic state, along with a small increase in the local magnetic moment as seen by muon spin relaxation[4]. We have begun a study of the magnetic excitations in this material throughout the Brillouin zone as a function of temperature and with different levels of Sr doping (on the Ba site) using RIXS at the iridium L_3-edge. The data in Fig. 2 show magnetic excitations near 50 meV in the phase at 180 K, but the excitation is not visible at 7 K in our (limited) data, probably indicating a change in magnetic structure at the 26 K phase transition. We are not certain if the magnetic excitations are completely gone or just located at different points in reciprocal space. The excitations do not appear to disperse, which is probably indicative of localized magnetic excitations.

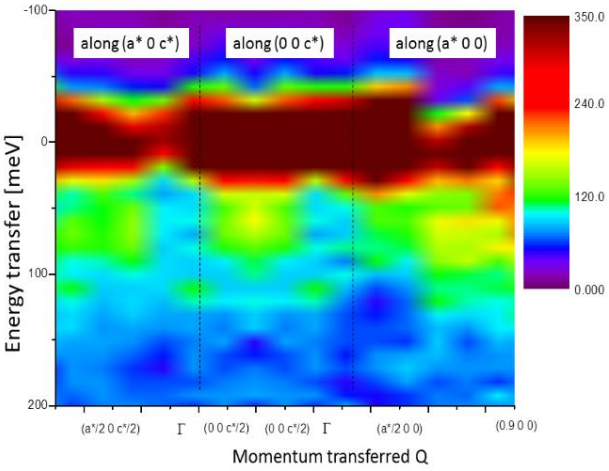


Fig. 2. Magnetic Scattering from excitations in magnetically ordered $BaIrO_3$ at 180 K. The dark red corresponds to elastic scattering and the magnetic excitation is visible near 50 meV along certain directions.

Future Plans

- We will take measurements on iridates using the polarization analysis at the new inelastic scattering sector (Sector 27) being built as part of the APS upgrade when the sector becomes available.
- We will carry out further studies of the magnetic excitations in $BaIrO_3$; in particular, we are interested in seeing how the magnetic excitations change at the transition and with Sr doping on the Ba site.
- For the 2015-2016 academic year I will be on sabbatical at SSRL and Stanford. At SSRL I will mostly work on resonant scattering (with Jun Sik Lee) and I will be collaborating with Ian Fisher and his group in Applied Physics at Stanford.

References

1. X. Gao, C. Burns, D. Casa, M. Upton, T. Gog, J. Kim and C. Li, Review of Scientific Instruments 82, 113108 (2011).
2. G. Cao, J. Crow, R. Guertin, P. Henning, C. Homes, M. Strongin, D. Basov and E. Lochner, Solid State Communications 113, 657-662 (2000).
3. T. Nakano and I. Terasaki, Physical Review B 73, 195106 (2006).
4. M. Brooks, S. Blundell, T. Lancaster, W. Hayes, F. Pratt, P. Frampton and P. Battle, Physical Review B 71, 220411 (2005).

Publications

1) J. Park, B.-G. Cho, K. D. Kim, J. Koo, H. Jang, K.-T. Ko, J.-H. Park, K.-B. Lee, J.-Y. Kim, D. R. Lee, C. A. Burns, S. S. A. Seo and H. N. Lee, "Oxygen-Vacancy-Induced Orbital Reconstruction of Ti Ions at the Interface of $LaAlO_3/SrTiO_3$ Heterostructures: A Resonant Soft-X-Ray Scattering Study", Physical Review Letters, **110**, 017401 (2013).
2) Yu. V. Shvyd'ko, J. P. Hill, C. A. Burns, D. S. Coburn, B. Brajuskovic, D. Casa, K. Goetze, T. Gog, R. Khachatryan, J.-H. Kim, C. N. Kodituwakku, M. Ramanathan, T. Roberts, A. Said, H. Sinn, D. Shu, S. Stoupin, T. Toellner, M. Upton, M. Wieczorek, H. Yava, "MERIX - next generation medium energy resolution inelastic x-ray scattering instrument at the APS", Journal of Electron Spectroscopy and Related Phenomena 188, 140 (2013).
3) Naresh Kujala, Albert Macrander, Xianbo Shi, Ruben Reininger, Xuan Gao, and Clement Burns, "Ray tracing simulation of 1-BM beamline at the Advanced Photon Source for polarization analyses of synchrotron optics", Proceedings of the SPIE, in press.

Ph. D. Theses

Xuan Gao, "Development of Polarization Analysis of Resonant Inelastic X-ray Scattering", Western Michigan University Ph. D. in Physics, December 2013.

Chengyang Li, "Studies of the Quantum Phase Transition in Chromium Using Inelastic X-ray Scattering and Ab Initio Methods", Western Michigan University Ph. D. in Physics, June 2014.

Interfacial bonding and properties of ultrathin topological insulator films

Tai C. Chiang, Department of Physics, University of Illinois at Urbana-Champaign

Program Scope

Our work has focused on ultrathin topological insulator (TI) films, their interactions with the substrates, and their unusual properties. Topological order is a bulk property, but interesting physics happens at surfaces and interfaces. When topological insulators are prepared as ultrathin films on substrates, coupling between the surface and the substrate states becomes important, and so does quantum confinement of the bulk states. Our work aims to clarify the interplay of interfacial bonding, quantum coupling, and dimensional crossover effects that may lead to interesting physical behavior.

Recent Progress

Interfacial topological states are a key element of interest for topological insulator thin films, and their properties can depend sensitively on the atomic bonding configuration. We employ *in situ* non-resonant and resonant surface X-ray scattering to study the interfacial and internal structure of a prototypical topological film system: Bi_2Te_3 grown on Si(111). The results reveal a Te-dominated buffer layer, a large interfacial spacing, and a slightly relaxed and partially strained bottom quintuple (QL) layer of an otherwise properly stacked bulk-like Bi_2Te_3 film. The presence of the buffer layer indicates a nontrivial process of interface formation and a mechanism for electronic decoupling between the topological film and the Si(111) substrate.

In prior studies using angle-resolved photoemission, we have established that Bi_2Te_3 films grown on Si(111) exhibit an electronic structure that resembles what is expected for a freestanding film. The implied very weak interfacial bonding is verified by our x-ray scattering experiments

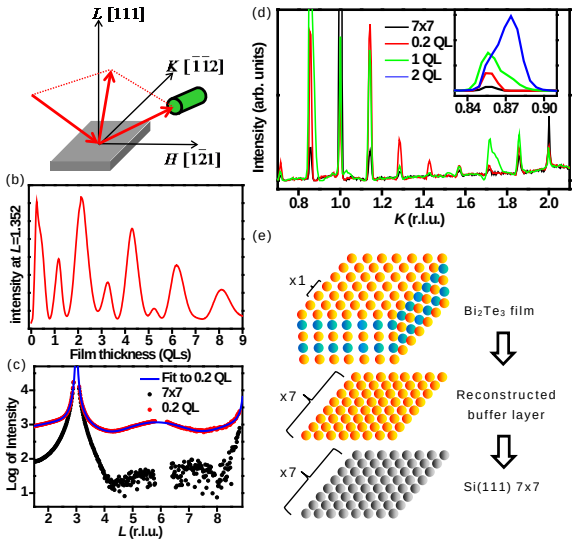


Fig. 1. (a) Experimental geometry for surface X-ray scattering. $\mathbf{k}_i$, and $\mathbf{k}_f$ are the incident and reflected photon wave vectors. A hexagonal surface coordinate of Si(111) substrate is used in this discussion. (b) Intensity oscillation at (H, K, L) = (0, 0, 1.352) in Si reciprocal lattice units (r.l.u.) as a function of film thickness. The chosen L value is close to an anti-Bragg reflection of Bi_2Te_3. (c) Specular reflectivity data (H = 0, K = 0) for the Si(111)-(7x7) surface (0 QL) and buffer-layer-capped surface (0.2 QL). A fit to the latter data set is shown. (d) A line scan along K (H = 0, L = 0.2) for the Si(111)-(7x7) surface, buffer-capped Si(111), and the same with the addition of 1 and 2 QLs. The inset shows the data near a bulk Bi_2Te_3 peak (K = 0.88), which is very close to the 6/7 fractional peak (K = 0.86) from the 7x7 reconstruction of Si(111). The intensity variations of the two peaks indicate that the 1 QL film is partially strained relative to the bulk case, but additional QLs are unstrained. (e) Schematic atomic structure. A buffer layer, commensurate with the Si(111)-7x7 substrate, is formed prior to the growth of Bi_2Te_3 films.

carried out at the Advanced Photon Source. A schematic diagram of the experimental configuration is shown in Fig. 1(a). Figure 1(b) shows measured real-time oscillations in the reflected intensity near an anti-Bragg position of Bi_2Te_3 during the film growth. The intensity increases rapidly to a maximum at a nominal film thickness of ~0.2 QLs, after which it undergoes damped bi-QL oscillations. The sharp peak at 0.2 QL is unusual and indicates a nontrivial growth mode. It is caused by the formation of a buffer layer. The ensuing bi-QL oscillations indicate QL-by-QL growth above the buffer layer. The measured specular reflectivity ($H = K = 0$) from the (7×7) substrate and buffer-capped surface (0.2-QL coverage) is shown in Fig. 1(c). In regions away from the Si Bragg peaks at $L = 3$ and 9, the reflectivity increases substantially with the addition of the buffer layer. Fitting of the data (blue curve over red data points) reveals a buffer layer sitting at ~2.7 Å above the top Si layer. This buffer layer has a (7×7) structure commensurate with the Si(111)-(7×7) substrate, as evidenced by simultaneous intensity increases for all of the 1/7 fractional peaks in in-plane scans; an example of *K*-scan at $H = 0$ and $L = 0.2$ is shown in Fig. 1(d). Further deposition beyond 0.2 QL results in intensity increases only at $K \sim 0.87$ and 1.74, indicating formation of 1×1 Bi_2Te_3 films. A close inspection of the peak at $K \sim 0.87$ [inset in Fig. 1(d)] reveals that there are actually two closely spaced peaks at $K = 0.86$ and 0.88, which correspond to the Si 6/7 fractional peak and the bulk Bi_2Te_3 peak, respectively. Evidently, this near-6/7 fractional match determines the epitaxial relationship. The intensities of both peaks grow with the film thickness increasing from 0.2 to 1 + 0.2 QL, but further deposition of another QL results in increase of the bulk Bi_2Te_3 peak only. A similar behavior is observed for the peak near $K = 1.74$. Thus, the first QL is partially strained by the substrate, and additional QLs assume the bulk structure within the plane. The deduced sample configuration at 1 + 0.2 QL is shown schematically in Fig. 1(e). Further experimental work based on resonant scattering confirms the presence of the buffer layer.

In summary, our X-ray study shows that the growth of the topological insulator Bi_2Te_3 on the most important electronic substrate material Si is epitaxial with a near 6/7 fractional lattice match. The buffer layer keeps the Bi_2Te_3 film atop essentially bulk-like and largely decoupled from the substrate, in agreement with our ARPES observations of a tunneling gap in this system when the film is thin.

Future Plans

We will continue the work on various topological insulator films with a focus on the entanglement of effects related to topological order, quantum confinement, surface chemical reactions, and interfacial bonding. ARPES spectroscopy, x-ray diffraction, and ab-initio calculations will be performed, where appropriate, to extract the essential physics of these systems. Circularly polarized light and spin detection will be employed for ARPES mapping of the surface band structure and spin texture. A spin-ARPES system is under construction at the Advanced Light Source.

Future work will also include thin film systems involving topological crystalline insulators, metals, semiconductors, Dirac semi-metals, highly correlated materials, and charge density compounds. Our theoretical modeling has indicated interesting behavior in some of the combinations. Experiments will follow to test the predictions and to explore new frontiers where detailed and quantitative theoretical predictions are not available or difficult.

Publications

1. Xiaoxiong Wang, Guang Bian, T. Miller, and T.-C. Chiang, "Topological spin-polarized charge layer above the surface of Ca-terminated Bi_2Se_3," Phys. Rev. B **87**, 035109 (2013).
2. Guang Bian, Xiaoxiong Wang, T. Miller, and T.-C. Chiang, "Topological phase transition and Dirac fermion transfer in Bi_2Se_3 films," EuroPhys. Lett. **101**, 27004 (2013), selected for EPL Highlights of 2013.
3. P.J. Kowalczyk, O. Mahapatra, S.A. Brown, G. Bian, X. Wang, and T.-C. Chiang, "Electronic size effects in three-dimensional nanostructures," Nano Lett. **13**, 43 (2013).
4. Xiaoxiong Wang, Guang Bian, T. Miller, and T.-C. Chiang, "Topological quantum well resonances in metal overlayers," Phys. Rev. B **87**, 235113 (2013).
5. A. Gray, Yang Liu, Hawoong Hong, and T.-C. Chiang, "X-ray diffraction studies of trilayer oscillations in the preferred thickness of In films on Si(111)," Phys. Rev. B **87**, 19541 (2013).
6. G. Bian, X. Wang, T. Miller, and T.-C. Chiang, "Origin of the giant Rashba spin splitting in Bi/Ag surface alloys," Phys. Rev. B **88**, 085427 (2013).
7. Y. Liu, H.-H. Wang, G. Bian, Z. Zhang, S. S. Lee, P. A. Fenter, J. Z. Tischler, H. Hong, and T.-C. Chiang, "Interfacial bonding and structure of Bi_2Te_3 topological insulator films on Si(111) determined by surface X-ray scattering," Phys. Rev. Lett. **110**, 226103 (2013).
8. J. E. Lawler, J. Bisognano, R. A. Bosch, T. C. Chiang, M. A. Green, K. Jacobs, T. Miller, R. Wehlitz, D. Yavuz, and R. C. York, "Nearly copropagating sheared laser pulse FEL undulator for soft x-rays," J. Phys. D: Appl. Phys. **46**, 325501 (2013).
9. Y. I. Joe, X. M. Chen, P. Ghaemi, K. D. Finkelstein, G. A. de la Peña, Y. Gan, J. C. T. Lee, S. Yuan, J. Geck, G. J. MacDougall, T. C. Chiang, S. L. Cooper, E. Fradkin, P. Abbamonte, "Emergence of charge density wave domain walls above the superconducting dome in 1*T*-$TiSe_2$" Nature Phys. **10**, 421 (2014).
10. Xiaoxiong Wang and T.-C. Chiang, "Internal chiral spin structure of topological-insulator/metal superlattices," EuroPhys. Lett. **106**, 37008 (2014).
11. Shih-Chang Weng, Ruqing Xu, Ayman H. Said, Bogdan M. Leu, Yang Ding, Hawoong Hong, Xinyue Fang, M. Y. Chou, A. Bosak, P. Abbamonte, S. L. Cooper, E. Fradkin, S.-L. Chang, and T.-C. Chiang, "Pressure-induced antiferrodistortive phase transition in $SrTiO_3$: common scaling of soft-mode with pressure and temperature " EuroPhys. Lett. **107**, 36006 (2014).
12. P.J. Kowalczyk, O. Mahapatra, S.A. Brown, G. Bian, and T.-C. Chiang, "STM driven modification of bismuth nanostructures," Surf. Sci. **621C**, 140 (2014).
13. Xiaoxiong Wang and T.-C. Chiang, "Topological states in Bi_2Se_3 surfaces created by cleavage within a quintuple layer – analysis in terms of the Shockley criterion," Phys. Rev. B **89**, 125109 (2014).
14. M. K. Dalai, B. R. Sekhar, D. Biswas, S. Thakur, T. -C. Chiang, D. Samal, C. Martin, and K. Maiti, "Valence band study of $Sm_{0.1}Ca_{0.9-x}Sr_xMnO_3$ using high resolution ultra-violet photoelectron spectroscopy," Phys. Rev. B **89**, 245131 (2014).
15. G. Bian, X. Wang, T. Miller, T.-C. Chiang, P. J. Kowalczyk, O. Mahapatra, and S. A. Brown, "First-principles and spectroscopic studies of Bi(110) films: thickness-dependent Dirac modes and property oscillations," (submitted).
16. Guang Bian, T. Miller, and T.-C. Chiang, "Rashba splitting and dichroism of surface states in Bi/Ag surface alloy," J. Elect. Spectro. Rel. Phenom. (accepted).

17. Man-Hong Wong, G. Bian, T. Miller, and T.-C. Chiang, "Topological phase transitions in antimony without gap parity reversal," (submitted).
18. Jie Ren, Guang Bian, Li Fu, Chang Liu, Tao Wang, Gangqiang Zha, Wanqi Jie, Madhab Neupane, T. Miller, M. Z. Hasan, and T.-C. Chiang, "Electronic structure of quantum spin Hall parent compound CdTe and related topological issues," (submitted).

Oxide Interfaces: Emergent Structure and Dynamics

PI: Roy Clarke, Applied Physics Program, University of Michigan, Ann Arbor MI 48109

Program Scope

The overall goals of this program are focused on the behavior of epitaxial oxide heterostructures at atomic length scales (Ångstroms), and correspondingly short time-scales (fs - ns). We aim to achieve a better basic understanding of structural and electronic correlations and how these can be exploited for technological applications, especially energy conversion and harvesting. Topics of interest include: probing the microscopic behavior of epitaxial interfaces and buried layers; novel materials structures that emerge from ionic and electronic reconfiguration at epitaxial interfaces; ultrahigh-resolution mapping of the atomic structure of heterointerfaces using synchrotron-based x-ray surface scattering, including direct methods of phase retrieval; using ultrafast lasers to study the effects of transient strain on coherent manipulation of multi-ferroic order parameters; and investigating structural ordering and relaxation processes in real-time. Fig. 1 illustrates the atomic-scale detail that can be achieved by direct methods (COBRA), a capability that made possible the recent accomplishment of a new ferroelectric heterostructure [1] based on the $SrTiO_3$ – $LaAlO_3$ interface [2,3].

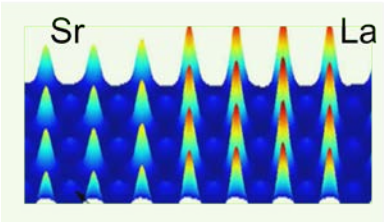


Fig. 1: COBRA map of interface between $SrTiO_3$ and $LaAl_3$.

Recent Progress

We have studied the thickness dependence of the $BiFeO_3$ thin film structure in the ultra-thin regime under moderate compressive strain (~ -1.4%) from (001) $SrTiO_3$ substrates. The samples were prepared in Schlom's MBE lab at Cornell. We found that a structural transition occurs from monoclinic to tetragonal, accompanied by a change in the octahedral tilt pattern from $a^-a^-b^0$ to $a^0a^0c^-$ when the film thickness is less than 20 unit cells. This definitively establishes the ultrathin-film structure as tetragonal which is important for several reasons: first, device applications normally require a single-domain state, which the lower-symmetry bulk-like mononclinic phases do not generally support; and secondly, the new tetragonal phase favors a polar alignment *normal* to the plane of the film, a geometry that is favorable for planar devices. The work reveals a novel "untilting" mechanism driven by the epitaxial heterointerface with $SrTiO_3$, which itself is untilted under ambient conditions. This in turn drives the transition to tetragonal symmetry. The work is published in APL materials. [4] We also studied the effect of epitaxial strain on this structural transition. Samples of $BiFeO_3$ grown on $LaAlO_3$ substrates, grown by pulsed laser deposition in the group of Hans Christen at Oak Ridge National Laboratory have a significantly larger mismatch (-4.3%). Interestingly, these highly strained

films grown on LAO also show the disappearance of the monoclinic peak splitting in the ultrathin regime. The larger compressive stress apparently drives the transition thickness to smaller dimensions, indicating again that the substrate interface plays a crucial role in the formation of the tetragonal phase. We have also studied the structure of these ultrathin samples down to low temperatures (~30K). These studies are ongoing.

Future Plans

Continuing experiments are planned at the Advanced Photon Source, focusing on multiferroic systems. In particular we are planning to investigate the role of strain in more detail by preparing epitaxial samples (in Christen's lab) on a range of different substrates to determine if we can stabilize the tetragonal phase of $BiFeO_3$ over a wider range of thicknesses relevant to devices. A detailed study of the atomic structure of the ultrathin tetragonal phase of $BiFeO_3$, using the COBRA direct phase retrieval technique, is continuing. Experiments on the dynamics of the metal-insulator transition in LSMO are also continuing at Sectors 11 and 7 at the Advanced Photon Source using time-resolved laser pump- x-ray probe techniques. We are particularly interested to study the intruiging effect shown in Fig. 2 where the laser-induced demagnetization of LSMO drives a transient structural transition on a ~130 ps time scale. This may point to a strong magnetoelastic coupling somewhat similar to the Invar effect in FePd and Fe-Ni alloys. We will investigate the dynamics of this coupled spin-lattice transition using x-ray pump-probe techniques correlated with asynchronous optical sampling (ASOPS) [6] measurements of the magnetization dynamics.

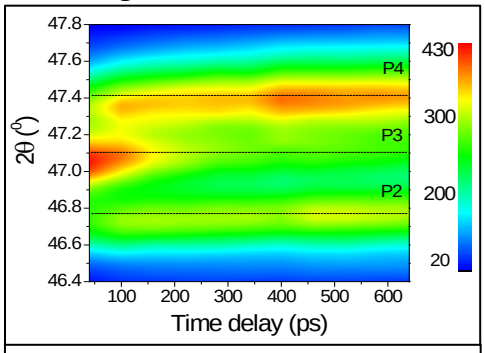


Fig. 2: Time-resolved x-ray scattering : transient relaxation after a 100 fs laser demagnetizes LSMO (P3) followed by slow lattice relaxation (P4) and spin-ordering . [5]

References

1. D.P. Kumah, Y.Yacoby, S.A. Pauli, P.R. Willmott, R.Clarke, *APL Mater.* **1**, 062107 (2013).

2. A. Ohtomo and H.Y. Wang, Nature (London) **427**, 423 (2004).

3. P.R. Willmott, S.A. Pauli, R. Herger, C.M. Schleputz, D. Martoccia, B.D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).

4. Y. Yang, C.M. Schlepütz, C. Adamo, D.G. Schlom, R. Clarke, *APL: Mater.* **1**, 052102 (2013).

5. V.A. Stoica, D.G. Schlom, and R. Clarke (to be published -2014).

6. V.A. Stoica, Y.-M. Sheu, D.A. Reis, and R. Clarke, *Optics Express* **16**, 2322 (2008).

Publications

1. Untilting $BiFeO_3$: the influence of substrate boundary conditions in ultra-thin $BiFeO_3$ on $SrTiO_3$, Yongsoo Yang, Christian M. Schlepütz, Carolina Adamo, Darrell G. Schlom, and Roy Clarke, *APL Materials* **1**, 052102 (2013).

2. La-doped $BaTiO_3$ heterostructures: compensating the polarization discontinuity, D. P. Kumah, Y. Yacoby, S. A. Pauli, P. R. Willmott, and R. Clarke, *APL Materials* **1**, 062107 (2013).

3. Structural transitions in highly-strained $BiFeO_3$ on $LaAlO_3$ (001) substrates, Y. Yang, C. Beekman, H. Christen, C.M. Schlepütz, R. Clarke, *Applied Physics Letters* (in preparation - 2014).

4. Spin-lattice coupling transition in $LaSrMnO_3$, V.A. Stoica, D.G. Schlom, and R. Clarke, *Nature Commun*. (submitted – 2014).

5. Growth and modeling of spherical crystalline morphologies of molecular materials, O. Shalev, S. Biswas, Y. Yang, T. Eddir, W. Lu, R. Clarke, M. Shtein, *Nature Commun.* (in press -2014).

6. Origin of stress and enhanced carrier transport in solution-cast organic semiconductor films, Ishviene Cour, Priya V. Chinta, Christian M. Schlepütz, Yongsoo Yang, Roy Clarke, Ron Pindak, and Randall L. Headrick, *Journal of Applied Physics* **114**, 093501 (2013).

7. Spatial Mapping of Morphology and Electronic Properties of Air-Printed Pentacene Thin Films, Shaurjo Biswas,Yongsoo Yang, Christian M. Schlepütz , Nadav Geva, Randall L. Headrick, Ron Pindak, Roy Clarke, Max Shtein, *Advanced Functional Materials* **24**, 3907-3916 (2014).

8. High-quality II-VI Films Grown on Amorphous Substrates using Tunable Tetradymite Templates, V.A. Stoica, L. Endicott, H.H. Shen, W. Liu, K. Sun, C. Uher, and R. Clarke, *Applied Physics Letters* (in press -2014).

9. I. Cour, P.V. Chinta, C.M. Schlepuetz, Y. Yang, R. Clarke, R. Pindak, R.L. Headrick, "Origin of stress and enhanced carrier transport in solution-cast organic semiconducting films", *J. Appl. Phys*. 114, 093501 (2013).

10. Yongsoo Yang, Synchrotron x-ray diffraction studies on oxide surfaces and interfaces; University of Michigan, Ph.D. Thesis: (*Thomson-Reuters,* May, 2014).

SIMES: Time- Resolved Soft X-ray Materials Science at the LCLS and ALS

T. P. Devereaux, Z.-X. Shen, A. Lindenberg, T. Heinz, D. Reis, W. Mao, W-S Lee, M. Trigo, H. Jiang

Program Scope

This program connects concepts of ultrafast time-domain science with those for momentum- and energy-domain x-ray spectroscopy. The combined activities bring a synergy to explore how materials behave under extreme conditions, driving lattice and charge conformational changes by applying short pulses, high fields, or high pressures. The purpose of this research is to develop a world-class program on the dynamics of complex materials using the x-ray beamlines available at LCLS to address the grand challenge problems of "emergence", non-equilibrium dynamics, and to probe model systems for deep insights on materials for energy conversion and transport.

Theoretical simulations conducted in parallel with experimental progress will help to establish a formalism for describing non-equilibrium physics of strongly correlated materials and provide additional insight to the generated experimental data. This activity requires the development of novel theoretical and computational tools designed to uncover the nature of the many-body state both in and out of equilibrium.

A new project aims to provide a fundamentally new approach to the modification and probing of key symmetry and topological properties of matter in the transition metal dichalcogenides (TMDCs. The focus will be on the use of circularly polarized light pulses to engineer electronic and structural response to combined dynamical breaking of sublattice and time-reversal symmetries. The research proposed provides a rich playground to explore the interplay of non-trivial quantum geometry with transport and optical measurements on one hand, while on the other hand serving to establish a firm theoretical and experimental basis to design and access practical valleytronics.

Recent Progress (*emphasis on theory)* A few examples of recent progress are illustrated below:

A. Theory for Resonant Inelastic X-ray Scattering in Strongly Correlated Materials

Using large-scale exact diagonalization, we investigated the nature of resonant inelastic x-ray scattering (RIXS) at the *L*-edge in cuprates, in particular the ability of RIXS to measure spin excitation in heavily-doped systems [1]. Utilizing large-scale numerics, we demonstrated that the experimental RIXS signal indeed corresponds to persistent spin excitations at high-energies along the anti-ferromagnetic zone boundary. Our results reconcile the RIXS experiments with previous investigations using inelastic neutron and Raman techniques. We predicted a striking asymmetry between hole- and electron-doped materials, which was recently confirmed in two separate experiments, one by members of the present FWP [2]. We have also demonstrated the ability of non-resonant and resonant inelastic x-ray scattering to provide both real-space and real-time information about the flow of energy and charge in condensed matter systems [3].

B. Numerical Algorithm and Code Development for Spectroscopy

We have developed numerical routines to obtaina microscopic understanding of lattice effects and the manifestation of electron-phonon coupling in RIXS spectra with the prospect of precisely

determine the mode coupling in condensed matter systems [4]. Our codes are scalable and adaptable to high performance computing (HPC). We have utilized HPC resources both in-house at SLAC as well as those available at DOE HPC centers (13,500,000 CPU-hrs allocation).

Future Plans (*emphasis on theory and TMDC project)*

The research will focus on the novel class of direct-gap two-dimensional materials provided by monolayer crystals of TMDCs. Recent findings have demonstrated experimentally the predicted valley-selective population of the energetically degenerate *K* and *K'* valleys. What is only beginning to be explored experimentally, however, and is of crucial importance, is the lifetime and relaxation channels for the valley polarization. This is both an important fundamental physics issue and critical for the use of the valley degree of freedom in solids. We will address this issue using time-resolved optical spectroscopy and time- and spin-resolved ARPES. In addition, the production of strongly nonequilibrium electronic populations, with an induced asymmetry between the *K* and *K'* points in the Brillouin zone, can lead the production of unusual nonequilibrium phonon populations that will be examined both through the use time-resolved Raman scattering and structural probes using short pulse x- rays at LCLS, the Advanced Photon Source (APS) and SSRL. It is the aim of these measurements with above-gap radiation to develop, in concert with theoretical efforts, a comprehensive understanding of the robustness of the valley degree of freedom. This will be achieved not only by direct measurements of the valley lifetime, but also by identifying decay channels (and retention of lowered symmetry characteristics) under conditions of varying temperature, carrier density, and magnetic field strength. This program thus aims at developing the physical principles that determine the importance and utility of the valley degree of freedom.

The investigations of the response of the material induced by circularly polarized above-gap radiation will be complemented by a new research direction motivated by theoretical predictions from our team. Theory predicts that for accessible field strengths with *below-gap circularly polarized radiation* the band structure of 2D materials can be dramatically modified. In addition to the identification of Floquet bands first reported for the surface states of topological insulators, recent theoretical work shows that the breaking of time-reversal symmetry provided by a circularly polarized optical pump beam can be transferred into a lifting of the *K/K'* degeneracy in the band structure of 2D materials. Thus, below gap-circularly circularly polarized radiation is also directly coupled to the valleytronic properties of the solid.

We will examine induced changes in the band structure of transition metal dichalcogenide monolayers by intense sub-gap electromagnetic fields. Particular emphasis will be given to the expected breaking of the *K* and *K'* to examine the energy of bands at the *K* and *K'* points as probed by optical absorption spectroscopy, time-resolved ARPES methods, and time-resolved RIXS. These approaches will be complemented by probes of nuclear displacement based on time-resolved Raman techniques and time-resolved x-ray diffraction at SSRL, APS and LCLS.

References

[1] C. J. Jia et al., *Nature Communications* **5**, 3314 (2014).
[2] W.-S. Lee et al, arXiv:1308.4740, to appear in *Nature Physics.*
[3] Y. Wang et al, *Phys. Rev. Lett.* **112**, 156402 (2014).
[4] J. J. Lee et al, *Phys. Rev. B* **89**, 041104(R) (2014) [Editors' Suggestion].

Publications

1. **Bandgap Closure and Reopening in $CsAuI_3$ at High Pressure,** Shibing Wang, Maria Baldini, Max Shapiro, Scott Riggs, Alexander F. Kemper, Zhao Zhao, Zhenxian Liu, Thomas P. Devereaux, Ted Geballe, Ian R Fisher, and Wendy L. Mao, Phys. Rev. B **89**, 245109 (2014).

2. **Real Space Visualization of Remnant Mott Gap and Magnon Excitations,** Yao Wang, Chunjing Jia, Brian Moritz, and Thomas Devereaux, *Phys. Rev. Lett.* **112**, 156402 (2014).

3. **Narrowing of Band Gaps in Thin Films and Linear Arrays of Ordered TiO_2 Nanoparticles**, Yu Liu, James Taing, Cheng-Chien Chen, Adam P. Sorini, Ming H. Cheng, Alexandria M. Margarella, Hendrik Bluhm, Thomas P. Devereaux, and John C. Hemminger, submitted to *J. Phys. Chem*.

4. **Asymmetry in Collective Excitations of Electron and Hole Doped Cuprate Superconductors**, W. S. Lee, J. J. Lee, E. A. Nowadnick, W. Tabis, S. W. Huang, V.N. Strocov, E. M. Motoyama, B. Moritz, M. Greven, T. Schmitt, Z. X. Shen, and T. P. Devereaux, arXiv:1308.4740, submitted to *Nat. Phys*.

5. **Ultrafast Lattice Dynamical Response to the Electronic Excitation of the Charge Density Wave in $TbTe_3$**, R. G. Moore, W. S. Lee, P. S. Kirchmann, Y. D. Chuang, A. F. Kemper, M. Trigo, L. Patthey, D. H. Lu, O. Krupin, M. Yi, D. A. Reis, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, G. Hay, P. Hering, T. Benson, J. -H. Chu, T. P. Devereaux, I. R. Fisher, Z. Hussain, and Z. -X. Shen, submitted to *Phys. Rev. Lett*.

6. **Persistent Spin Excitations in Doped Antiferromagnets Revealed by Resonant Inelastic Light Scattering**, C. J. Jia, E. A. Nowadnick, K. Wohlfeld, C.-C. Chen, S. Johnston, T. Tohyama, B. Moritz, and T. P. Devereaux, *Nat. Commun.* **5**, 3314 (2014).

7. **Charge-Orbital-Lattice Coupling Effects in the *dd*-Excitation Profile of One Dimensional Cuprates**, J. J. Lee, B. Moritz, W. S. Lee, M. Yi, C. J. Jia, A. P. Sorini, K. Kudo, Y. Koike, K. J. Zhou, C. Monney, V. Strocov, L. Patthey, T. Schmitt, T. P. Devereaux, and Z. X. Shen, *Phys. Rev. B* **89**, 041104(R) (2014) [Editors' Suggestion].

8. **Existence of Orbital Order and its Fluctuation in Superconducting $Ba(Fe_{1-x}Co_x)_2As_2$ Single Crystals Revealed by X-ray Absorption Spectroscopy**, Y. K. Kim, W. S. Jung, G. R. Han, K.-Y. Choi, K.-H. Kim, C.-C. Chen, T. P. Devereaux, A. Chainani, J. Miyawaki, Y. Takata, Y. Tanaka, M. Ouara, S. Shin, A. P. Singh, J.-Y. Kim, C. Kim, *Phys. Rev. Lett.* **111**, 217001 (2013).

9. **Time-Dependent Charge and Spin Order Recovery in Striped Systems**, Y. F. Kung, C.-C. Chen, A. F. Kemper, W.-S. Lee, B. Moritz, A. P. Sorini, and T. P. Devereaux, *Phys. Rev. B* **88**, 125114 (2013).

10. **Mapping of the Unoccupied States and Relevant Bosonic Modes Via the Time Dependent Momentum Distribution,** A. F. Kemper, M. Sentef, B. Moritz, C. C. Kao, Z. X. Shen, J. K. Freericks, and T. P. Devereaux, *Phys. Rev. B* **87**, 235139 (2013).

11. **The Role of Lattice Coupling in Establishing Electronic and Magnetic Properties in Quasi-1D Cuprates**, W. S. Lee, S. Johnston, B. Moritz, J. Lee, M. Yi, K. J. Zhou, T. Schmitt, L. Patthey, V. Strocov, K. Kudo, Y. Koike, J. van den Brink, T. P. Devereaux, and Z. X. Shen, *Phys. Rev. Lett.* **110**, 265502 (2013).

12. **Doping Evolution of Oxygen K-edge X-ray Absorption Spectra of Cuprate Superconductors Using a Three-Orbital Hubbard Model**, C.-C. Chen, M. Sentef, Y. F. Kung, C. J. Jia, R. Thomale, B. Moritz, A. P. Kampf, T. P. Devereaux, *Phys. Rev. B* **87**, 165144 (2013).

13. **Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered $La_{1.75}Sr_{0.25}NiO_4$ Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction,** Y.D. Chuang, W. S. Lee, Y.F. Kung, A.P. Sorini, B. Moritz, R. G. Moore, L. Patthey, M. Trigo, D. H. Lu, P. S. Kirchmann, M. Yi, O. Krupin, M. Langner, Y. Zhu, S. Y. Zhou, D. A. Reis, N. Huse, J. S. Robinson, R. A. Kaindl, R. W. Schoenlein, S.L. Johnson, M. Forst, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, T. Sasagawa, Z. Hussain, Z. X. Shen, and T. P. Devereaux, *Phys. Rev. Lett.* **110**, 127404 (2013).
14. **X-ray Emission Spectroscopy of Cerium Across the γ-α Volume Collapse Transition**, M. J. Lipp, A. P. Sorini, J. Bradley, B. Maddox, K. T. Moore, H. Cynn, T. P. Devereaux, Y. Xiao, P. Chow, and W. J. Evans, *Phys. Rev. Lett.* **109**,195705 (2012)
15. **Uncovering selective excitations using the resonant profile of indirect inelastic x-ray scattering in correlated materials: observing two-magnon scattering and relation to the dynamical structure factor**, C. J. Jia, C.-C. Chen, A. P. Sorini, B. Moritz, and T. P. Devereaux, *New J. Phys.* **14**,113038 (2012)
16. **Large-Amplitude Spin Dynamics Driven by a THz Pulse in Resonance with an Electromagnon,** T. Kubacka, J.A. Johnson, M.C. Hoffmann, C. Vicario, S. de Jong, P. Beaud, S. Grübel, S-W. Huang, L. Huber, L. Patthey, Y-D. Chuang, J.J. Turner, G.L. Dakovski, W-S. Lee, W. Schlotter, R. G. Moore, C. Hauri, S.M. Koohpayeh, V. Scagnoli, G. Ingold, S.L. Johnson, U. Staub, *Science* **343**, 1333 (2014).
17. **Melting of Charge Stripes in Vibrationally Driven $La_{1.875}Ba_{0.125}CuO_4$: Assessing the Respective Roles of Electronic and Lattice Order in Frustrated Superconductors,** M. Först, R. I. Tobey, H. Bromberger, S. B. Wilkins, V. Khanna, A. D. Caviglia, Y.-D. Chuang, W. S. Lee, W. F. Schlotter, J. J. Turner, M. P. Minitti, O. Krupin, Z. J. Xu, J. S. Wen, G. D. Gu, S. S. Dhesi, A. Cavalleri, and J. P. Hill, *Phys. Rev. Lett.* **112**, 157002 (2014).
18. **Photoinduced melting of magnetic order in the correlated electron insulator $NdNiO_3$,** A. D. Caviglia, M. Först, R. Scherwitzl, V. Khanna, H. Bromberger, R. Mankowsky, R. Singla, Y.-D. Chuang, W. S. Lee, O. Krupin, W. F. Schlotter, J. J. Turner, G. L. Dakovski, M. P. Minitti, J. Robinson, V. Scagnoli, S. B. Wilkins, S. A. Cavill,*, M. Gibert, S. Gariglio, P. Zubko, J.-M. Triscone, J. P. Hill, S. S. Dhesi, and A. Cavalleri, *Phys. Rev. B,* **88**, 220401 (2013).
19. **Ultrafast charge localization in a stripe-phase nickelate,** G. Coslovich, B. Huber, W. S. Lee, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H.A. Bechtel, M.C. Martin, Z.-X. Shen, R.W. Schoenlein and R.A. Kaindl, *Nature Comm*. **4**, 2643 (2013).
20. **Speed Limit of the insulator-metal transition in magnetite,** S. de Jong, R. Kukreja, C. Trabant, N. Pontius, C. F. Chang, T. Kachel, M. Beye, F. Sorgenfrei, C. H. Back, B. Brauer, W. F. Schlotter, J. J. Turner, O. Krupin, M. Doehler, D. Zhu, M. A. Hossain, A. O. Scherz, D. Fausti, F. Novelli, M. Esposito, W. S. Lee, Y. D. Chuang, D. H. Lu, R. G. Moore, M. Yi, M. Trigo, P. Kirchmann, L. Pathey, M. S. Golden, M. Buchholz, P. Metcalf, F. Parmigiani, W. Wurth, A. Fohlisch, C. Schussler-Langegeine, and H. A. Durr, *Nature Matt.* **12**, 882 (2013).
21. **Real-time visualization of nanocrystal solid-solid transformation pathways**, J.S. Wittenberg, T.A. Miller, E. Szilagyi, K. Lutker, F. Quirin, W. Lu, H. Lemke, D. Zhu, M. Chollet, J. Robinson, H. Wen, K. Sokolowski-Tinten, A.P. Alivisatos, A.M. Lindenberg, *Nano Lett.* **14**, 1995 (2014).

22. **Measurement of transient atomic displacements in thin films with picosecond and femtometer resolution**, M. Kozina, T. Hu, J.S. Wittenberg, E. Szilagyi, M. Trigo, T.A. Miller, C. Uher, A. Damodaran, L. Martin, A. Mehta, J. Corbett, J. Safranek, D.A. Reis and A.M. Lindenberg, *Struct. Dyn.* **1**, 034301 (2014).
23. **Ultrafast sub-threshold photo-induced response in crystalline and amorphous GeSbTe thin films**, M. J. Shu, I. Chatzakis, Y. Kuo, P. Zalden, A. M. Lindenberg, *Appl. Phys. Lett.* **102**, 201903 (2013).
24. **Intense THz pulses from SLAC electron beams using coherent transition radiation**, Z. Wu, A.S. Fisher, J. Goodfellow, M. Fuchs, D. Daranciang, M. Hogan, H. Loos, A.M. Lindenberg, *Rev. Sci. Instrum*. **84**, 022701 (2013).
25. **The mechanism of ultrafast structural switching in superionic copper (I) sulfide nanocrystals,** T.A. Miller, J.S. Wittenberg, H. Wen, S. Connor, Y. Cui, A.M. Lindenberg, *Nat. Commun.* **4**, 1369 (2013).
26. **Ultrafast electric-field-induced processes in GeSbTe phase-change materials**, M. Shu, P. Zalden, F. Chen, B. Weems, I. Chatzakis, F. Xiong, R. Jeyasingh, M. Hoffmann, E. Pop, H.-S.P. Wong, M. Wuttig, A.M. Lindenberg (Submitted to *Appl. Phys. Lett*.).(2014).
27. **Below gap optical absorption in GaAs driven by intense, single-cycle coherent transition radiation,** J. Goodfellow, M. Fuchs, D. Daranciang, S. Ghimire, F. Chen, H. Loos, D. Reis, A.S. Fisher, A.M. Lindenberg. *(*Submitted to *Optics Express).* (2014)
28. **Femtosecond x-ray tomography of nanocrystals at extreme strains**, E. Szilagyi, J. Wittenberg, T.A. Miller, E. Szilagyi, K. Lutker, F. Quirin, H. Lemke, D. Zhu, M. Chollet, J. Robinson, H. Wen, K. Sokolowski-Tinten, A.P. Alivisatos, A.M. Lindenberg. (Submitted to *Nature Nanotech*.) (2014)
29. **Evidence for photo-induced monoclinic metallic VO_2 under high pressure,** W.-P. Hsieh, M. Trigo, D. A.Reis, G. Andrea Artioli, L. Malavasi, and W. L. Mao, *Applied Physics Letters* **104,** 021917 (2014).
30. **Fourier-transform inelastic x-ray scattering from time- and momentum-dependent phonon-phonon correlations,** M. Trigo, M. Fuchs, J. Chen, M. P. Jiang, M. Cammarata, S. Fahy, D. M. Fritz, K. Gaffney, S. Ghimire, A. Higginbotham, S. L. Johnson, M. E. Kozina, J. Larsson, H. Lemke, A. M. Lindenberg, G. Ndabashimiye, F. Quirin, K. Sokolowski-Tinten, C. Uher, G. Wang, J. S. Wark, D. Zhu, and D. A. Reis. *Nat Phys*. **9,** 790 (2013).
31. **Fractional Non-Cubic Power Law for Density of Metallic Glasses,** Q. Zeng, Y. Kono, Y. Lin, Z. Zeng, J. Wang, S. V. Sinogeikin, C. Y. Park, Y. Meng, W. Yang, H.-k. Mao, and W. L. Mao, *Phys. Rev. Lett.*, accepted.
32. **Pressure induced novel triple layered and metallic phases of Ag2Se,** Z. Zhao, S. Wang, A. Oganov, P. Chen, Z. Liu, W. L. Mao, *Phys. Rev. B*, accepted.
33. **Pressure induced second-order structural and electronic transition in Sr3Ir2O7,** Z. Zhao, S. Wang, T. F. Qi, Q. S. Zeng, S. Hirai, P. P. Kong, L. Li, C. Park, S. J. Yuan, C. Q. Jin, G. Cao, W. L. Mao, *J. Phys.: Condens. Matter,* accepted.
34. **High pressure Raman and X-ray diffraction study of [121] Tetramantane,** F. Yang, Y. Lin, J. E. P. Dahl, R. M. K. Carlson, W. L. Mao, *J. Phys. Chem. C,* doi:10.1021/jp500431, 2014.
35. **Strain derivatives of Tc in HgBa2CuO4□□: The CuO2 plane alone is not enough,**S. Wang, J. Zhang, J. Yan, X-J Chen, V. V. Struzhkin, W. Tabis, N. Barisic, M. Chan, C. Dorow, X. Zhao, M. Greven, W. L. Mao, T. Geballe, *Phys. Rev. B* **89**, 024515 (2014).

36. **Densification process of GeO2 glass: High pressure transmission x-ray microscopy study,** Y. Lin, Q. S. Zeng, W. Yang, and W. L. Mao, *Appl. Phys. Lett.* **103**, 261909 (2013).
37. **High-pressure Raman spectroscopy of phase change materials,**W. P. Hsieh, P. Zalden, M. Wuttig, A. M. Lindenberg, and W. L. Mao, *Appl. Phys. Lett.* **103**, 191908 (2013).
38. **Pressure induced structural transitions and metallization in Ag2Te,** Z. Zhao, S. Wang, H. Zhang, and W. L. Mao, *Phys. Rev. B* **88**, 024120 (2013).
39. **The effect of composition on pressure-induced devitrification in metallic glasses,** Q.S. Zeng, W. L. Mao, H. Sheng, Z. Zeng, Q. Hu, Y. Meng, H. Lou, F. Peng, W. Yang, S. V. Sinogeikin and J. Z. Jiang, *Appl. Phys. Lett.* **102**, 171905 (2013).
40. **Pressure-induced tetragonal-orthorhombic phase transitions in CeRuPO,**S. Hirai, Y. Kamihara, A. Wakatsuki, M. Matoba, and W. L. Mao, *Appl. Phys. Lett.* **102**, 051917 (2013).
41. **Novel pressure-induced transitions in Co3O4,** S. Hirai and W. L. Mao, *Appl. Phys. Lett.* **102,** 041912, (2013).
42. **Theoretical Description of High-Order Harmonic Generation in Solids**, A. F. Kemper, B. Moritz, J.K. Freericks, and T. P. Devereaux, New J. Phys. **15**, 023003 (2013).
43. **Giant displacement at a magnetic transition in metastable Mn3O4** S. Hirai, A. M. dos Santos, M. Shapiro, J. J. Molaison, N. Pradhan, M. Guthrie, C. A. Tulk, I. R. Fisher, W. L. Mao, Phys. Rev. B **87**, 014417 (2013).
44. **Time- and momentum-resolved probe of heat transport in photo-excited bismuth**, J. Chen, M. Trigo, S. Fahy, E. D. Murray, Y. M. Sheu, T. Graber, R. Henning, Y. J. Chien, C. Uher, and D. A. Reis. Appl. Phys. Lett. **102**, 181903 (2013).
45. **Microscopic origin of spin-orbital separation in Sr2CuO3**, Krzysztof Wohlfeld, Satoshi Nishimoto, Maurits W. Haverkort, and Jeroen van den Brink, accepted in Phys. Rev. B (2013).
46. **Orbital superexchange and crystal field simultaneously at play in YVO3: Resonant inelastic xray scattering at the V L edge and the O K edge**, E. Benckiser, L. Fels, G. Ghiringhelli, M. Moretti Sala, T. Schmitt, J. Schlappa, V. N. Strocov, N. Mufti, G. R. Blake, A. A. Nugroho, T. T. M. Palstra, M. W. Haverkort, K. Wohlfeld, and M. Grueninger; accepted as a regular paper in Physical Review B.
47. **Optical probing of ultrafast electronic decay in Bi and Sb with slow phonons.** J. J. Li, J. Chen, D. A. Reis, S. Fahy, and R. Merlin. Phys. Rev. Lett. **110,** 047401 (2013).

Terahertz Control of Electrons & Spins on the Nanoscale

Hermann Dürr, Matthias Hoffmann, Alex Reid, Joachim Stöhr
SLAC National Accelerator Laboratory, Stanford University

Program Scope

The 'Magnetization & Dynamics' FWP at SLAC focuses on the emergence of nanscale spin & charge order in the far from equilibrium states that occur when solid-state devices used for instance in information technology are operated near their speed limits given by the fundamental laws of physics. We aim at addressing the grand scientific challenges related to these areas by developing a fundamental understanding of the evolution of materials properties determined by the flow of energy and angular momentum as the magnetic and charge state is switched by external stimuli. We employ the unique x-ray capabilities at SLAC to access the nm lengthscale on the complementary fs (LCLS) and ps (SSRL) timescales for probing: (1) all-optical magnetic switching in metallic alloys (see abstract by Alex Reid), (2) spectroscopy of non-equilibrium spin transport in spintronics (see abstract by Joachim Stöhr) and (3) electric field driven metal-insulator transitions in strongly correlated materials (this abstract). The latter aims at making use of intense THz fields generated by fs lasers and the relativistic electron beams available at SLAC. A timely basic understanding developed in this FWP leading to the control of such phenomena is expected to influence future generations of magnetic data storage devices and field effect transistors possibly to the same degree as the discovery of giant magneto-resistance and basic semiconductor research did in the past.

Recent Progress

We studied the insulator-metal transition in magnetite (see Fig. 1), the first oxide in which a relationship between electrical conductivity and fluctuating/localized electronic order was discovered. Recently, three-Fe-site lattice distortions called trimerons were identified as the characteristic building blocks of the low-temperature insulating electronically ordered phase [Senn 2012]. Investigating the Verwey transition in the time domain demonstrates how trimerons become mobile on a 1.5 ± 0.2 picosecond timescale to yield residual insulating and metallic regions. This establishes the speed

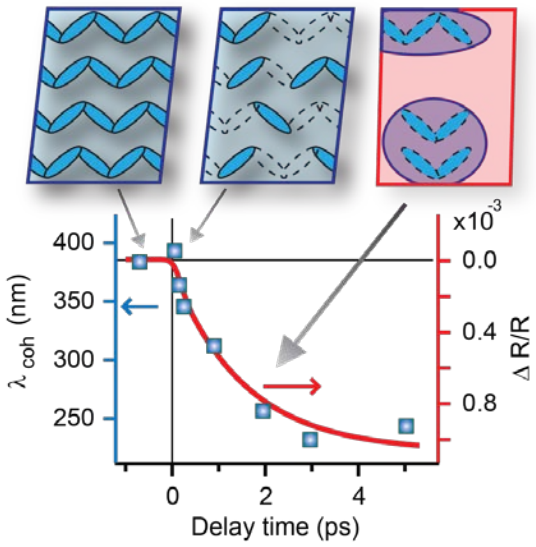


Figure 1: Sketch of the local ordering in magnetite as it goes through the Verwey transition following laser excitation (blue – insulator phase, red – metallic phase). [Jong 2013]

limit for switching in future oxide electronics [Jong 2013].

An important ingredient in the external control of conductivity is the material's propensity to display phenomena such as insulator-metal transitions. We used the archetypal correlated oxide compound vanadium dioxide (VO_2), to show that the metal–insulator transition temperature of thin can be changed continuously by varying the orbital occupation via epitaxial strain as probed with soft x-ray spectroscopy (see Fig. 2) [Nagaphani 2013].

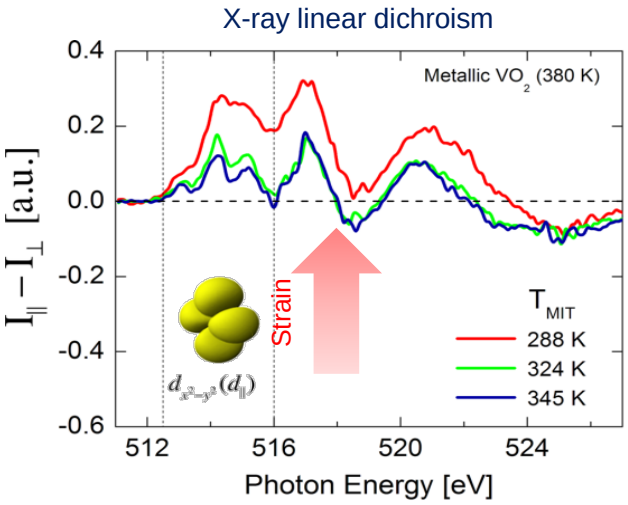


Figure 2: Changes in Vanadium *d*- orbital occupation measured by x-ray linear dichroism as the transition temperature is varied with strain in ultrathin, epitaxial VO_2 films. [Nagaphani 2013]

Future Plans

We aim at driving insulator-metal transitions by intense, ultrashort electric field pulses [Liu 2012]. On the one hand this serves to demonstrate if energy efficient switching, i.e. without energy dissipation to the lattice, can be achieved in field-effect devices based on oxide electronics. On the other hand, transient electric field pulses shorter than typical electronic relaxation times offer a new way to modify the electron kinetic energy and control electronic interactions on an ultrafast timescale.

References

[Senn 2012] Senn, M. S., Wright, J. P. & Attfield, J. P. *Charge order and three-site distortions in the Verwey structure of magnetite*, Nature **481**, 173 (2012).

[Jong 2013] S. de Jong, et al. *Speed limit of the insulator-metal transition in magnetite*, Nature Materials **12**, 882 (2013).

[Nagaphani 2013] A.B Nagaphani, et al. *Towards Wide Temperature Range Control of the Metal-Insulator Transition in Vanadium Dioxide by Modifying Orbital Occupancy*, Nature Physics **9**, 661 (2013).

[Liu 2012] M. Liu, et al *Terahertz-field-induced insulator-to-metal transition in vanadium dioxide metamaterial*, Nature **487**, 345 (2012).

Publications (FY 13/14)

1. Y. P. Cai, K. Chesnel, M. Trevino, A. Westover, R. G. Harrison, J. M. Hancock, S. Turley, A. Scherz, A. Reid, B. Wu, C. Graves, T. Wang, T. Liu, H. Dürr, *Orbital and spin moments of 5 to 11 nm Fe_3O_4 nanoparticles measured via x-ray magnetic circular dichroism*, J. Appl. Phys. **115**, 17B537 (2014)
2. A. Fognini, G Salvatella, T.U. Michlmayr, C. Wetli, U. Ramsperger, T. Bähler, F. Sorgenfrei, M. Beye, A. Eschenlohr, N. Pontius, C. Stamm, F. Hieke, M. Dell'Angela, S. de Jong, R. Kukreja, N. Gerasimova, V. Rybnikov, H. Redlin, J. Raabe, A. Foehlisch, H.A. Dürr, W. Wurth, D. Pescia, A. Vaterlaus, Y. Acremann, *The role of space charge in spin-resolved photoemission experiments*, New J. Phys. **16**, 043031 (2014).
3. A. Fognini, T.U. Michlmayr, G. Salvatella, C. Wetli, U. Ramsperger, T. Baehler, F. Sorgenfrei, M. Beye, A. Eschenlohr, N. Pontius, C. Stamm, F. Hieke, M. Dell'Angela, S. de Jong, R. Kukreja, N. Gerasimova, V. Rybnikov, A. Al-Shemmary, H. (Redlin, J. Raabe, A. Foehlisch, H.A. Dürr, W. Wurth, D. Pescia, A. Vaterlaus, Y. Acremann, *Ultrafast reduction of the total magnetization in iron*, Appl. Phys. Lett. 104, 032402 (2014).
4. Nagaphani B. Aetukuri, Alexander X. Gray, Marc Drouard, Matteo Cossale, Li Gao, Alexander H. Reid, Roopali Kukreja, Hendrik Ohldag, Catherine A. Jenkins, Elke Arenholz, Kevin P. Roche, Hermann A. Dürr, Mahesh Samant, Stuart S.P. Parkin, *Towards Wide Temperature Range Control of the Metal-Insulator Transition in Vanadium Dioxide by Modifying Orbital Occupancy,* Nature Physics **9**, 661 (2013).
5. Tianhan Wang, Virat Mehta, Yoshihiro Ikeda, Hoa Do, Kentaro Takano, Sylvia Florez, Bruce D. Terris, Benny Wu, Catherine Graves, Michael Shu, Ramon Rick, Andreas Scherz, Joachim Stöhr, Olav Hellwig, *Magnetic design evolution in perpendicular magnetic recording media as revealed by resonant small angle x-ray scattering,* Appl. Phys. Let. **103**, 112403 (2013).
6. C.E. Graves, A.H. Reid, T. Wang, B. Wu, S. de Jong, K. Vahaplar, I. Radu, D.P. Bernstein, M. Messerschmidt, L. Müller, R. Coffee, M. Bionta, S.W. Epp, R. Hartmann, N. Kimmel, G. Hauser, A. Hartmann, P. Holl, H. Gorke, J. H. Mentink, A. Tsukamoto, A. Fognini, J.J.

Turner, W.F. Schlotter, D. Rolles, H. Soltau, L. Strüder, Y. Acremann, A.V. Kimel, A. Kirilyuk, Th. Rasing, J. Stöhr, A.O. Scherz, H.A. Dürr, *Nanoscale spin reversal by nonlocal angular momentum transfer following ultrafast laser excitation in ferrimagnetic GdFeCo*, Nature Materials **12**, 293 (2013).

7. S. de Jong, R. Kukreja, C. Trabant, N. Pontius, C. F. Chang, T. Kachel, M. Beye, F. Sorgenfrei, C. H. Back, B. Bräuer, W. F. Schlotter, J. J. Turner, O. Krupin, M. Doehler, D. Zhu, M. A. Hossain, A. O. Scherz, W. S. Lee, Y. D. Chuang, D. H. Lu, R. G. Moore, M. Yi, M. Trigo, P. Kirchman[1], L. Pathey, M. S. Golden, M. Buchholz, P. Metcalf, W. Wurth, A. Föhlisch, C. Schüßler-Langeheine, H. A. Dürr, *Speed limit of the insulator-metal transition in magnetite*, Nature Materials **12**, 882 (2013).
8. M.A. Hussain, M.H. Burkhardt, S. Sarkar, H. Ohldag, Y.D. Chuang, A. Scholl, A.T. Young, A. Doran, D.S. Dessau, H. Zheng, J.F. Mitchel, H.A. Dürr, J. Stöhr, *Interplay between intrinsic and stacking-fault magnetic domains in bi-layered magnanites, Appl. Phys. Lett.* **101**, 132402 (2012).

Dynamical Control of Nanoscale Order in Complex Oxides

Paul G. Evans, Materials Science and Engineering, University of Wisconsin-Madison, 1509 University Ave., Madison, WI 53706 evans@engr.wisc.edu

Program Scope

The rapid evolution of x-ray coherent scattering and time-resolved diffraction techniques provides the opportunity to obtain new insight into the dynamics of ferroic complex oxides. The response of ferroelectric and multiferroic oxides spans a range of length scales and time scales, and depends on the interaction of local atomic distortion with long-range order. We have focused on the electric field excitation of dynamics, which allows an accurate thermodynamic interpretation of the applied perturbation. In addition, coherent scattering techniques allow us to search for equilibrium dynamics that are not apparent in incoherent scattering studies. Here we summarize recent results in two areas and plans for the near future.

I. Recent Progress

I.1. Equilibrium dynamics of striped domains

Thin layers of ferroic materials often have a complex nanoscale domain structure that reduces the total electrostatic or magnetic energy. We have extensively studied the atomic-scale structural distortion induced by applied electric fields in these systems, including observations of slow piezoelectric dynamics in disordered materials.[1] At a larger scale, superlattices consisting of alternating $PbTiO_3$ and $SrTiO_3$ layers exhibit a striped domain pattern in which the polarization is either along or opposite to the surface normal, with a short in-plane coherence length and a nearly isotropic distribution of the orientations of domain walls. Applied fields distort the structure of the domains,[5] and subsequently produce a uniform polarization state. In equilibrium, in the absence of applied fields, we have used coherent x-ray nanobeam scattering to show that the ferroelectric nanodomain system exhibits a disordered spatial pattern accompanied by fluctuations of the domain pattern at room temperature. Coherent synchrotron x-ray nanobeam scattering yields a diffuse scattering pattern shown in schematically in Fig. 1(a), which exhibits a speckle pattern when illuminated by coherent x-ray radiation. Speckle patterns, as in Fig. 1(b) and (c), lack correlation between spatially separated locations, indicating that the domain pattern does not have a repeating geometric pattern. Fig.

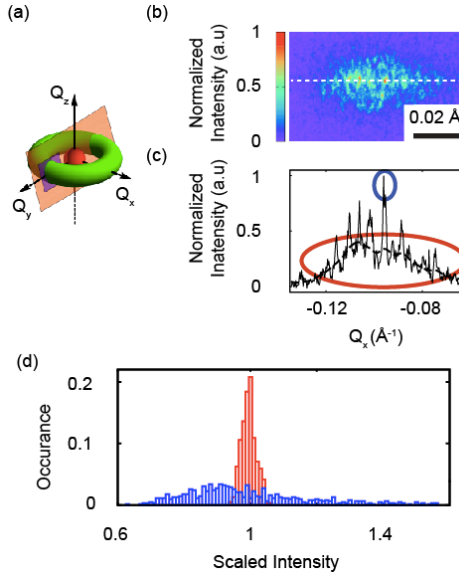


Fig. 1 (a) Reciprocal space schematic showing the intersection of the Ewald sphere (green surface) with the 002 superlattice Bragg reflection (red sphere) and the ring of domain diffuse scattering (blue ring). (b) Coherent scattering pattern with speckles from disordered domain structures. (c) Line profile along the dashed line in (b). (d) Intensity histogram for the single speckle indicated by the blue circle in (c) and blue bar in (d) and for the entire domain scattering satellite indicated by the red circle in (c) and red bar in (d).

1(d) shows that histogram of the intensity of a single speckle is varies over a wide range as the position of the beam is scanned, and that the total domain diffuse scattering intensity is constant. The scattering patterns become increasingly decorrelated as a function of elapsed time following a compressed exponential time dependence, typical of disordered systems in which metastable states are formed in part due to the distortion of the spatial pattern away from equilibrium. The rate of decorrelation varies among samples produced with same structure but varying defect densities, suggesting that the dynamics are related to the microstructure of the superlattice.[12]

I.2. Ultrafast structural dynamics in complex oxide ferroelectrics

In a collaboration with Haidan Wen, Yuelin Li, and others at the Advanced Photon Source and at Argonne's Center for Nanoscale Materials we have shown that intense fs laser pulses can induce transient strains of up to 0.5% in multiferroic $BiFeO_3$ thin films.[4,6] Further study in collaboration with Matthias Bargheer's group at Univ. of Potsdam shows that the time interval over which the strain is developed is not sufficient for carrier transport to the surface and interface, thus pointing to a mechanism for strain generation in which carriers are not separated by more than a few nanometers.[9]

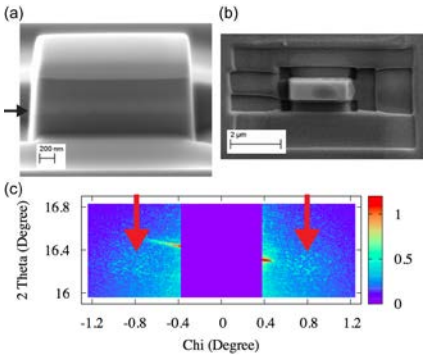


Fig. 2 (a) and (b) Side and plan-view SEM images of a 625 nm × 2 μm ridge designed to provide lateral confinement for the stripe domains in a PTO/STO superlattice. The location of the PTO/STO layer beneath the W and C thin films protecting the surface during ion milling is indicated by the arrow in (a). (c) Domain coherent x-ray diffraction pattern of the 625 nm × 2 μm PTO/STO ridge, acquired with a photon energy of 11 keV. Domain diffuse scattering satellites appear at chi=±0.8° (red arrows). The areas of low intensity at the center of the diffraction pattern arises from the attenuation of the superlattice Bragg rod that would saturate the detector at chi=0.

II. Future Plans

II.1. Dynamics in confined systems

We have begun to test the hypothesis that mechanical boundary conditions can be used to modify dynamics and geometry of ferroelectric superlattice striped nanodomain patterns by patterning striped domain structures in which the physical extent of the entire PTO/STO crystal is not significantly larger than the typical coherence length of the domain pattern, as in Fig. 2. Pillars created by FIB have ranged from 150 to 800 nm, or approximately 10 to 200 coherence lengths of the domain pattern. Initial coherent scattering studies show that the stripe domains persist in the pattern structures and that their geometric distribution is modified by the boundaries.

II.2. Facilities and Instrumentation

We are developing instrumentation for nanodiffraction that allows optical pumping using a highly stable <2 μm diameter fs laser spot is produced by delivering the pulse to the sample stage via a single mode fiber optic and focusing with precisely positioned objective. This instrument permits precise control of the optical geometry and introduces far smaller total power to the sample, improving the stability of optically pumped nanobeam experiments. We have also contributed to the scientific cases of future time-resolved and coherent scattering facilities.[7,8,11]

Publications

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. B. Adams, M. Borland, L. X. Chen, P. Chupas, N. Dashdorj, G. Doumy, E. Dufresne, S. Durbin, H. Dürr, P. Evans, T. Graber, R. Henning, E. P. Kanter, D. Keavney, C. Kurtz, Y. Li, A. M. March, K. Moffat, A. Nassiri, S. H. Southworth, V. Srajer, D. M. Tiede, D. Walko, J. Wang, H. Wen, L. Young, X. Zhang and A. Zholents, "*X-ray Capabilities on the Picosecond Timescale at the Advanced Photon Source*," Synchrotron Radiation News **25**, 6 (2012).
3. 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).
4. H. Wen, P. Chen, M. P. Cosgriff, D. A. Walko, J. H. 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 $BiFeO_3$*," Phys. Rev. Lett. **110**, 037601 (2013).
5. P. Chen, M. P. Cosgriff, Q. Zhang, S. J. Callori, B. W. Adams, E. M. Dufresne, M. Dawber, and P. G. Evans, "*Field-Dependent Domain Distortion and Interlayer Polarization Distribution in $PbTiO_3/SrTiO_3$ Superlattices*," Phys. Rev. Lett. **110**, 047601 (2013).
6. Y. Li, H. Wen, P. Chen, M. P. Cosgriff, D. Walko, J. H. Lee, C. Adamo, R. Schaller, C. Rowland, C. Schlepuetz, E. Dufresne, Q. Zhang, C. Giles, D. Schlom, J. Freeland and P. Evans, "*Ultrafast Photostriction in Thin Film Bismuth Ferrite and its Correlation to Electronic Dynamics*," MRS Online Proc. Lib. **1528**, mrsf12-1528-vv11-09 (2013).
7. P. G. Evans, "*Opportunities for a Free Electron Laser Oscillator in Nanomaterial Phonon Characterization and Complex Oxide Dynamics*," International Committee for Future Accelerators Beam Dynamics Newsletter, **60**, 39 (2013).
8. R. Reininger, E. M. Dufresne, M. Borland, M. A. Beno, L. Young, K.-J. Kim, and P. G. Evans, "*Optical design of the short pulse x-ray imaging and microscopy time-angle correlated diffraction beamline at the Advanced Photon Source*," Rev. Sci. Instrum. **84**, 053013 (2013).
9. D. Schick, M. Herzog, H. Wen, P. Chen, C. Adamo, P. Gaal, D. G. Schlom, P. G. Evans, Y. Li, and M. Bargheer, "*Localized Excited Charge Carriers Generate Ultrafast Inhomogeneous Strain in the Multiferroic $BiFeO_3$*," Phys. Rev. Lett. **112**, 097602 (2014).
10. D. M. Paskiewicz, D. E. Savage, M. V. Holt, P. G. Evans, and M. G. Lagally, "*Nanomembrane-based materials for Group IV semiconductor quantum electronics*," Scientific Reports **4**, 4218 (2014).

11. R. Reininger, E. M. Dufresne, M. Borland, M. A. Beno, L. Young, and P. G. Evans, "*A short-pulse X-ray beamline for spectroscopy and scattering*," J. Synchrotron Rad. **21**, 1194 (2014).
12. Q. Zhang, P. Chen, J. Park, M. P. Cosgriff, M. Yusuf, Z. Cai, R. Harder, S. J. Callori, M. Dawber, and P. G. Evans, "*Domain Pattern Fluctuation in Ferroelectric/Dielectric $PbTiO_3/SrTiO_3$ Superlattices*," submitted (2014).

Interfacial Reactivity and Dynamics

Dillon Fong, Paul Fuoss, Stephan Hruszkewycz, Brian Stephenson, Hoydoo You
Materials Science Division, Argonne National Laboratory

Program Scope

Hard x-rays from third generation sources permit the study of catalytically active surfaces under realistic conditions. Complex oxides, in addition to exhibiting a wide array of electromagnetic functionalities [1, 2], have recently demonstrated high activities for different redox reactions [3, 4]. In this thrust, we employ multiple synchrotron x-ray techniques for *in situ* studies on the redox behavior of model complex oxide surfaces.

Recent Progress

Redox reactions are essential to a wide range of energy technologies, from storage to conversion [5-7]. Currently, there is substantial interest in developing and optimizing oxide materials for driving these technologies since they are generally chemically and thermally stable, cheaper than many metallic catalysts, and many of them can be tuned for electronic / ionic transport, depending on the particular application [8, 9]. However, most of the reaction pathways for these materials remain unknown and their activity-stability relationships have yet to be established.

We have grown and conducted the first catalytic studies of $SrCoO_{2.5}$, a complex oxide that is catalytically active but has been difficult to stabilize as a single phase in bulk form [10]. Utilizing the technique of epitaxial strain stabilization and a new apparatus built for *in situ* catalytic studies employing gas chromatography and mass spectrometry [11], we have shown that the material can exhibit high activity for the CO oxidation reaction even at temperatures approaching 300°C (Figure 1) [12]. The activities are higher than that of other well-known oxide catalysts and depend strongly on the crystallographic orientation of the film. More recently, with real-time *in situ* synchrotron x-ray scattering and exploiting a reflection highly sensitive to the oxygen form factor, we observe that CO removes oxygen from the $SrCoO_{2.5}$, while an oxygen environment serves to replenish the $SrCoO_{2.5}$ (Figure 2a), as may be expected for a Mars-van Krevelen reaction mechanism.

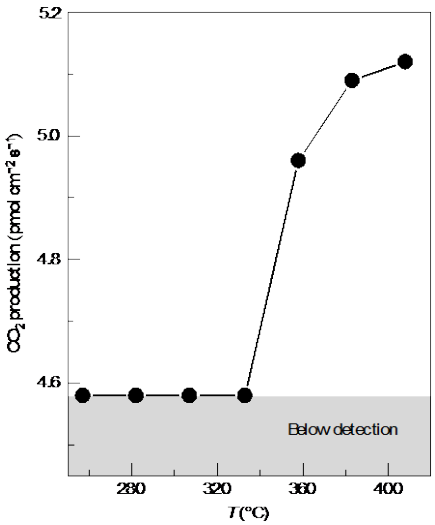


Figure 1. Gas phase catalysis. Temperature-programmed CO oxidation reaction over a $SrCoO_{3-\delta}$ / $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$ (001) heterostructure. CO_2 production shows catalytic activity above 320°C.

Future Plans

In the next two years, we will investigate the kinetics and dynamics of reactions on (La, Sr)CoO_x oxide surfaces, looking at the effects of temperature, strain and orientation, CO/O_2 ratios, and total pressures. We will employ *in situ* resonant scattering and x-ray absorption spectroscopy techniques to examine which films are the most catalytically active and structurally robust and study which oxygen ions participate in the reaction (e.g., those in the CoO_x plane vs those in the SrO plane). For detailed studies on the Mars-van Krevelen mechanism [13], we intend to perform a series of isotopic oxygen experiments to isolate the degree of film-supplied oxygen to CO_2 production.

Figure 2b shows the 0 0 ½ reflection from a $SrCoO_x$ film held at 200°C under 0.1 mbar of oxygen partial pressure, as it undergoes reduction. We have monitored the behavior of this reflection as a function of temperature and oxygen partial pressure. In future studies with a coherent beam, we will be able to monitor time correlations in the speckle from this reflection, enabling studies of the space-time correlations in the evolving oxygen vacancy superstructure.

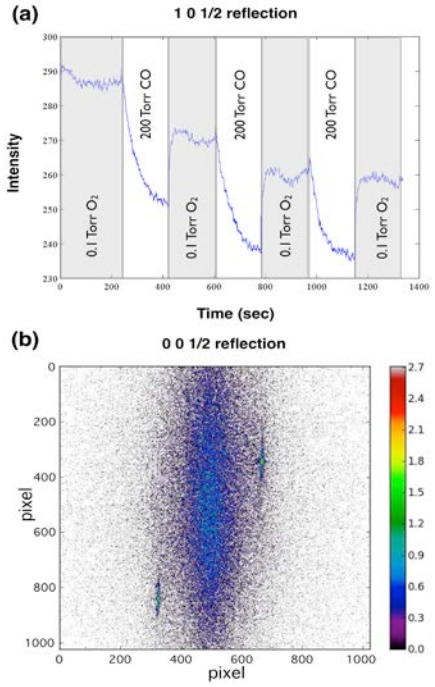


Figure 2. (a) Intensity of the 1 0 ½ reflection during reduction (CO) and oxidation (O_2). (b) *In situ* XPCS measurements from a $SrCoO_{3-\delta}$ / $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$ (001) heterostructure held at 200°C under 0.1 mbar oxygen partial pressure. The time dependence of the speckle will be used to determine the dynamics of oxygen tetrahedral ordering.

References

[1] H.-U. Habermeier, *Materials Today*, **10,** 34 (2007).
[2] H. Y. Hwang, et al. *Nature Materials*, **11,** 103 (2012).
[3] E. Bakken, et al. *J. Mater. Chem.*, **12,** 317 (2001).
[4] H. Jeen, et al. *Adv. Mater.*, **25,** 6459 (2013).
[5] P. Nolte, et al. *Science*, **321,** 1654 (2008).
[6] Y. Liang, et al. *Nature Materials* **10,** 780 (2011).
[7] A. Kumar, et al. *Nature Chemistry*, **3,** 707 (2011).
[8] J. Suntivich, et al. *Science*, **334,** 1383 (2011).
[9] J. Suntivich, et al. *Nature Chemistry*, **3,** 546 (2011).
[10] H. Jeen, et al. *Adv. Mater.*, **25,** 3651 (2013).
[11] C. M. Folkman, et al. *Rev. Sci. Instrum.*, **84,** 025111 (2013).
[12] H. Jeen, et al. *Nature Materials*, **12,** 1057 (2013).
[13] M. A. Vannice, *Catalysis Today*, **123,** 18 (2007).

Publications since last PI meeting: See complete list on Fuoss abstract

Control of Emergent Phases using Nickelate Heterostructures

John W. Freeland, Advanced Photon Source

Co-PI of Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures, DE-SC-0012375

Program Scope

Dynamic processes in materials underpin many facets of energy science such as efficient energy conversion and transport. We propose an interdisciplinary team to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales studying two broad classes of phenomena: (1) strongly electron correlated oxides exhibiting metal-insulator transitions, and (2) "hidden phases" in ferroelectrics and multiferroics. Fundamental research goals that will be addressed by the team are to: (a) Establish materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions.

Recent Progress

Oxide heterostructures offer new opportunities to control the phases of strongly correlated electrons and to seek out phases that do not exist in the bulk counterparts (see Ref. 1 and references therein). Through the utilization of strain, confinement, interfacial charge transfer, and putting distinct phases in close proximity, one can create new boundary conditions in the search for new quantum many-body phenomena. Of the many materials of interest to our project, here I will discuss the use of epitaxial nickelate architectures created with unit cell precision to illustrate our understanding to date of how one can control the static phases in this class of materials. As a starting point, consider the bulk phase diagram (see Fig. 1) that shows how one can move from purely metallic and paramagnetic phases in $LaNiO_3$ to systems that display strong metal-insulator transitions (MIT) associated with charge and antiferromagnetic order (for a review see Ref. 2).

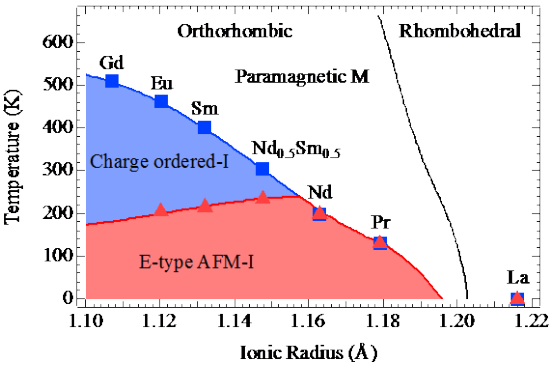


Figure 1 Phase diagram for the bulk nickelates illustrating the variety of phases with chemical pressure, which range from metallic (M) to insulating (I) together with charge order and antiferromagnetism (AFM). Reproduced from J.-S. Zhou, J. B. Goodenough, Phys Rev B **68**, 144406 (2003).

In moving to epitaxial layers, strain becomes an important control parameter as seen in the phase diagram in Fig. 2a (work together with co-PI J. Chakhalian). As one crosses from tensile to compressive strain it is possible to sweep across the entire available phase space from phases still

possessing an MIT to purely metallic phases with strong non-Fermi liquid behavior [3], which is indicative of possible quantum critical behavior in the cross-over regime. The shift to superlattices (Fig. 2b and c) makes use of the interfacial interactions, which can be harnessed to control the orbital character that is normally not active in bulk nickelates[4,5]. Recent predictions suggest topological phase can be created by altering the epitaxial orientation to the hexagnonal lattice of the (111) orientation (see references in Ref. 1).

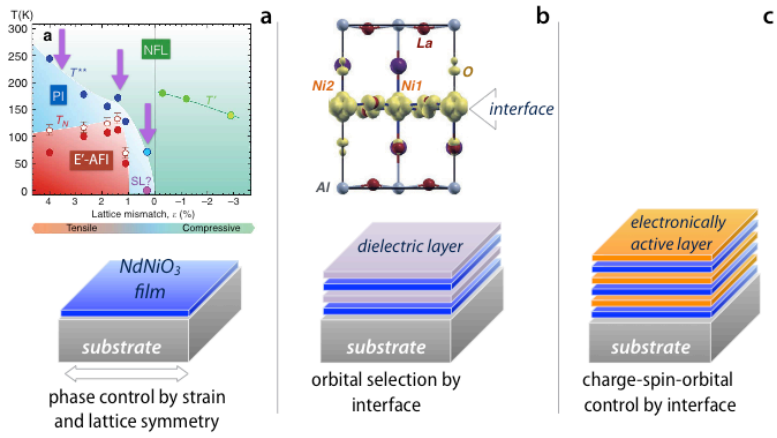


Figure 2 Architectures for control of strongly correlated electrons arising from the Ni 3d states that range from strain (a) to ultra-thin superlattices with dielectric (b) and electronically active (c) spacers

Future Plans

To this point the focus has been on the control of static phases. Now we want to utilize this phase control to expand understanding into the dynam ic realm in the search of materials with tunable response to mode selective excitation with the goal of designing energy efficient photo-responsive materials (Lead-PI V. Gopalan). Since many degrees of freedom are active in complex oxides, one needs to explore the structural, electronic, and magnetic behavior in the time-domain using the ultrafast X-ray tools at the LCLS and APS (with co-PI H. Wen), which will be directly correlated with findings of optical probes (co-PIs R. Averitt, V. Gopalan, and D. Basov). However, in this project we want to go beyond simply tracking behavior to integrate the experimental findings within a theoretical framework to provide a mechanistic understanding needed for the rational design of new mode selective materials (co-PIs J. Rondinelli and A. Millis). As well we are seeking pathways to suppress particular degrees of freedom in the system (e.g. structure) to simplify the problem and enable use to disentangle the nature of photo-excited correlated electron states.

References

[1] J. Chakhalian, J.W. Freeland, A.J. Millis, C. Panagopoulos, and J.M. Rondinelli, Rev. Mod. Phys. **86**, 1189 (2014).

[2] G. Catalan, Phase Transitions, **81**, 729 (2008).

[3] Jian Liu et al. Nature Comm. **4**, 2714 (2013)

[4] J.W. Freeland et al. Euro. Phys. Lett., **96**, 57004 (2011).

[5] J. Liu et al. Phys. Rev. Lett., **109**, 107402 (2012).

Evolution of heterogeneous materials: Atomic-scale surface structure and dynamics during growth

Paul Fuoss, Dillon Fong, Stephan Hruszkewycz, Brian Stephenson, Hoydoo You

Materials Science Division, Argonne National Laboratory

Program Scope

The development of high flux coherent x-ray sources opens new domains for study of equilibrium and non-equilibrium fluctuations in materials. We now have the opportunity to study phase transitions, nucleation and synthesis processes not only as statistical averages, but also as events resolved in both time and space. This thrust uses advanced synchrotron x-ray techniques for in situ studies of epitaxial film growth.

Recent Progress

To date, wurtzite-structure GaN thin films have most often been grown with a c-plane (0 0 0 1) surface because high quality epitaxial films are most easily grown in this orientation. However, the inherent polarization-induced electric field normal to the c-plane impedes the efficiency of light emitters because of the poor overlap of electron and hole wave functions in quantum wells [1]. Non-polar GaN with m-plane (1 0 -1 0) and a- plane (1 1 -2 0) surface orientations have attracted significant interest as a route to minimize polarization-induced fields across device interfaces [2].

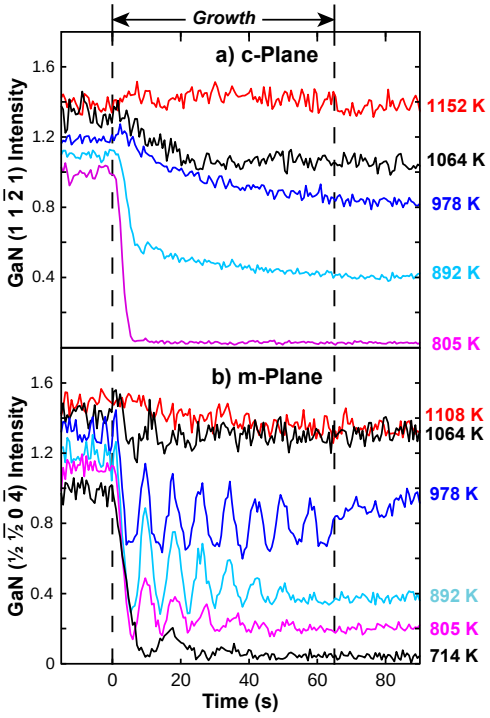


Figure 1: X-Ray CTR measurements demonstrating different growth modes as a function of temperature but at the same growth rate on a) +c-plane and b) m-plane surfaces of GaN. The m-plane shows a window of 2D layer-by-layer growth absent for the +c-plane surface.

We have carried out the first studies of homoepitaxial growth modes on m-plane GaN single crystals during metal-organic vapor phase epitaxy (MOVPE) using real-time in-situ synchrotron x-ray surface scattering [3]. On the m-plane surface, we observe all three growth modes (step-flow, layer-by-layer, and three-dimensional) as a function of temperature and growth rate. In contrast, the c-plane surface exhibits a direct crossover between step-flow and 3D growth, with no layer-by-layer regime. The apparent activation energy of 2.8 eV observed for the growth rate at the layer-by-layer to step-flow boundary on the m-

plane surface is consistent with those observed for MOVPE growth of other III-V compounds [4,5], indicating a large critical nucleus size for islands.

Future Plans

Using our recently enhanced facility for *in situ* x-ray studies, we will compare growth on the polar c-plane surface, the semi-polar r-plane, and the non-polar m-plane, to understand effects of anisotropic transport, dislocation dynamics and catalytic decomposition of ammonia that differ with orientation.

Figure 2 shows time dependent oscillations of diffuse scattering measured around the CTR anti-Bragg position of an m-plane crystal during layer-by-layer growth. Study of coherent x-ray speckle in such diffuse scattering will reveal the space/time correlations of island positions, providing unprecedented insight into the atomic-scale mechanisms of growth in the MOVPE environment.

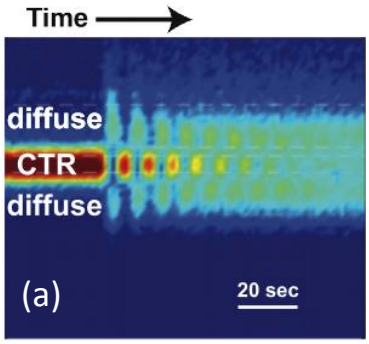


Figure 2: The time-resolved diffuse scattering near a CTR anti-Bragg position (½ 0 -½ -2) of m-plane GaN surface as surface islands form and coalesce under layer-by-layer growth conditions. Coherent x-ray techniques will reveal space/time correlations in island positions and potentially allow imaging of island evolution.

In addition to probing homoepitaxial growth, we will use x-ray techniques, and in particular coherent diffraction imaging, to probe the complex behavior associated with growing InGaN alloys. The alternative GaN crystal planes have shown distinct and promising results in terms of indium incorporation and device performance [6,7]. Despite these promising results, the underlying mechanisms that determine film crystal quality, composition, and defect incorporation are still poorly understood [8] since these different crystal faces vary in electronic properties, crystal symmetry, and catalytic properties.

References

[1] P. Waltereit et al., Nature **406**, 865 (2000).
[2] S. P. DenBaars et al., Acta Mater. **61**, 945 (2013).
[3] E. Perret et al., Appl. Phys. Lett. **105**, 051602 (2014)
[4] D. W. Kisker et al., J. Cryst. Growth **163**, 54 (1996).
[5] G. B. Stephenson et al., Appl. Phys. Lett. **74**, 3326 (1999).
[6] F.K. Yam and Z. Hassan, Superlattices Microstruct. **43**, 1 (2008).
[7] M. Adachi et al., Appl. Phys. Express **3**, 121001 (2010).
[8] R.M. Farrell, E.C. Young, F. Wu, S.P. DenBaars, and J.S. Speck, Semicond. Sci. Technol. **27**, (2012).

Publications since last PI meeting

- ***Real-time x-ray studies of crystal growth modes during metal-organic vapor phase epitaxy of GaN on c- and m-plane single crystals***
  E. Perret, M.J. Highland, G.B. Stephenson, S.K. Streiffer, P. Zapol, P.H. Fuoss, A. Munkholm and C. Thompson, Applied Physics Letters, **105**, 051602 (August 2014), doi:10.1063/1.4892349.

- ***Dynamic layer rearrangement during growth of layered oxide films by molecular beam epitaxy***
  J.H. Lee, G. Luo, I.C. Tung, S.H. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S.M. Nakhmanson, J.A. Eastman, H. Hong, J. Jellinek, D. Morgan, D.D. Fong and J.W. Freeland, Nature Materials, (August 2014), doi:10.1038/nmat4039.

- ***Growth of arrays of oriented epitaxial platinum nanoparticles with controlled size and shape by natural colloidal lithography***
  V. Komanicky, A. Barbour, M. Lackova, M. Zorko, C. Zhu, M. Pierce, H. You, Nanoscale Research Letters, **9**, 336(July 2014), doi:10.1186/1556-276X-9-336.

- ***Strain Imaging of Nanoscale Semiconductor Heterostructures with X-Ray Bragg Projection Ptychography***
  M.V. Holt, S.O. Hruszkewycz, C.E. Murray, J.R. Holt, D.M. Paskiewicz, P.H. Fuoss, Physical Review Letters, **112**, 165502(April 2014), doi:10.1103/PhysRevLett.112.165502.

- ***Full-field X-ray reflection microscopy of epitaxial thin-films***
  N. Laanait, Z. Zhang, C.M. Schlepütz, J. Vila-Comamala, M.J. Highland and P. Fenter, Journal of Synchrotron Radiation, **21**, (April 2014), doi:10.1107/S1600577514016555.

- ***Interfacial charge and strain effects on the ferroelectric behavior of epitaxial (001) $PbTiO_3$ films on (110) $DyScO_3$ substrates***
  M.J. Highland, D.D. Fong, G.B. Stephenson, T.T. Fister, P.H. Fuoss, S.K. Streiffer, C. Thompson, M.I. Richard, J.A. Eastman, Applied Physics Letters, **104**,132901 (March 2014), doi:10.1063/1.4869579.

- ***Octahedral rotations in strained LaAlO3/SrTiO3 (001) heterostructures***
  T.T. Fister, H. Zhou, Z. Luo, S.S.A. Seo, S.O. Hruszkewycz, D.L. Proffit, J.A. Eastman, P.H. Fuoss, P.M. Baldo, H.N. Lee and D.D. Fong, APL Materials, **2**, 021102 (2014), doi:10.1063/1.4865160.

- ***Influence of hydrostatic pressure on superconducting properties of niobium thin films***
  G. Pristas, S. Gabani, E. Gazo, V. Komanicky, M. Orendac, H. You, Thin Solid Films, **556**, 470 (January 2014), doi:10.1016/j.tsf.2014.01.062.

- ***Coherent Bragg nanodiffraction at the hard X-Ray Nanoprobe beamline***
  S.O. Hruszkewycz, M.V. Holt, J. Maser, C.E. Murray, M.J. Highland, C.M. Folkman and P.H. Fuoss, Philosophical Transactions of the Royal Society A, **372**, 20130118 (January, 2014), doi:10.1098/rsta.2013.0118.

- ***Universal features in the photoemission spectroscopy of high-temperature superconductors***
  J. Zhao, U. Chatterjee, D. Ai, D.G. Hinks, H. Zheng, G.D. Gu, J.P. Castellan, S. Rosenkranz, H. Claus, M.R. Norman, M. Randeria, and J.C. Campuzano, Proceedings of the National Academy of Sciences, **110**, 17774 (October 2013), doi:10.1073/pnas.1302932110.

- ***Electrocatalytic activity of surface oxides on platinum nanofacets and surfaces***
  V. Komanicky, D.C. Hennessy, H. Iddir, P. Zapol, and H. You, Electrochimica Acta, **109**, 440 (October 2013), doi:10.1016/j.electacta.2013.07.098.

- ***In Situ X-ray studies of film cathodes for solid oxide fuel cells***
  P. Fuoss, K.-C. Chang, H. You, J. of Electron Spectroscopy and Related Phenomena, **190**, 75 (October 2013), doi:10.1016/j.elspec.2013.02.003.

- ***Coherently strained epitaxial $Pb(Zr_{1-x}Ti_x)O_3$ thin films***
  R.L. Johnson-Wilke, D.S. Tinberg, C. Yeager, W. Qu, D.D. Fong, T.T. Fister, S.K. Streiffer, Y. Han, I.M. Reaney and S. Trolier-McKinstry, J. of Applied Physics, **114**, 164104 (October 2013), doi:10.1063/1.4825215.

- ***Single shot speckle and coherence analysis of the hard X-ray free electron laser LCLS***
  S. Lee, W. Roseker, C. Gutt, B. Fischer, H. Conrad, F. Lehmkühler, I. Steinke, D. Zhu, H. Lemke, M. Cammarata, D.M. Fritz, P. Wochner, M. Castro-Colin, S.O. Hruszkewycz, P.H. Fuoss, G.B. Stephenson, G. Grubel, and A. Robert, Optics Express, **21**, 24647 (October 2013), doi:10.1364/OE.21.024647.

- ***Reversible redox reactions in an epitaxially stabilized $SrCoO_x$ oxygen sponge***
  H. Jeen, W.S. Choi, M.D. Biegalski, C.M. Folkman, I.-C. Tung, D.D. Fong, J.W. Freeland, D. Shin, H. Ohta, M.F. Chisholm, and H.N. Lee, Nature Materials, **12**, 1057 (August 2013), doi:10.1038/nmat3736.

- ***Imaging Local Polarization in Ferroelectric Thin Films by Coherent X-Ray Bragg Projection Ptychography***
  S.O. Hruszkewycz, M.J. Highland, M.V. Holt, D. Kim, C.M. Folkman, C. Thompson, A. Tripathi, G.B. Stephenson, S. Hong, and P.H. Fuoss, Physical Review Letters, **110**, 177601 (April 2013), doi:10.1103/PhysRevLett.110.177601.

- ***Surface diffraction on a ψ-circle diffractometer using the χ-axis geometry***
  T.T. Fister, P.H. Fuoss, D.D. Fong, J.A. Eastman, C.M. Folkman, S.O. Hruszkewycz, M.J. Highland, H. Zhou, and P. Fenter, Journal of Applied Crystallography, **46**, (April 2013), doi:10.1107/S0021889813007693.

- ***Modular instrument mounting system for variable environment in operando X-ray experiments***
  C.M. Folkman, M.J. Highland, E. Perret, S.K. Kim, T.T. Fister, H. Zhou, P.M. Baldo, S. Seifert, J.A. Eastman, P.H. Fuoss, and D.D. Fong, Review of Scientific Instruments, **84**, 025111 (February 2013), doi:10.1063/1.4791799.

- ***Resonant X-ray scattering studies of epitaxial complex oxide thin films***
  E. Perret, C. Park, D.D. Fong, K.-C. Chang, B.J. Ingram, J.A. Eastman, P.M. Baldo, and P.H. Fuoss, Journal of Applied Crystallography, **46**, 76 (January 2013), doi:10.1107/S0021889812047620.

- ***Synchrotron X-ray diffraction and fluorescence study of the astrolabe***
  M. Notis, B. Newbury, B. Stephenson, G.B. Stephenson, Applied Physics A, **111**, 129 (December 2012), doi:10.1007/s00339-012-7480-7.

- ***High Contrast X-ray Speckle from Atomic-Scale Order in Liquids and Glasses***
  S. Hruszkewycz, M. Sutton, P. Fuoss, B. Adams, S. Rosenkranz, K. Ludwig, W. Roseker, D. Fritz, M. Cammarata, D. Zhu, S. Lee, H. Lemke, C. Gutt, A. Robert, G. Grubel, and G. Stephenson, Physical Review Letters, **109**, 185502 (November 2012), doi:10.1103/PhysRevLett.109.185502.

- ***Coherent x-ray scattering experiments of Pt(001) surface dynamics near a roughening transition***
  M.S. Pierce, A. Barbour, V. Komanicky, D. Hennessy, and H. You, Physical Review B, **86**, 184108 (November 2012), doi:10.1103/PhysRevB.86.184108.

- ***Study of electrode surface dynamics using coherent surface X-ray scattering***
  H. You, M. Pierce, V. Komanicky, A. Barbour, and C. Zhu, Electrochimica Acta, **82**, 570 (November 2012), doi:10.1016/j.electacta.2012.03.069.

- ***Momentum spectrometer for electron-electron coincidence studies on superconductors***
  R. Wallauer, S. Voss, L. Foucar, T. Bauer, D. Schneider, J. Titze, B. Ulrich, K. Kreidi, N. Neumann, T. Havermeier, M. Schöffler, T. Jahnke, A. Czasch, L. Schmidt, A. Kanigel, J.C. Campuzano, H. Jeschke, R. Valenti, A. Müller, G. Berner, M. Sing, R. Claessen, H. Schmidt-Böcking, and R. Dörner, Review of Scientific Instruments, **83**, 103905 (October 2012), doi:10.1063/1.4754470.

- ***Electronic surface compensation of polarization in $PbTiO_3$ films***
  J. He, G.B. Stephenson and S.M. Nakhmanson, Journal of Applied Physics, **112**, 054112 (September 2012), doi:10.1063/1.4750041.

- ***A DFT study of reaction pathways of NH_3 decomposition on InN (0001) surface***
  W. Walkosz, P. Zapol, and G. Brian Stephenson, The Journal of Chemical Physics, **137,** 054708 (August, 2012), doi:10.1063/1.4739309.

Ultrafast Electronic and Structural Dynamics in Quantum Materials

Nuh Gedik, MIT, Department of Physics, Cambridge, MA 02139

Program Scope

Topological insulators (TIs) are novel materials that do not conduct electricity in their bulk but possess exceptional properties at the surface. When a topologically ordered phase is interfaced with an ordinary phase that has a different topological invariant (including the vacuum), dissipationless metallic states appear at the boundary, even if both materials are insulating. These conducting surface electrons have a number of highly unusual characteristics: (i) they behave like massless relativistic particles (Dirac fermions) similar to photons (ii) their spin is locked perpendicular to their momentum and (iii) this state is robust against moderate disorder. These surface states are topologically protected by time reversal symmetry (TRS). When TRS is broken, the Dirac fermions acquire mass and the resultant state display highly exotic properties such as quantum anomalous Hall effect or unusual magneto-optical effects. Understanding and characterizing unique properties of these materials can lead to novel applications such as current induced magnetization or extremely robust quantum memory bits.

The goal of this program is to use ultrashort laser pulses to probe and control properties of the topological surface states. Utilizing the short duration of these pulses, we aim to use time resolved techniques to probe the temporal evolution of optical and electronic properties with time, energy and momentum resolutions in response to photoexcitation.

Recent Progress

We have used time and angle resolved photoemission spectroscopy to probe the evolution of the band structure of a TI after excitation by a laser pulse. When the energy of the excitation pulse is higher than the bulk band gap, we observe generation of photoexcitations across the bulk band gap. Subsequent relaxation dynamics of bulk and surface excitations reveal that the interaction between the two populations is mediated by phonons [1].

When the energy of the photoexcitation pulse is below the bulk band gap of the TI, we observed that surface electrons and laser photons form hybrid states known as Floquet-Bloch states [2]. These photon-dressed surface bands exhibit polarization-dependent band gaps at avoided crossings. Circularly polarized photons induce an additional gap at the Dirac point, which is a signature of broken time-reversal symmetry on the surface. These observations establish the Floquet-Bloch bands in solids and pave the way for optical manipulation of topological quantum states of matter.

Floquet theorem states that a Hamiltonian periodic in time has quasistatic eigenstates that are evenly spaced by the drive photon energy. These so-called Floquet states can be regarded as a time analog of Bloch states, which are the eigenstates of a Hamiltonian periodic in space. Combining the two situations, a periodic excitation on a crystalline lattice induces Floquet-Bloch bands that repeat in both momentum and energy. Just as different Bloch bands hybridize and develop band gaps at the crossing points, the crossing points between different orders (n) of the Floquet-Bloch bands open dynamic gaps.

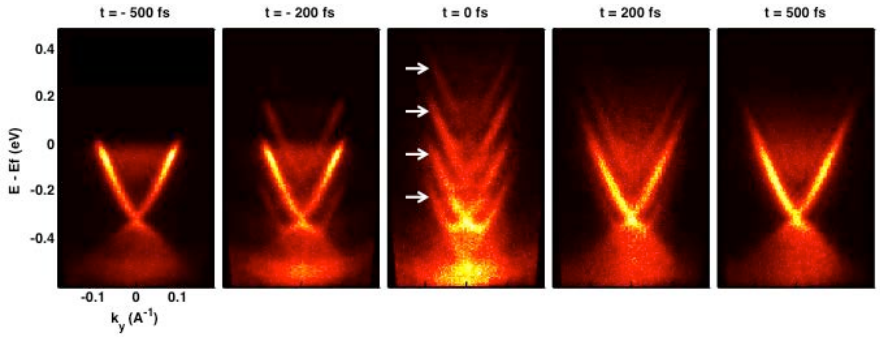


Figure 1 Evolution of the surface band structure of Bi_2Se_3 under strong linearly polarized mid-infrared (MIR) light with photon energy 165 meV. White arrows show the Floquet-Bloch bands.

Future Plans

We will use this new ability to break TRS with light to achieve experimental realization of several fascinating effects in 3D TIs. First, we hope to achieve a complete understanding of the nature of Floquet-Bloch states and the photoinduced TRS broken phase in topological insulators. Then, we will use this light induced TRS broken state to realize several theoretically predicted exotic phenomena in TIs. In particular, we will search for light induced quantum anomalous hall effect, low frequency magneto-optical effects and one-dimensional chiral edge modes. This new field of Floquet physics in TIs is ripe for exploration, the importance of which extends well beyond understanding topological materials. The ability to change electronic band structure with light could fundamentally change the way we think about generating materials with novel properties.

References

1. *"Measurement of intrinsic Dirac fermion cooling on the surface of a topological insulator Bi_2Se_3 using time- and angle-resolved photoemission spectroscopy"* Y. H. Wang, D. Hsieh, E. J. Sie, H. Steinberg, D. R. Gardner, Y. S. Lee, P. Jarillo-Herrero, and N. Gedik ***Phys. Rev. Lett. (2012)***

2. "*Observation of Floquet-Bloch States in a Topological Insulator*" Y.H. Wang, Hadar Steinberg, P. Jarillo-Herrero, and N. Gedik ***Science 342,*** 453 (2013)

Publications

1. "*Trion induced negative photoconductivity in monolayer MoS_2*" C. H. Lui, A. J. Frenzel, D. V. Pilon, Y.-H. Lee, X. Ling, G. M. Akselrod, J. Kong, N. Gedik, *to appear in* ***Phys. Rev. Lett.,*** (2014)

2. "*Semiconducting-to-metallic photoconductivity crossover and temperature-dependent Drude weight in graphene*" A. J. Frenzel, C. H. Lui, Y. C. Shin, J. Kong, N. Gedik ***Phys. Rev. Lett. 113,*** 056602 (2014)

3. "*Observation of Floquet-Bloch States in a Topological Insulator*" Y.H. Wang, Hadar Steinberg, P. Jarillo-Herrero, and N. Gedik ***Science 342,*** 453 (2013)

4. "*Driven Electronic States at the Surface of a Topological Insulator*" Benjamin M. Fregoso, Y.H. Wang, N. Gedik, Victor Galitski ***Phys. Rev. B 88***, 155129 (2013)

5. "*Observation of suppressed terahertz absorption in photoexcited graphene*" A.J. Frenzel, C.H. Lui, W. Fang, N.L. Nair, P.K. Herring, P. Jarillo-Herrero, J. Kong, and N. Gedik ***Appl. Phys. Lett. 102*** 113111 (2013)

6. *"Spin Induced Optical Conductivity in the Spin Liquid Candidate Herbertsmithite"* Daniel V. Pilon, Chun Hung Lui, Tianheng Han, David B. Shrekenhamer, Alex J. Frenzel, William J. Padilla, Young S. Lee and Nuh Gedik ***Phys. Rev. Lett. 111***, 127401 (2013)

7. *"Circular dichroism in angle-resolved photoemission spectroscopy of topological insulators"* Yihua Wang and Nuh Gedik Phys. ***Status Solidi RRL 7*** , No. 1–2, 64–71 (2013)

8. *"Measurement of intrinsic Dirac fermion cooling on the surface of a topological insulator Bi_2Se_3 using time- and angle-resolved photoemission spectroscopy"* Y. H. Wang, D. Hsieh, E. J. Sie, H. Steinberg, D. R. Gardner, Y. S. Lee, P. Jarillo-Herrero, and N. Gedik ***Phys. Rev. Lett. (2012)***

9. "*Theoretical and Experimental Study of Second Harmonic Generation from the Surface of the Topological Insulator Bi_2Se_3*" J. W. McIver, D. Hsieh, S.G. Drapcho, D.H. Torchinksy, D.R. Gardner, Y.S. Lee, and N. Gedik Phys. ***Rev. B 86,*** 035327 (2012)

10. *"Control over topological insulator photocurrents with light polarization"* J. W. McIver*, D. Hsieh*, H. Steinberg, P. Jarillo-Herrero and N. Gedik ***Nature Nanotechnology 7,*** 96–100 (2012)

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures (Grant No.: DE-SC0012375, Start Date: 8/15/2014)

V. Gopalan (PI, Penn State), R. Averitt (UCSD), D. Basov (UCSD), J. Chakhalian (U. Arkansas), R. Engel-Herbert (Penn State), J. Freeland (Argonne), L. Martin (Berkeley), A. Millis (Columbia), J. Rondinelli (Northwestern), H. Wen (Argonne)

Program Scope

Dynamic processes in materials underpin many facets of energy science such as efficient energy conversion and transport. Our project aims to address two of the grand challenges of materials research put forth by the BES, namely to uncover hidden phases in transition metal oxides by controlling dynamic trajectories in a complex energy landscape by preferentially exciting specific degrees of freedom, while developing the experimental and theoretical tools to control matter away from equilibrium. We propose an interdisciplinary team to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales (**Figure 1**) studying two broad classes of phenomena: strongly electron correlated oxides exhibiting metal-insulator transitions, and "hidden phases" in ferroelectrics and multiferroics. Fundamental research goals that will be addressed by the team are to: (a) Establish materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions.[1,2] In order to probe transient states, the team has assembled experts in a new generation of ultrafast and ultrabright light sources in terahertz, infrared and hard X-ray free electron lasers, as well as pioneers in the development of nanoscale diffraction, spectroscopy, and ultrafast multimodal microscopy techniques such as ultrafast infrared near-field nanospectroscopy[3]. The team consists of experienced users and resident scientists at national X-ray user facilities including the Linac

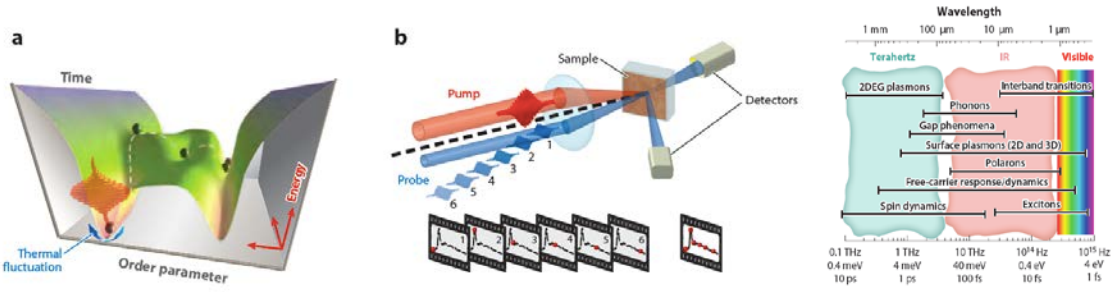


Figure 1: Pathway for photoinduced phase transition. (a) along the dynamical free-energy landscape as a function of time after pump excitation. (*b*) Ultrafast spectroscopy and switching of materials. A pump pulse (*red*) creates a nonequilibrium state. By sweeping the probe pulses (*blue*) at different delays (labeled with *numbers*) and by measuring the reflection or transmission of a probe beam, snapshots of the transient state are taken to temporally resolve the nonequilibrium dynamics. Pump beam may be in the visible, mid-IR, or the THz and determines mode selectivity. (*c*, right) Energy scales associated with different optical and elementary excitations in complex oxides for the proposed mode selectivity.

Coherent Light Source (LCLS) and the Advanced Photon Source (APS). They are complemented by material growers, who utilize state-of-the-art hybrid and laser molecular beam epitaxy with unit cell level control, and theorists who bring materials-by-design density functional and non-equilibrium dynamical mean field theories to the team.[4,5]

Recent Progress

This team has recently discovered new electronic phases in strained nickelate films,[6] "hidden" magnetic phase in a paramagnetic manganite film through photoexcitation,[7] and low symmetry metastable phases in classic ferroelectrics exhibiting large property enhancements that can be created and melted with fields.[8] These will be some of the building blocks going forward. Our recent progress (in the past few months) has been as follows: (1) Established regular biweekly teleconferences for research planning, updates, and team building for the past two months. (2) Interviewing and hiring of students and postdocs is being actively pursued. (3) We have developed a plan for direct phonon pumping (both experiments and theory) through extensive team discussions. A document with the current plans was submitted to Lane Wilson. (4) Successfully secured beamtime for Advanced Photon Source towards probing hidden states in ferroelectrics and nickelates. Experiments are planned this Fall. (5) Ultrafast optical experiments for phonon pumping are being setup.

Future Plans

Our central goal is to use irradiation to create (transiently, i.e. for the duration of the irradiation) a system with enhanced or new properties not found in presently known equilibrium bulk materials. We will explore the phenomena of metal insulator transitions, charge ordering, magnetism, ferroelectricity, and multiferroicity in complex oxides.[9] The specific materials systems are: Manganites, Nickelates, Tintanates, Vanadates, Ferrites, and Cobaltites. Chakhalian (thermal MBE), Engel-Herbert (Hybrid MBE), and Martin (Laser MBE) will synthesize samples.

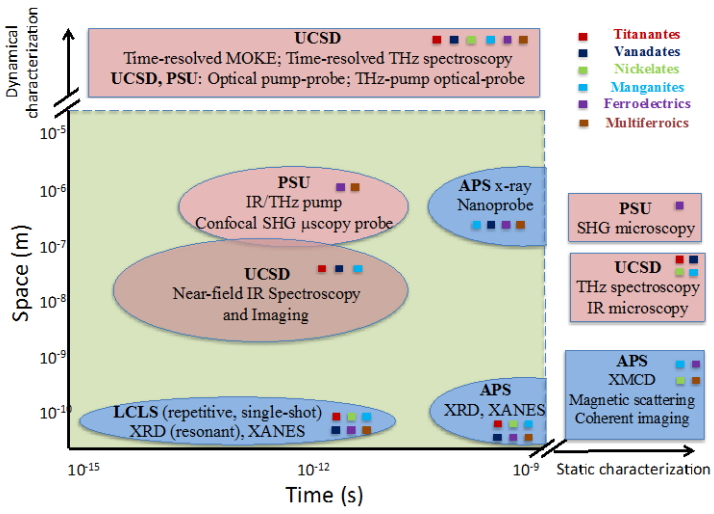


Figure 2: Ultrafast X-ray and optical techniques proposed by this team and how UCSD, Penn State and Argonne team members complement each other.

Pump-probe techniques using optical/infrared/THz pumping, and Xray/optical/infrared/THz probing will be performed (**Figure 2**). We plan to employ two broad modalities: Electronic excitation and Phonon excitation. The phonon pumping will be achieved with direct infrared and THz pumping, as well as impulsively stimulated coherent phonon pumping. Synergy

between proposed techniques between different team members (Gopalan, Averitt, Basov, Wen, Freeland) is depicted in Figure 2.

The key questions to be addressed with theory (Rondinelli and Millis) are: which materials to investigate? Which phonons to excite? How hard does the electronic and atomic systems need to be driven to have the potential of producing an interesting effect? What are the other effects of the excitation? Our approach will be the computation of phonon nonlinearities,[10] computation of dipole matrix elements, and the computation of effects and material responses from pumping.

The details of the proposed work above and our approach are in the original proposal, as well as in the "Phonon Pumping plan" submitted to Lane Wilson.

Publications

None

References

[1] Zhang, J. & Averitt, R.D., Dynamics and Control in Complex Transition Metal Oxides. *Annu. Rev. Mater. Res.* 44 (1), in print (2014). http://www.annualreviews.org/doi/abs/10.1146/annurev-matsci-070813-113258

[2] Basov, D., Averitt, R., van der Marel, D., Dressel, M., & Haule, K., Electrodynamics of correlated electron materials. *Rev. Mod. Phys.* 83 (2), 471-542 (2011). http://rmp.aps.org/abstract/RMP/v83/i2/p471_1

[3] Wagner, M., Fei, Z., McLeod, A.S., Rodin, A.S., Bao, W., Iwinski, E.G., Zhao, Z., Goldflam, M., Liu, M., Dominguez, G., Thiemens, M., Fogler, M.M., Castro Neto, A.H., Lau, C.N., Amarie, S., Keilmann, F., & Basov, D.N., Ultrafast and Nanoscale Plasmonic Phenomena in Exfoliated Graphene Revealed by Infrared Pump–Probe Nanoscopy. *Nano Lett.* 14 (2), 894-900 (2014). http://dx.doi.org/10.1021/nl4042577

[4] Rondinelli, J., May, S., & Freeland, J., Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery. *MRS Bull.* 37 (03), 261-270 (2012). http://journals.cambridge.org/action/displayAbstract?aid=8511543

[5] Lau, B. & Millis, A.J., Theory of the Magnetic and Metal-Insulator Transitions in $RNiO_3$ Bulk and Layered Structures. *Phys. Rev. Lett.* 110 (12), 126404 (2013). http://link.aps.org/doi/10.1103/PhysRevLett.110.126404

[6] Liu, J., Kargarian, M., Kareev, M., Gray, B., Ryan, P.J., Cruz, A., Tahir, N., Chuang, Y.-D., Guo, J., Rondinelli, J.M., Freeland, J.W., Fiete, G.A., & Chakhalian, J., Heterointerface engineered electronic and magnetic phases of $NdNiO_3$ thin films. *Nat. Commun.* 4 (2013). http://dx.doi.org/10.1038/ncomms3714

[7] J. Zhang, X. Tan, M. Liu, S. W. Teitelbaum, K. A. Nelson, D. N. Basov, W. Wu, R.D. Averitt, Cooperative photoinduced metastable phase control in strained manganite films. *submitted* (2014).

[8] Lummen, T.T.A., Gu, Y., Wang, J., Lei, S., Xue, F., Kumar, A., Barnes, A.T., Barnes, E., Denev, S., Belianinov, A., Holt, M., Morozovska, A.N., Kalinin, S.V., Chen, L.-Q., & Gopalan, V., Thermotropic phase boundaries in classic ferroelectrics. *Nat. Commun.* 5 (2014). http://dx.doi.org/10.1038/ncomms4172

[9] Chakhalian, J., Millis, A.J., & Rondinelli, J., Whither the oxide interface. *Nat. Mater.* 11 (2), 92 (2012). http://www.nature.com/nmat/journal/v11/n2/full/nmat3225.html

[10] Subedi, A., Cavalleri, A., Georges, A. Theory of nonlinear phononics for coherent light control of solids, *Phys. Rev. B*, **89**, 220301(R) (2014). http://journals.aps.org/prb/abstract/10.1103/PhysRevB.89.220301

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures (Grant No.: DE-SC0012375, Start Date: 8/15/2014)

Metastable Low Symmetry Phases in Ferroelectrics with Enhanced Properties

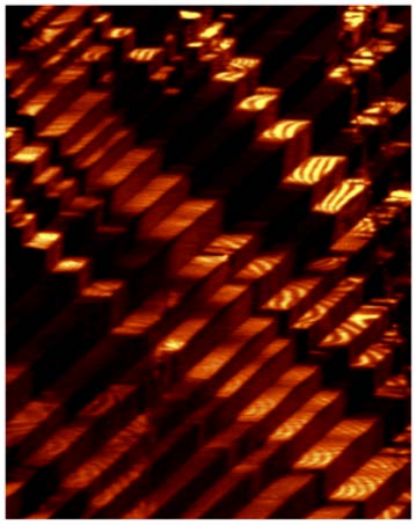
Venkatraman Gopalan, Pennsylvania State University

Program Scope

Dynamic processes in materials underpin many facets of energy science such as efficient energy conversion and transport. We propose an interdisciplinary team to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales studying two broad classes of phenomena: strongly electron correlated oxides exhibiting metal-insulator transitions, and "hidden phases" in ferroelectrics and multiferroics. Fundamental research goals that will be addressed by the team are to: (a) Establish materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions.[1]

Recent Progress

Gopalan group has recently discovered metastable low symmetry phases in single crystals of classic ferroelectrics of $BaTiO_3$ and $KNbO_3$ (Supported by the NSF DMR-0820404).[2,3] While both these materials show a series of rhombohedral-orthorhombic-tetragonal-cubic (ROTC) phase transitions upon heating, the equilibrium phase diagram does not indicate any other phase. Nonetheless, using optical second harmonic generation microscopy (developed in Gopalan's lab) combined with nanoscale Xray diffraction imaging (at Argonne National Labs), we have discovered that low symmetry monoclinic phase exists at room temperature coexisting with the tetragonal phase. This phase is metastable, and can easily be perturbed with temperature and field. Using phase-field modeling, we show that this phase is (meta)stabilized through local fields and stresses generated by domain microstructure, or externally applied. Such susceptibility is shown to lead to an increase in nonlinear optical coefficients and piezoelectric coefficients in this phase by a factor of up to 440%.



Optical second harmonic generation microscopy reveals a new metastable monoclinic phase (bright regions) coexisting with conventional tetragonal phase (darker regions).

Future Plans

In this DOE project, we plan to broadly explore metastable and transient ferroelectric phases in crystals, thin films and heterostructures (grown by Martin and Engel-Herbert) on ultrafast time scales and nanometer length scales. In particular, we plan to excite phonon modes that can break inversion symmetry and lead to a ferroelectric order, as well as couple it to magnetism in multiferroic systems. Phonon pumping (Gopalan, Averitt) will be performed through impulsively stimulated Raman Scattering, as well as direct pumping with THz and infrared radiation (details of the phonon pumping was plan separately submitted to Lane Wilson). Both John-Teller distortion mechanism, as well as improper mechanisms involving oxygen octahedral rotations (Rondinelli predictions) [4] will be explored through phonon pumping. The ferroic order will be probed on ultrafast time scale with nonlinear optics, Raman spectroscopy and Xray diffraction imaging. The optical second harmonic generation microscope at Penn State now has variable temperature stage for imaging down to 4K with ~500nm spatial resolution. We will complement the system with pump-probe microscopy, where optical and THz pumping and nonlinear optical and Raman probing will be performed in the confocal microscopy mode. In parallel, we have successfully acquired beamtime at the Argonne National Labs in Fall 2014 (with Wen, Freeland, Averitt) for ultrafast pump-probe experiments using THz and optical pumping / Xray diffraction imaging probe. Nanoscale imaging spectroscopy of metastable phase creation will be performed in collaboration with Basov.

Publications

None

References

[1] Zhang, J. & Averitt, R.D., Dynamics and Control in Complex Transition Metal Oxides. *Annu. Rev. Mater. Res.* 44 (1), in print (2014). http://www.annualreviews.org/doi/abs/10.1146/annurev-matsci-070813-113258

[2] Lummen, T.T.A., Gu, Y., Wang, J., Lei, S., Xue, F., Kumar, A., Barnes, A.T., Barnes, E., Denev, S., Belianinov, A., Holt, M., Morozovska, A.N., Kalinin, S.V., Chen, L.-Q., & Gopalan, V., Thermotropic phase boundaries in classic ferroelectrics. *Nat. Commun.* 5 (2014). http://dx.doi.org/10.1038/ncomms4172

[3] Gu, Y., Xue, F., Lei, S., Lummen, T. T. A., Wang, J., Gopalan, V., Chen, L-Q., Monoclinic phases arising across thermal inter-ferroelectric phase transitions, *Phys. Rev. B* **90**, 024104 (2014). http://journals.aps.org/prb/abstract/10.1103/PhysRevB.90.024104

[4] Rondinelli, J., May, S., & Freeland, J., Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery. *MRS Bull.* 37 (03), 261-270 (2012). http://journals.cambridge.org/action/displayAbstract?aid=8511543

Fundamental Physics of Topological Matter and Novel Excitation Modes

M. Zahid Hasan

Department of Physics, Princeton University, Princeton, NJ 08544, USA

Tel: +1-609-258-3044 Fax: +1-609-258-1006
email: mzhasan@princeton.edu

In this talk, report our recent results on topological quantum phase transition leading to the realization of 3D Graphene, topological Dirac semimetals (TDSM), topological Crystalline Insulators (TCI), topological Kondo Insulators (TKI) and topological superconductors (T-SC) [1-11]. Some recent results on thin-film topological superconductors as a robust platform for exotic fermions would be presented. These new phases of electronic matter collectively reveal the emergence of a topological revolution in condensed matter physics with potential for application. I also briefly describe our recent results on the **ultrafast (time-resolved ARPES) electron dynamics** observed in topological matter.

References (work supported by DOE)

1. M.Z. Hasan & C.L. Kane; Topological Insulators *REVIEWS of MODERN PHYSICS* 82, 3045 (2010).

2. M.Z. Hasan *et.al.,* "Experimental Discovery of Topological Surface States: A New type of 2D Electron Systems (2DES)" Chapter in edited book volume "Topological Insulators" edts Franz & Molenkamp, Elsevier/Oxford (2013).

3. D. Hsieh *et.al., NATURE* 452, 970 (2008); D. Hsieh *et.al., SCIENCE* 323, 919 (2009).

4. D. Hsieh *et.al., NATURE* 460, 1101 (2009); Y. Xia *et.al., NATURE PHYS* 05, 398 (2009).

5. L.A. Wray *et.al., NATURE PHYS* 06, 855 (2010); *NATURE PHYS* 07, 32 (2011).

6. S.-Y. Xu *et.al., SCIENCE* 332, 560 (2011); *NATURE PHYSICS* 08, 616 (2012).

7. Y. Okada *et.al., SCIENCE* 341, 6153 (2013); Zeljkovic *et.al., NATURE PHYSICS* 10, 572 (2014).

8. Y. Xu *et.al., NATURE PHYSICS* (in press) (2014). *NATURE MATERIALS* (submitted) (2014).

9. M. Neupane *et.al., NATURE COMMUN*. 05, 3786 (2014); *NATURE COMMUN*. 04, 2991 (2013).

10. S.-Y. Xu *et.al.,* Helical Topological Superconductor *NATURE PHYSICS* (in press) (2014).

11. S.-Y. Xu *et.al., SCIENCE* (submitted) (2014).

X-ray Scattering Studies of Strongly Correlated Electron Systems

J.P. Hill and M.P.M. Dean,

Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory

Program Scope

The central objective of this program is to carry out basic studies of the structural, electronic and magnetic properties of strongly correlated electron systems using advanced x-ray scattering techniques. Particular emphasis is placed on electronic and magnetic structure and phase behavior, on collective excitations and on non-equilibrium dynamics and how these relate to high-temperature superconductivity. The proposed research has a long-term goal of understanding and ultimately controlling the properties of these materials. Inelastic x-ray scattering and hard and soft x-ray resonant scattering experiments will be carried out as part of a broader effort within CMPMSD and more generally at BNL to address these questions. To carry out these objectives, the X-ray Scattering Group also develops instrumentation and is involved in the development and use of two sectors at the APS, and three beamlines at NSLS-II.

Recent Progress

The ubiquity and importance of short-range charge correlations in the cuprate phase diagram has recently become clear. We have used soft x-ray resonant scattering to show that these correlations in the so-called "214" system of $La_{2-x}Ba_xCuO_4$ and in the "123" system $YB_2C_3O_{6.6}$ have order parameters of a similar size, despite having different wave-vectors [1]. Further, we have observed rotated charge stripe ordering for the first time in orthorhombic $La_{2-x}Sr_xCuO_4$ and showed that again this ordering has a similar integrated intensity [2]. These results lend strong support to the idea that there is a common motif to the charge order in all cuprate families. Our ultra-fast experiements on $La_{2-x}Ba_xCuO_4$, show that this charge order is melted with an mid-IR photon pump on a time scale of a few hundred femtoseconds [3]. This is much faster than the response of the LTT structural distortion, which in equilibrium is tied to the charge order. This is significant because similar MIR pumps have previously been shown to induce superconductivity in non-superconducting, stripe ordered $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$ [4] and to increase the strength of the superconducting condensate in $La_{1.875}Ba_{0.125}CuO_4$ [5]. Our results are consistent with a picture where, in equilibrium, the charge order inhibits the 3D phase coherence the 2D planes (even though these have strong superconducting correlations). The mid-IR pump then destroys charge order and allows the formation of 3D phase-coherent superconductivity [4]. Using inelastic scattering, we have also looked for renormalization of the spin correlations as a result of the charge correlations. With resolution available today, no such effects were observed [6].

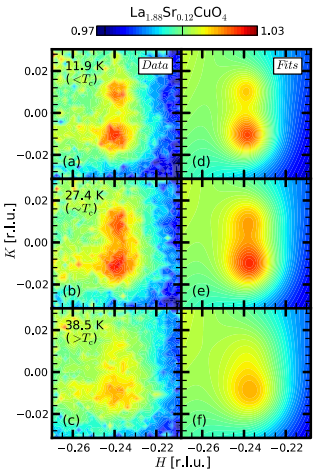


Fig 1. Scattered intensity arising from stripe order in $La_{1.88}Sr_{0.12}CuO_4$. The split peak shows the stripe order is rotated away from the CuO bonds.

Future Plans

There are a number of central questions that need to be addressed in regard to the charge correlations in the cuprates. First, what is their doping dependence? Several scenarios are possible (see figure). Current experiments can only detect charge order when the correlations length is relatively long. Higher sensitivity is required in order to definitively determine whether the presence of such correlations is related to a quantum critical point, or to the pseudogap phase. The CSX beamline at NSLS-II, which will have a factor of 500x the flux of the NSLS where the previous experiments were performed [1,2], together with MBE films grown by Ivan Bozovic, will enable the first such comprehensive studies.

Second, what is the real space organization of these charge correlations and what is their dynamical behavior? Key issues include what determines the correlation length, are there glassy dynamics at any temperature, and what, if any, is the role of impurities? By observing the time dependence of the "speckle" pattern in coherent x-ray scattering experiments at CSX, we will extract real-space movies of the charge correlations on time scales to 1 μs (the limit of NMR experiments) and length scales to 5 nm.

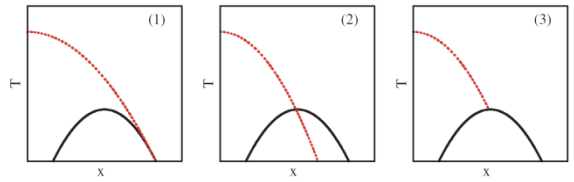


Fig 2.Possible phase diagrams for the charge correlations as a function of doping. The intensity at NSLS-II will allow these various scenarios to be distinguished (taken from ref [7]).

Third, is the superconducting condensate in fact a pair density wave state? If so a new pair density wave diffraction peak should be observed at half the wavevector of the charge density wave. With the large flux of NSLS-II, we will carry out a search for this peak. Observing it would be a significant advance in our understanding of high-temperature superconductivity.

In a parallel thrust, we will investigate doped iridates such $Sr_2Rh_{1-x}Ir_xO_4$. These large spin orbit coupled systems have many analogies with the curpates. Here key questions include, do these systems also exhibit incommensurate charge and spin correlations? More generally, how do the spin excitations evolve with doping? Unlike the cuprates, the useful resonance, the Ir L_3, is in the hard x-ray regime (11.2 keV) allowing the full Brillouin zone to be probed. Related to this, we will also investigate the evolution of the magnetic and orbital excitation spectrum of Sr_2IrO_4, following the application of at MIR pulse. This will both reveal the microscopic mechanism of the MIR pump for the first time, and allow the evolution of the magnetic Hamiltonian to be followed in real time.

References

*[1] Thampy, et al., Phys. Rev. B 88, 024505 (2013)
*[2] Thampy, V., et al., Phys. Rev. B 90, 100510(R) (2014)
*[3] Först, M., et a., Phys. Rev. Lett. 112, 157002 (2014)
[4] Fausti, D., et al., Science 331 189-191 (2011)
*[5] Nicoletti, D., et al., Phys. Rev. B 90, 100503(R) (2014)
[6] Dean, M. P. M., et al., Phys. Rev. B 88, 020403(R) (2013)
[7] Norman, M. R., Pines, D., Kallin, C., Advances in Phys. 54, 715-733 (2005)
***** Funded by this FWP

Publications

2014

1. Burriel, M., Wilkins, S., Hill, J.P., Muñoz-Márquez, M.A., Brongersma, H.H., Kilner, J.A., Ryan, M.P., and Skinner, S.J. Absence of Ni on the outer surface of Sr doped La2NiO4 single crystals. Energy Environ. Sci. 7, 311-316 (2014).
2. Caviglia, A.D., Först, M, Scherwitzl, R., Khanna, V., Bromberger, H., Mankowsky, R., Singha, R., Chuang, Y.-D., Lee, W.S., Krupin, O., Schlotter, W.F., Turner, J.J., Dakovski, G.L., Minitti, M.P., Robinson, J., Scagnoli, V., Wilkins, S.B., Cavill, S.A., Gibert, M., Gariglio, S., Zubko, P., Triscone, J.-M., Hill, J.P., Dhesi, S.S., and Cavalleri, A. Photo-induced melting of magnetic order in the correlated electron insulator NdNiO3. Phys. Rev. B 88, 220401(R) (2013). (published 12/2/2013).
3. De Vries, M.A., Loving, M., McLaren, M., Brydson, R.M.D., Liu, X., Langridge, S., Lewis, L.H., and Marrows, C.H. Asymmetric "melting" and "freezing" kinetics of the magnetostructural phase transition in B2-ordered FeRh epilayers. Appl. Phys. Lett. 104, 232407 (2014).
4. Först, M, Tobey, R., Bromberger, H., Wilkins, S., Khanna, V., Caviglia, A., Chuang, Y.-D., Lee, W.S., Schlotter,W., Turner, J., Minitti, M., Krupin,O., Xu, Z.J., Wen, J.S., Gu, G.D., Dhesi, S.S., Cavalleri, A., and Hill, J.P. Melting of charge stripes in vibrationally driven La1.875Ba0.125CuO4: Assessing the respective roles of electronic and lattice order in frustrated superconductors. Phys. Rev. Lett. 112, 157002 (2014).
5. Först, M., Mankowsky, R., Bromberger, H., Fritz, D.M., Lemke, H., Zhu, D., Chollet, M., Tomioka, Y., Tokura, Y., Merlin, R., Hill, J.P., Johnson, S.L., and Cavalleri, A. Nonlinear phononics viewed by Femtosecond X-ray diffraction. New J. of Phys. (submitted).
6. Langridge, S., Watson, G.M., Gibbs, D., Betouras, J.J., Gidopoulos, N.I., Pollmann, F., Long, M.W., Vettier, C., and Lander, G.H. Distinct magnetic phase-transition at the surface of an antiferromagnet. Phys. Rev. Lett. 112, 167201 (2014).
7. Leiner, J., Thampy, V., Christianson, A.D., Abernathy, D.L., Stone, M.B., Lumsden, M.D., Sefat, A.S., Sales, B.C., Hu, J., Mao, Z., Bao, W., and Broholm, C. Modified magnetism within the coherence volume of superconducting Fe1+∂SexTe1-x. Phys. Rev. B 90, 100501(R) (2014).
8. Li, Qing'an, Gray, K.E.,Wilkins, S.B., et al. Prediction and experimental evidence for thermodynamically stable charged orbital domain walls. Phys. Rev. X 4, 031028 (2014).
9. Nicoletti, D., Casandruc, E., Laplace, Y., Khanna, V., Hunt, C.R., Kaiser, S., Dhesi, S.S., Gu, G.D., Hill, J.P., and Cavalleri, A. Optically-induced superconductivity in striped La2-xBaxCuO4 by polarization-selective excitation in the near infrared. Phys. Rev. B 90, 100503(R) (2014).
10. Öztürk, H., Yan, H., Hill, J.P., and Noyan, I. Sampling statistics of diffraction from nanoparticle power aggregates. J. Appl. Cryst. 47, 1016-1025 (2014).

11. Seman, T., Liu, X., Hill, J.P., van Veenendaal, M., and Ahn, K. Momentum dependence in K-edge resonant inelastic x-ray scattering and its application to screening dynamics in CE-phase La0.5Sr1.5MnO4. Phys. Rev. B 90, 045111 (2014).
12. Thampy, V., Dean, M.P.M., Christensen, N.B., Steinke, L., Islam, Z., Oda, M., Ido, M., Momono, N., Wilkins, S.B., and Hill, J.P. Rotated stripe order and its competition with superconductivity in La1.88Sr0.12CuO4. Phys. Rev. B 90, 100510(R) (2014).

2013

13. Burrows, C.W., Dobbie, A., Myronov, M., Hase, T.P.A., Wilkins, S., Walker, M., Mudd, J.J., Maskery, I., Lees, M.R., McConville, C.F., Leadley, D.R., and Bell, G.R. Heteroepitaxial growth of ferromagnetic MnSb(0001) films on Ge/Si(111) virtual substrates. Cryst. Growth Des. 13, 4923-4929 (2013).
14. Dean, M.P.M., Dellea, G., Springell, R.S., Yakhou-Harris, F., Kummer, K., Brookes, N.B., Liu, X., Sun, Y.-J., Strle, J., Schmitt, T., Braicovich, L., Ghiringhelli, G., Bozovic, I., and Hill, J.P. Persistence of magnetic excitations in La2−xSrxCuO4 from the undoped insulator to the heavily overdoped non-superconducting metal. Nature Materials 12, 1019 (2013).013
15. Dean, M.P.M., James, A.J.A., Springell, R.S., Liu, X., Monney, C., Zhou, K.J., Konik, R.M., Wen, J.S., Xu, Z.J., Gu, G.D., Strocov, V.N., Schmitt, T., and Hill, J.P. High-energy magnetic excitations in the cuprate superconductor Bi2Sr2CaCu2O8+δ: Towards a unified description of its electronic and magnetic degrees of freedom. Phys. Rev. Lett. 110, 147001 (2013).
16. Dean, M.P.M., Dellea, G., Minola, M., Wilkins, S.B., Konik, R.M., Gu, G., Le Tacon, M., Brookes, N.B., Yakhou-Harris, F., Kummer, K., Hill, J.P., Braicovich, L., and Ghiringhelli, G. Magnetic excitations in stripe-ordered La1.875 Ba0:125CuO4 studied using resonant inelastic x-ray scattering. Phys. Rev. B 88, 020403(R) (2013).
17. Först, M., Mankowsky, R., Bromberger, H., Fritz, D.M., Lemke, H., Zhu, D., Chollet, M., Tomioka, Y., Tokura, Y., Merlin, R., Hill, J.P., Johnson, S.L., and Cavalleri, A. Displacive lattice excitation through nonlinear phononics viewed by femtosecond X-ray diffraction. Solid State Communications 169, 24-27 (2013).
18. Först, M., Mankowsky, R., Bromberger, H., Fritz, D.M., Lemke, H., Zhu, D., Chollet, M., Yomioka, Y., Tokura, Y., Merlin, R., Hill, J.P., Johnson, S.L., and Cavalleri, A. Displacive lattice excitation through nonlinear phononics viewed by Femtosecond x-ray diffraction. Solid State Communications 169, 24-27 (2013).
19. Garcia-Fernandez, M., Wilkins, S., Lu, M., Li, Q., Gray, K., Zheng, H., Mitchell, J., and Khomskii, D. Antiferromagnetic domain structure in bilayer manganite. Phys. Rev. B 88, 075134 (2013).
20. Gretarsson, H., Clancy, J., Liu, X., Hill, J.P., Bozin, E., Singh, Y., Manni, S., Gegenwart, P., Kim, J.H., Said, A.H., Casa, D., Gog, T., Upton, M.H., Kim, H.-S., Yu, J., Katukuri,

V.M., Hozoi, L., van den Brink, J., and Kim, Y.-J. Crystal-field splitting and correlation effect on the electronic structure of A2IrO3. Phys. Rev. Lett. 110, 076402 (2013).
21. Gretarsson, H., Clancy, J.P., Singh, Y., Gegenwart, P., Hill, J.P., Kim, J., Upton, M., Said, A., Casa, D., Gog, T., and Kim, Y.-J. Magnetic excitation spectrum of Na2IrO3 probed with resonant inelastic x-ray scattering. Phys. Rev.B 87, 220407 (2013).
22. Gretarsson, H., Clancy, J.P., Liu, X., Hill, J.P., Bozin, E., Singh, Y., Manni, S., Gegenwart, P., Kim, J., Said, A.H., Casa, D., Gog, T., Upton, M.H., Kim, H.-S., Yu, J., Katukuri, V.M., Hozoi, L., van den Brink, J., and Kim, Y.-J. Crystal-field splitting and correlation effect on the electronic structure of
23. Juhas, P., Davis, T., Farrow, C.L., and Billinge, S.L. PDFgetX3: a rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions. J. Appl. Cryst. 46, 560 (2013).
24. Kim, M., Soh, J., Lang, J., Choi, Y., Dean, M.P.M., Thaler, A., Bud'ko, S.L., Canfield, P., Bourret-Courchesne, E., Kreyssig, A., Goldman, A.I., and Birgeneau. Spin polarization of Ru in superconducting Ba(Fe0.795Ru0.205)2As2 studied by x-ray resonant magnetic scattering. Phys. Rev. B 88, 014424 (2013).
25. Kim, M.G., Soh, J., Lang, J., Dean, M., Thaler, A., Bud'ko, L., Canfield, P.C., Bourret-Courchesne, E., Dreyssig, A., Gpoldman, A.I., and Birgeneau, R.J. Spin polarization of Ru in superconducting Ba(Fe0.795Ru0.205)2As2 studied by x-ray resonant magnetic scattering. Phys. Rev. B 88, 014424 (2013).
26. Liu, X., Katukuri, V., Hozoi, L., Yin, W.-G., Dean, M., Upton, M., Kim, J., Casa, D., Said, A., Gog, T., Qi, T.F., Cao, G., Tsvelik, A., van den Brink, J., and Hill, J.P. Testing the validity of the strong spin-orbit-coupling limit for octahedrally coordinated iridates in a model system Sr3CuIrO6. Phys. Rev. Lett. 109, 157401 (2012).
27. Liu, X., Seman, T.F., Ahn, K.H., van Veenendaal, M., Casa, D., Prabhakaran, D., Boothroyd, A.T., Ding, H., and Hill, J.P. Strongly momentum-dependent screening dynamics in La0.5Sr1.5MnO4 observed with resonant inelastic x-ray scattering. Phys. Rev. B 87, 201103(R) (2013).
28. Lu, X., Gretarsson, H., Zhang, R., Liu, X., Luo, H., Tian, W., Laver, M., Yamani, Z., Kim, Y.-J., Nevidomskyy, A., Si, Q., and Dai, P. Avoided quantum criticality and magnetoelastic coupling in BaFe2-xNixAs2. Phys. Rev. Lett. 110, 257001 (2013).
29. Shvyd'ko, Y., Hill, J.P., Burns, C.A., Coburn, D.S., Brajuskovic, B., Casa, D., Goetze, K., Gog, T., Khachatryan, R., Kim, J.-H., Kodituwakku, C.N., Ramanathan, M., Roberts, t., Said, A., Sinn, H., Shu, D., Stoupin, S., Upton, M., Wiezorek, M., and Yavas, H., MERIX – next generation medium energy resolution inelastic x-ray scattering instrument at the APS. J. Electron Spectroscopy and Related Phenomena 188, 140-149 (2013).
30. Thampy, V., Blanco-Canosa, S., Garcia-Fernandez, M., Dean, M.P.M., Gu, G., Forst, M., Loew, T., Keimer, B., Le Tacon, M., Wilkins, S.B., and Hill, J.P. Comparison of charge modulations in La1.875Ba0.125CuO4 and YBa2Cu3O6.6. Phys. Rev. B 88, 024505 (2013).

31. Xu, Z., Wen, J., Zhao, Y., Matsuda, M., Ku, W., Liu, X., Gu, G., Lee, D.-H., Birgeneau, R.J., Tranquada, J.M., and Xu, Guangyong. Temperature-dependent transformation of the magnetic excitation spectrum on approaching superconductivity in Fe1+y(Ni/Cu)xTe0.5Se0.5. Phys. Rev. Lett. 109, 227002 (2012).
32. Yin, W.-G., X. Liu, A.M. Tsvelik, M.P.M. Dean, M.H. Upton, J. Kim, D. Casa, A. Said, T. Gog, T.F. Qi, G. Cao, and J.P. Hill. Ferromagnetic exchange anisotropy from antiferromagnetic auperexchange in the mixed 3d - 5d transition-metal compound Sr3CuIrO6. Phys. Rev. Lett. 111, 057202 (2013).
33. Zhu, P., Cao, J., Zhu, Y., Geck, J., Hidaka, Y., Pjerov, S., Ritschel, T., Berger, H., Shen, Y., Tobey, R., Hill, J.P., and Wang, X.J. Dynamic separation of electron excitation and lattice heating during the photoinduced melting of the periodic lattice distortion in 2H-TaSe2. Appl. Phys. Lett. 103, 071914 (2013).

Design of Molecular Solar Cells via Feedback from Soft X-ray Spectroscopy

F. J. Himpsel, Department of Physics, University of Wisconsin-Madison, 1150 University Ave., Madison, WI 53706-1390

Program Scope

While most work on photovoltaics has aimed at improving the efficiency of a specific design, this project asks a more general question: What limits the performance of a generic solar cell, which consists of a light absorber sandwiched between an electron donor and an electron acceptor. There are two distinct contributions, one from the position of the four relevant energy levels and the other from the dominant mechanism for carrier loss. In the past we have addressed the first contribution by combining synchrotron-based XAS and XPS with optical and electrochemical techniques [1]-[3].

Recent Progress

Recently, we have pursued two avenues (with different sets of collaborators). The first has been the search for a transparent, wide-gap electron donor material that can act as counterpart to the widely-used TiO_2 acceptor. Highly boron-doped diamond films were be able to play this role. The combination of diamond with CIGS, a well-studied solar cell material, was investigated by building working solar cells and measing their energy levels. A combination of many techniques was used, including XAS and hard X-ray photoemission at the ALS, in order to allow for cross-checks between different methods (see [3]). The lead author is the postdoc who was supported by this starter project.

The other program involves nanostructured photoelectrodes for solar fuel synthesis, such as hematite (a-Fe_2O_3) nanorods, a collaboration with Lionel Vayssieres. In that case we wanted to see how dramatic changes in device performance (for example two orders of magnitude in the photocurrent after annealing) are reflected in the energy level structure (see [2]). The observed changes generally were subtle. This led us to the conclusion that the determination of carrier lifetimes and loss mechanisms will be critical to fully understand and optimize such devices.

Future Plans

Looking forward, it has become clear that the lifetimes of the photo-generated carriers and their decay mechanisms are at least as important as the energy levels. Ultrafast pump-probe experiments have been performed for quite some time in the UV/visible [4],[5]. But these would greatly benefit from the atom- and bond-specific character of core level spectroscopy with soft X-rays [6]. A dream experiment will be discussed where the carriers are followed in real time on their way from the absorber to the contact electrodes, using atom-selective pump-probe techniques at a future generation of laser-like soft X-ray light sources. It is proposed to prepare for such experiments using available UV lasers and fluorescent markers, as used in biochemistry experiments.

References

[1] I. Zegkinoglou et al., *Spectroscopy of Donor-π-Acceptor Porphyrins for Dye-Sensitized Solar Cells*, J. Phys. Chem. C **117**, 13357 (2013).

[2] C. X. Kronawitter et al., *Titanium Incorporation into Hematite Photoelectrodes: Theoretical Considerations and Experimental Observations*, Energy Environ. Sci. **7**, 3100 (2014).

[3] M. Kapilashrami et al., *B-Doped Diamond Films as Electron Donors in Photovoltaics: An X-Ray Absorption and Hard X-Ray Photoemission Study*, J. Appl. Phys. **116**, 143702 (2014).

[4] G. Duvanel, J. Grilj, and E. Vauthey, *Ultrafast Long-Distance Excitation Energy Transport in Donor−Bridge−Acceptor Systems*, J. Phys. Chem. A **117**, 918 (2013).

[5] J.-L. Bredas, *When Electrons Leave Holes in Organic Solar Cells*, Science **343**, 492 (2014).

[6] B. E. Van Kuiken et al., *Probing the Electronic Structure of a Photoexcited Solar Cell Dye with Transient X-ray Absorption Spectroscopy*, J. Phys. Chem. Lett. **3**, 1695 (2012).

Publications supported by this grant (2013, 2014)

F. J. Himpsel, P. L. Cook, G. de la Torre, J. M. Garcia-Lastra, R. Gonzalez-Moreno, J.-H. Guo, R. J. Hamers, C. X. Kronawitter, P. S. Johnson, J. E. Ortega, D. Pickup, M.-E. Ragoussi, C. Rogero, A. Rubio, R. E. Ruther, L. Vayssieres, W. Yang, I. Zegkinoglou, *Design of Solar Cell Materials via Soft X-ray Spectroscopy*, J. Electron Spectrosc. Relat. Phenom. **190**, 2 (2013).

C. X. Kronawitter, Ioannis Zegkinoglou, S. Shen, J.-H. Guo, F. J. Himpsel, S. S. Mao, L. Vayssieres, *On the orbital anisotropy in hematite nanorod-based photoanodes*, Communication: Phys. Chem. Chem. Phys. **15**, 13483 (2013).

C. X. Kronawitter, I. Zegkinoglou, S.-H. Shen, P. Liao, I. S. Cho, O. Zandi, Y.-S. Liu, K. Lashgari, G. Westin, J.-H. Guo, F. J. Himpsel, E. A. Carter, X. L. Zheng, T. W. Hamann, B. E. Koel, S. S. Mao, L. Vayssieres, *Titanium Incorporation into Hematite Photoelectrodes: Theoretical Considerations and Experimental Observations*, Energy Environ. Sci. **7**, 3100 (2014).

M. Kapilashrami, G. Conti, I. Zegkinoglou, S. Nemšák, C. S. Conlon, T. Törndahl, V. Fjällström, J. Lischner, Steven G. Louie, R. J. Hamers, L. Zhang, J.-H. Guo, C. S. Fadley, and F. J. Himpsel, *Boron-Doped Diamond Films as Electron Donors in Photovoltaics: An X-Ray Absorption and Hard X-Ray Photoemission Study*, J. Appl. Phys., **116**, 143702 (2014).

Localized Structures and Strains in Materials

Stephan Hruszkewycz, Dillon Fong, Paul Fuoss, Brian Stephenson, Hoydoo You

Materials Science Division, Argonne National Laboratory

Program Scope

This thrust of the Synchrotron Radiation Studies program at ANL focuses on the development and use of coherent diffraction imaging techniques that can map, with unprecedented sensitivity and resolution, strain fields around both isolated objects and within continuous films. We aim to measure, with nanoscale spatial resolution, heterogeneous strain and lattice distortions in thin films and correlate these strains with the properties and performance of energy materials in realistic environments, thereby capitalizing on the ever-improving coherence properties of current and next generation DOE light sources.

Recent Progress

In recent years, we have developed a new coherent x-ray diffraction structural microscopy method, Bragg projection ptychography (BPP) [1], and we have used it to measure nanoscale lattice distortions associated with local polarization in a single crystal ferroelectric thin film [2] and strain fields within nanoelectronic device components [3]. BPP applies 2D ptychographic phase-retrieval principles [4,5] to the Bragg geometry, such that the advantages of ptychography (i.e. nanoscale spatial resolution, numerical robustness, flexible field of view) are combined with the exquisite structural sensitivity of x-ray diffraction. BPP maps the projected in-plane spatial distribution of the complex Bragg structure factor, a quantity that can be linked to specific distortions in a crystal lattice.

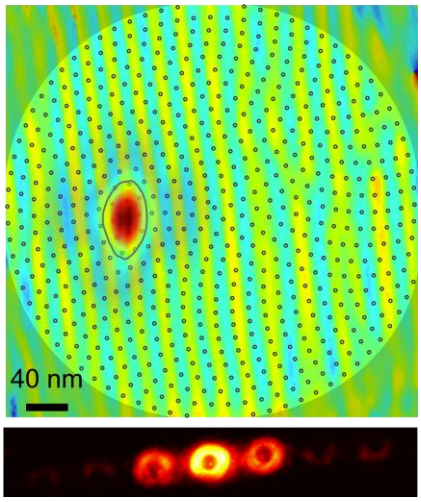


Figure 1: The top panel shows ferroelectric stripe domains reconstructed from coherent diffraction images taken on a spiral grid indicated by the gray points. The reconstructed footprint of the beam is superimposed on the reconstruction. The bottom panel shows a typical coherent diffraction pattern from which the image is reconstructed.

As shown in Figure 1, using BPP, a set of overlapping, scanning probe coherent Bragg diffraction patterns was reconstructed into a quantitative, complex real-space image of the structure factor in a ferroelectric film. We developed a method to quantify this image in terms of unit cell distortions responsible for local polarization in ferroelectric materials, and mapped polar domains with a spatial resolution of 5.7 nm. Similarly, in a nanoelectronic prototype device, we used BPP to simultaneously resolve two distinct lattice deformations – lattice contraction and lattice rotation – near the vertical interfaces between two heterogeneous device materials in a study that further demonstrated the versatility and potential of BPP for noninvasive structural imaging.

Future Plans

We plan to explore the development and application of new three-dimensional Bragg ptychography methods that enable 3D structural imaging from two-dimensional diffraction patterns. We will build on BPP with new algorithms that make 3D imaging possible from coherent diffraction measurements that currently yield only two-dimensional (2D) images. In collaboration with the Institut Fresnel, we have invented a highly dose-efficient Bragg ptychography method, 3D Bragg projection ptychography (3DBPP). This technique uses a major conceptual advance achieved by integrating concepts of tomography (back-projection and Radon transformations [6]) with ptychography to enable 3D imaging of nanoscale crystals from a 2D array of Bragg diffraction patterns. 3DBPP greatly simplifies 3D structural imaging of nanoscale crystals, decreases sample measurement time, and reduces sample dose by two orders of magnitude.

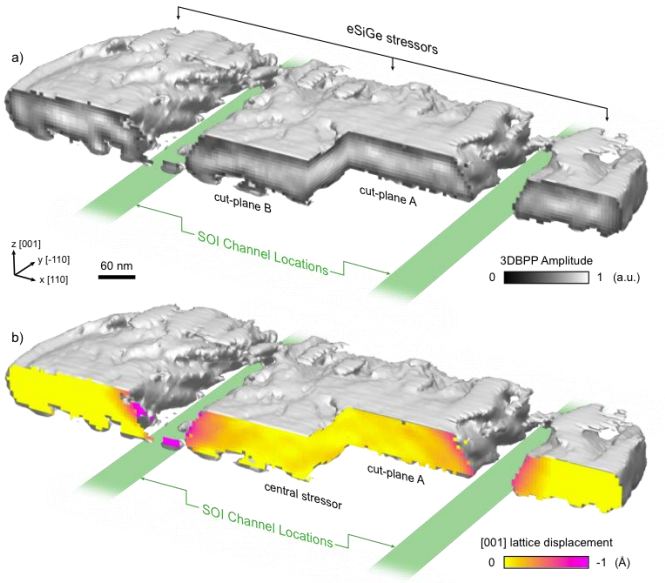


Figure 2: A 3DBPP reconstruction of the lattice structure within an embedded crystalline SiGe component of a nanoelectronic device is shown in terms of (a) scattering electron density and (b) lattice displacement along [001].

Based on our preliminary results in which we imaged the 3D distribution of out-of-plane lattice displacement within a nanoelectronic prototype device component (Figure 2), we plan to further develop the 3DBPP method and apply it to imaging 3D strain distributions of faceted islands that form during the growth of InGaN [7]. We will also use 2D and 3D Bragg projection ptychography to visualize local surface structures that play crucial roles during catalysis, synthesis, and decomposition. Finally, we also plan to develop innovative experiments and algorithms that allow dynamic structures in materials to be imaged, opening new doors to understanding transient structural states via time-resolved ptychography.

References

[1] Hruszkewycz, et. al., Nano Letters 12 (5148), 2012.
[2] Hruszkewycz, et. al., PRL 110 (177601), 2013.
[3] Holt, et. al., PRL 112 (165502), 2014.
[4] Thibault, et. al., Ultramicroscopy 109 (339), 2009.
[5] Faulkner, et. al, PRL 93 (023903), 2004.
[6] Radon, IEEE Trans. Med. Imaging 5 (170), 1986
[7] Heying, et. al., J. Appl. Phys. 85 (6470), 1999.

Publications since last PI meeting: See complete list on Fuoss abstract

Dynamics, Imaging, and Reactivity of Heterogeneous Interfaces

Hoydoo You, Dillon Fong, Paul Fuoss, Stephan Hruszkewycz, Brian Stephenson
Materials Science Division, Argonne National Laboratory

Program Scope

The dynamics of heterogeneous materials and their interfaces is one of the important characteristics governing physical and chemical processes directly relevant to energy conversion processes. While dynamics measurements alone can be sufficient for some systems, combination with imaging can greatly enhance our understanding of reactivity and selectivity. In this thrust we will further develop interface-sensitive coherent x-ray techniques and apply them to heterogeneous interfaces of energy materials such as electrocatalysts.

Recent Progress

In coherent x-ray scattering studies, we developed an interface-sensitive ptychographic imaging technique.[1] We established a proof-of-concept by imaging atomic-scale surface morphology of Pt(111) using reflection ptychography. We showed that ptychography can be used to image atomic steps from coherent diffraction patterns recorded along the crystal truncation rod. Due to the penetration power of x-rays, this method can find interesting applications for the study of atomic surface structures under buried interfaces or in harsh environments. In electrocatalysis research, we found that a nanoscale platinum surface with bilayer oxides exhibits a significantly higher and more stable CO oxidation activity than a bare platinum surface. A series of electrochemistry and x-ray measurements showed that a high-index Pt surface can form stable nanoscale oxides that can oxidize carbon monoxide (model fuel) efficiently at low voltages and sustain indefinitely the reactivity.[2] We proposed a bifunctional mechanism where the metallic part activates carbon monoxide while the oxide part activates water to OH, allowing efficient reactions between CO and OH.

Future Plans

In coming years, by expanding the bi-functionality mechanism, we will take an electrodeposition approach for understanding and possibly improving electrocatalysts. We will deposit submonolayer platinum on inexpensive metal substrates, where the platinum islands and the substrate perform separate reactions, using the self-limiting monolayer-level electrodeposition of platinum observed on gold substrates.[3] First, we will characterize the dynamics of electrodeposition of platinum from a precursor complex. We will also determine the structure and oxidation states of the precursors and substrate surfaces. These x-ray studies will be complemented with electrochemical activity measurements. Ultimately, we aim to identify the self-limiting deposition mechanism and expand the knowledge to other inexpensive metal substrates such as nickel and tungsten. We plan to apply the reflection ptychography technique that we developed to image the topography of the electrodeposition.

Dynamics measurements using coherent x-rays can reveal hidden order parameters of phase transitions. During phase transitions, driven thermally, chemically, or electrochemically,

we hypothesize that materials can exhibit properties qualitatively different from their stable, equilibrium, or steady-state phases. Here, we plan to explore the use of coherent x-rays to directly probe the dynamics of the phase transitions to investigate hidden order parameters. In work to date, we have shown that a previously unidentified transition of surface dynamic states exists on gold surfaces[4] and that there is a remarkable dynamic behavior at the previously known roughening transition on platinum surfaces.[5] In coming years, we will investigate whether it is possible to have a transition-like behavior of dynamic properties in the absence of established phase transitions. An example is an isosymmetry transition of multiferroic hexagonal manganites where domain dynamics manifests a discontinuity. The hexagonal manganites, such as $ErMnO_3$, are a class of multiferroic materials that are simultaneously ferroelectric and antiferromagnetic. They are 'improper' multiferroics[6] because a high-temperature transition sets the ferroic structure. However, the nature of high-temperature transition itself is still in dispute, despite that it is responsible for the improper multiferroic behavior. An ongoing debate is whether the para-to-ferro transition is actually two successive transitions as seen in lattice constants and dilatometry measurements, or simply a single phase transition.[7] A recent neutron powder diffraction experiment showed that there is no symmetry change[8] near the second transition temperature. Our preliminary measurements indicate that the second transition is an iso-symmetry transition with only a jump in the dynamics at the transition, as shown in Figure 1. The correlation time, measured from x-ray speckles on a specular surface rod sensitive to domain fluctuations, was found to have an order-of-magnitude jump at 880°C. We will complement this interesting time-domain dynamics study with energy-domain measurements such as high-resolution inelastic phonon scattering.

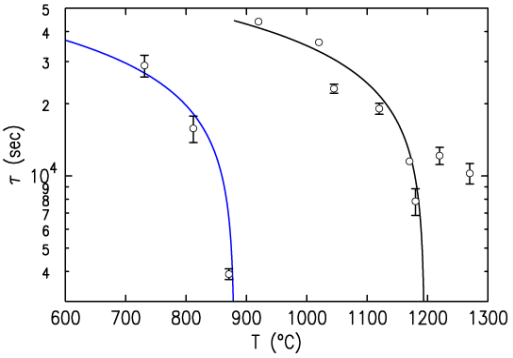


Figure 1. De-correlation of ferroic domains in $ErMnO_3$. There is a large discontinuity at 880° C as well as at the known transition at 1200° C.

[1] C. Zhu, et al. Appl. Phys. Lett., submitted (2014)
[2] V. Komanicky, et al., Electrochim. Acta, 109, 440 (2013)
[3] Y. Liu, et al., Science 338, 1327 (2012)
[4] M. S. Pierce, et al., Phys. Rev. Lett., 103, 165501 (2009)
[5] M.S. Pierce, et al., , Phys. Rev. B 86, 184108 (2012)
[6] S.-W. Cheong and M. Mostovoy, Nature Materials 6, 13 (2007)
[7] G. Nenert, et al., Journal of Physics-Condensed Matter **19** (2007).
[8] A. S. Gibbs, K. S. Knight, and P. Lightfoot, Physical Review B **83** (2011).

Publications since last PI meeting: See complete list on Fuoss abstract

Understanding valley spin coupling and two-dimensional exciton gases in layered materials at extreme magnetic fields

Denis Karaiskaj, University of South Florida, Tampa, Florida 33620, USA

David Hilton, University of Alabama at Birmingham, Birmingham, Alabama 35294, USA

Jie Shan, Pennsylvania State University, University Park, Pennsylvania 16802, USA

Program Scope

Probing the valley coupling in monolayer materials: The transition between two layers to single layers breaks the inversion symmetry of the crystal and leads to spin-coupled valleys. The degree of spin correlation between the degenerate K and K' valleys are a matter of intense debate. An important question is whether coherent manipulation can be performed on such valley pseudo-spins, analogous to that implemented using true spins in the quest for quantum technologies. **Understanding exciton, biexciton, and trion formation:** Recent theoretical studies have predicted a large exciton binding energy on the order of 1 eV in monolayers of semiconducting transition metal dichalcogenides. Such tightly bound excitons are expected to not only dominate the optical response, but also play a defining role in the optoelectronic processes, such as photoconduction and photocurrent generation in 2D semiconductors. **Exploring two-dimensional electron (hole) gases at extreme magnetic fields:** The objective is to perform coherent two-dimensional Fourier transform (2DFT) experiments at optical and THz frequencies on several two-dimensional monolayer samples to understand the nature of the inter Landau level coherence in these truly two-dimensional materials.

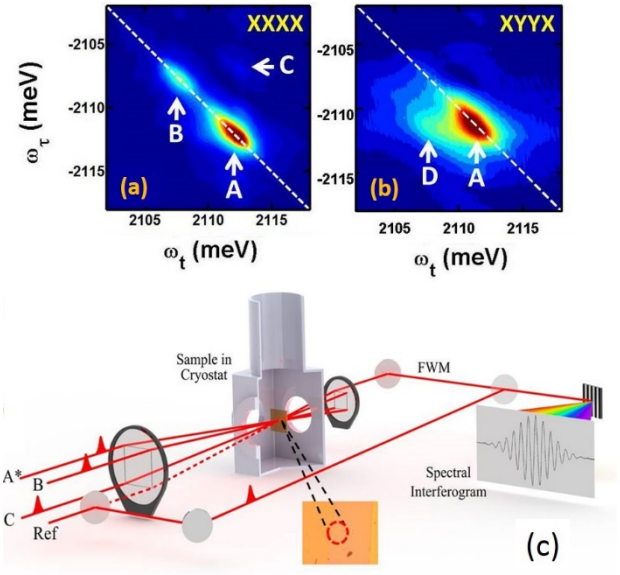
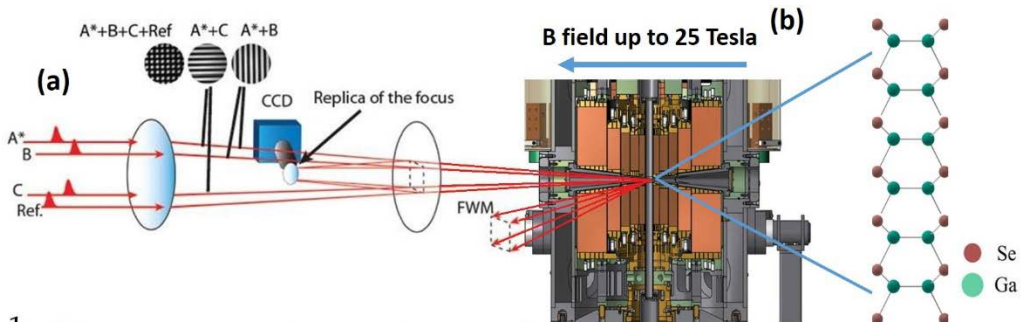


Figure 1: (a) Magnitude of the 2DFT spectra of atomically thin GaSe 1s exciton using co-linearly (XXXX) polarized excitation. The polarizations correspond to A*, B, C, and detection, respectively. Diagonal peaks are labeled as A and B, whereas the weak cross-peak in the 2DFT spectra above the diagonal is labeled as C (b) Magnitude and the 2DFT spectra of the GaSe 1s exciton using cross-linearly (XYYX) polarized excitation. Using the cross-polarized sequence the diagonal peaks are suppressed, revealing the existence of an off-diagonal peak, labeled as D. (c) The four phase stabilized linearly polarized beams obtained from the MONSTR instrument are focused on the sample, which is held in the cryostat at 5 K.

Recent Progress

Using nonlinear two-dimensional Fourier transform (2DFT) spectroscopy we examined the electronic structure of the excitonic ground state in GaSe. The polarization dependent 2DFT spectra shown in Fig 1 (a-b) reveal a spitting of the ground state into a singlet A and triplet B. By cross-polarizing the excitation beams, moderate biexciton formation is revealed (peak D). The Penn State U. group has recently performed two-photon photoluminescence excitation spectroscopy to investigate the exciton binding energy in monolayers of tungsten diselenide (WSe_2). These studies have determines the exciton binding energy to be 0.37eV, which renders the exciton excited states observable even at room temperature [1]. Furthermore, the Penn State group is working on several approaches including both sample transfer and CVD growth for achieving large samples of high quality for these measurements. The UAB team has developed a pump-probe setup and has demonstrated measurements at magnetic fields up to 25 Tesla [2]. A 2DFT THz apparatus is currently being completed.



Future Plans

Figure 2: (a) Four phase stabilized laser pulses are obtained the MONSTR. (b) The magnet shown is a realistic drawing of the 25 Tesla split coil magnet at the NHMFL in Tallahassee, Florida.

The 2DFT technique will be applied to several atomically thin and monoatomic materials, which include GaSe, InSe, $MoSe_2$ and WSe_2. The valley coupling in monolayer in $MoSe_2$ will be studied using polarization dependent 2DFT. A replica of the MOSTR operational at USF is being set up at the NHMFL in Tallahassee for measurements under high magnetic fields up to 25 Tesla (Fig. 2). THz measurements on bulk samples will start immediately since large samples are available. In order to study trion formation samples doped with both, donors and acceptors will be studied.

References

[1] K. He, N. Kumar, L. Zhao, Z. Wang, K.F. Mak, H. Zhao, and J. Shan, "*Tightly bound excitons in monolayer WSe_2*" Physical Review Letters **113**, 026803 (2014).

[2] Jeremy A. Curtis, Takahisa Tokumoto, Nicholas K. Nolan, Luke M. McClintock, Judy G. Cherian, Stephen A. McGill, and David J. Hilton, "*Ultrafast pump–probe spectroscopy in gallium arsenide at 25 T*", Optics Letters **39**, 5772 (2014)

Publications

P. Dey, J. Paul, N. Glikin, Z. D. Kovalyuk, Z. R. Kudrynskyi, A. H. Romero, A. Cantarero, D. J. Hilton, D. Karaiskaj "*The electronic structure of the excitonic ground state in GaSe*" submitted to Phys. Rev. B.

Nanoscale Dynamical Heterogeneity in Complex Magnetic Materials

Steve Kevan, Physics Department, University of Oregon, Eugene, OR. 97403

Program Scope

In this project, we to apply resonant, coherent soft x-ray scattering techniques we 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 emergent behaviors. Operating at a soft x-ray wavelength in resonance with various absorption edges, we can project nanoscale orbital, magnetic, and charge structures with elemental selectivity into a speckle-diffraction pattern that can be analyzed to understand spatial and temporal correlations (Fig. 1).[1] Our program is divided into two complementary efforts:

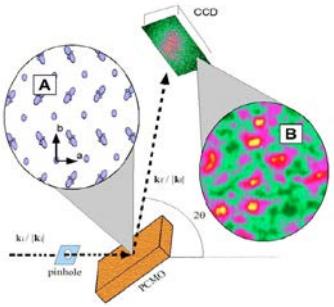


Fig. 1: Projecting orbital correlations in a PCMO manganite crystal.

1) Measuring nanoscale correlations in thin film magnetic domains to relate field-driven Barkhausen cascades to recently observed field-driven changes in local domain symmetries.
2) Measuring nanoscale correlations in helical spin structures, with particular focus on probing the structure and motion of topological skyrmions.

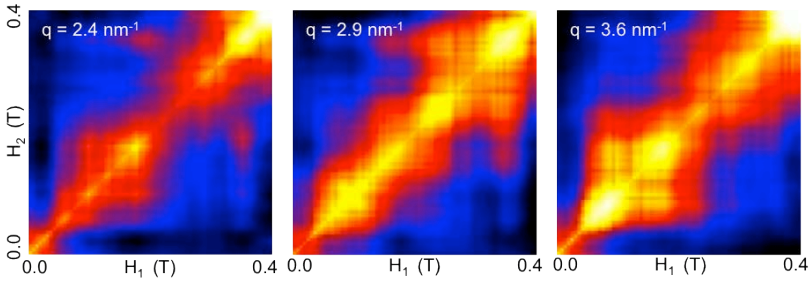


Fig. 2: Barkhausen intermittency in a CoPd magnetic film revealed in two-field correlation functions of magnetic speckle patterns.

Recent Progress

Fig. 2 illustrates progress on the first topic above. This shows 'q-resolved Barkhausen intermittency', probed with 2-field correlation functions of speckle patterns collected from a CoPd films having perpendicular anisotropy. The square structures along the diagonal reflect field-driven magnetic intermittent cascades. We are trying to understand the relationship between these cascades and 'hidden symmetries' also evident in the speckle patterns.[2,3] Such a relationship appears to be present, but we are hampered by the need for a statistical number of speckle patterns to isolate the underlying trends (see next section).

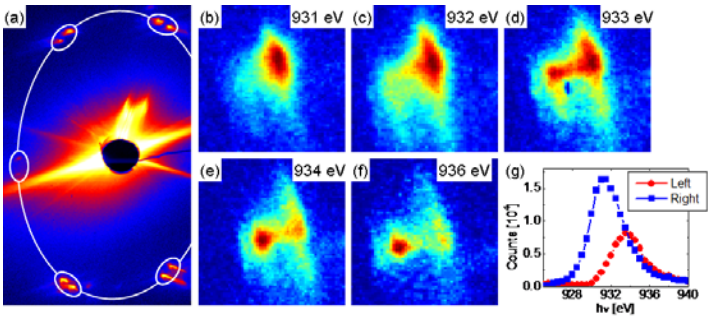


Fig. 3: Soft x-ray Bragg scattering off the skyrmion phase in Cu_2OSeO_3. The skyrmion superlattice peaks slit systematically as a function of T and H.

Fig. 3 illustrates progress on the second topic above. These results are the first observation of a skyrmion phase using soft x-ray scattering, in this case in the ferrimagnetic compound Cu_2OSeO_3.[4] These data were collected at the Cu L_3 resonance on the lowest order Bragg peak, and the skyrmion phases is reflected by the satellite peaks surrounding the blocked Bragg peak. We observed and explained a T- and H-dependent splitting of the skyrmion peaks.

Future Plans

Our plans for the future include

1) An extensive investigation of the relationship between intermittency and hidden symmetries in perpendicular magnetic films. We will benefit from commissioning the COSMIC beamline at the ALS in 2015, which will provide higher coherent flux and will have a faster detector so that a much larger data set will become possible.
2) We have recently started to image magnetic domain walls using soft x-ray ptychography. The COSMIC beamline will increase our capabilities in this area as well. In particular, the variable polarization undulator will enable sensitivity to the vector magnetization.
3) We plan increased focus on skyrmion systems. For example, we recently observed a skyrmion lattice in FeGe films at room temperature, and look forward to investigating the structure of this phase and it's response to applied fields.

References

1. S. Roy, D. Parks, K.A. Seu, R. Su, J.J. Turner, W. Chao, E.H. Anderson, S. Cabrini, and S.D. Kevan, Nature Photonics 5, 243 (2011).

2. P. Wochner, C. Gutt, T. Autenrieth, T. Demmer, V. Bugaev, A. Diaz Ortiz, A. Duri, F. Zontone, G. Grübel and H. Dosch, Proc. Nat. Acad. Sci 106, 11511 (2009).

3. Run Su, Keoki Seu, Daniel Parks, Jimmy J. Kan, Eric E. Fullerton, Sujoy Roy, Stephen D. Kevan, Phys. Rev. Lett. 107, 275204 (2011).

4. Langner, M.C., S. Roy, S.K. Misra, J.C.T. Lee, X.W. Shi, M.A. Hossain, Y-.D. Chuang, S. Seki, Y. Tokura, S.D. Kevan, and R.W. Schoenlien, Physical Review Letters 112, 167202 (2014).

Publications

1. Chesnel, K., J. Nelson, B. Wilcken, and S.D. Kevan “Mapping spatial and field dependence of magnetic domain memory by soft X-ray speckle metrology,” J. of Synch. Rad. **19**, 293 (2012).

2. Chesnel, K., B. Wilken, M. Rytting, S.D. Kevan and E.E. Fullerton, “Field and temperature dependence of magnetic domain memory induced by exchange couplings,” New J. Phys. **15**, 023016 (2013).

3. Pierce, M.S., J.E. Davies, J.J. Turner, K. Chesnel, E.E. Fullerton, J. Nam, R. Hailstone, S.D. Kevan, J.B. Kortright, Kai. Liu, L.B. Sorenson, B.R. York, and O. Hellwig, “Influence of structural disorder on magnetic domain formation in perpendicular anisotropy thin films,” Phys. Rev. B **87**, 184428 (2013).

4. “Development of coherent scattering and diffractive imaging and the COSMIC facility at the Advanced Light Source”, D. Shapiro, S. Roy, R. Celestre, W. Chao, D. Doering, M. Howells, S. Kevan, D. Kilcoyne, J. Kirz, S. Marchesini, K.A. Seu, A. Schirotzek, J. Spence, T. Tyliszczak, T. Warwick, D. Voronov and H.A. Padmore, J. Phys.: Conf. Ser. **425**, 192011 (2013).

5. “Altered magnetism and new electronic length scales in magneto-electric La2/3Sr1/3MnO3–BiFeO3 heterointerface”, Mazumdar, K. Tarafdar, Lin-Wang Wang, S. D. Kevan, C. Sanchez-Hanke, A. Gupta and S. Roy, New J. Phys. **15**, 113042 (2013).

6. "Partially Coherent X-ray Diff ractive Imaging of Complex Objects," Parks, D.H., X. Shi, and S.D. Kevan, Physical Review A **89**, 063824 (2014).

7. "Coupled Skyrmion Sublattices in Cu2OSeO3," Langner, M.C., S. Roy, S.K. Misra, J.C.T. Lee, X.W. Shi, M.A. Hossain, Y-.D. Chuang, S. Seki, Y. Tokura, S.D. Kevan, and R.W. Schoenlien, *Physical Review Letters* **112**, 167202 (2014).

Ultrafast Spectroscopy of Complex Materials

Alessandra Lanzara, Joseph W. Orenstein, Robert A. Kaindl
Materials Sciences Division, E. O. Lawrence Berkeley National Laboratory,
1 Cyclotron Road, Berkeley, CA 94720

Program Scope: The ultrafast materials program is focused on the application of ultrafast techniques to understand, control and induce novel properties in complex materials. Scientific areas of interest include understanding the emergence of unconventional superconductivity , metal-insulator transitions (lattice vs electronically driven), interplay of Coulomb correlations and spin-orbit coupling, and the formation of unusual collective electronic properties at interfaces. The generation of new phases of matter via tailored excitations (transient photodoping, vibrational pumping, and spin excitation) is of long-term interest.

This program utilizes a combination of state of the art spectroscopic tools to measure quasiparticle dynamics, including time-, spin-, and angle-resolved photoemission spectroscopy (trARPES and Spin-trARPES) to access quasiparticle dynamics throughout momentum space, and THz to visible optical spectroscopy. tr-ARPES experiments utilize two different but complementary setups, one in which 6 eV pulses are created using second harmonic generation in nonlinear crystals and the other using high harmonic generation (HHG) in Kr gas to generate photon energies above 20 eV. While former system features very high energy and momentum resolution, momentum space access is limited. In contrast, the latter system permits access to the entire Brillouin zone, but at present with less energy resolution. The all-optical pump probe tools are complementary to trARPES in that they can be used rapidly scan the vast space of materials, temperature, and pump laser intensity to identify those regimes (for example near phase transitions or crossovers) that are most promising for the more time-intensive studies by ARPES.

Recent Progress: An important science driver of recent work in this program has been the quest to understand the emergence of charge-ordered and superconducting phases in strongly-correlated oxides and their relation with the pseudogap phase. To first understand the dynamics of charge-ordered phases in isolation, we have studied the nickelate compound $La_{2-x}Sr_xNiO_4$ (LSNO) – a model system that is isostructural to the cuprate superconductor LSCO, yet exhibits charge and spin stripes without superconductivity. Our experiments – which comprise the first ultrafast mid-IR study of a stripe-phase correlated system - revealed ultrafast charge localization and lattice vibrational coupling as dynamic precursors of stripe formation [Cos13]. We found the opening of an infrared “pseudogap”, appearing at a crossover temperature T^* far above long-range stripe formation, that acts as a dynamic precursor to long-range stripe formation. As illustrated in Fig. 1, the pseudogap is characterized by femtosecond charge localization - which in turn drives the strong enhancement of electron-phonon coupling [Cos13]. When combined with transient THz spectroscopy studies, we capture snapshots of both the electronic and structural dynamics relevant to charge ordering, revealing an intriguing two-

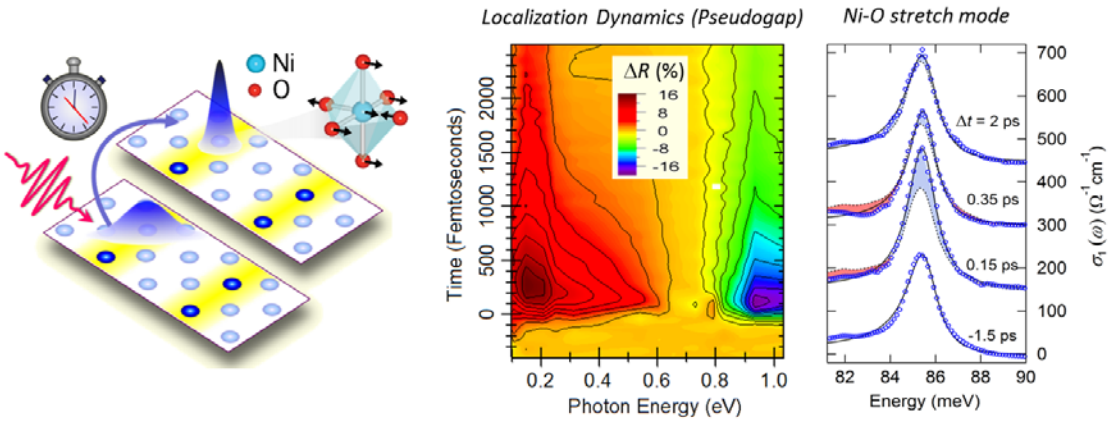


Figure 1 – Pseudogap dynamics in the transient reflectivity ΔR of the stripe-phase compound $La_{1.75}Sr_{0.25}NiO_4$ reveals ultrafast hole localization (left panel) inducing a rapid synchronous increase of electron-phonon coupling, as revealed by the ultrafast suppression and recovery of the Fano lineshape asymmetry (right side) of the Ni-O stretching mode. This provides new insight to the precursor role of charge localization in stripe ordering and demonstrates a dynamic dependence of electron-phonon coupling [Cos13].

component response, composed of a slower, picosecond-scale phonon splitting (stripe formation) and fast electronic dynamics (pseudogap).

The nature of the pseudogap phase and its interplay with superconductivity has also been investigated in cuprate superconductors by ultra-broadband THz and optical pump-probe spectroscopy. We observe significant ultrafast reflectivity changes in a Hg-based cuprate related to the condensate, gap dynamics and pseudogap formation. We found that as the pseudogap signal is suppressed there is a growth of the quasiparticle signal, which onsets near T* and evolves smoothly upon cooling. By looking at the relaxation dynamics we observe an increase of the PG relaxation with increasing doping and a cusp in the qp relaxation time at Tc which is washed out by a magnetic field. We propose that these results are evidence of the slowing down of fluctuating CDW order, which couples to the QP recombination time via coherence factors. Moreover, the doping dependence of this peak suggests that there may be multiple charge ordering instabilities at different points in the phase diagram.

As it is becoming more clear, electron-phonon interaction might be the precursor toward CDW formation in these materials. To investigate the nature of electron-boson coupling and how this is related to the relevant energy scale in the system, we have performed trARPES experiments [Zha14] that reveal that ultrafast laser excitation triggers a synchronous softening of the electron-boson interaction and the closure of the superconducting gap. The measurements show that this process culminates in a weakening of electron-boson coupling when the superconducting gap is fully quenched. In contrast, electron-boson coupling is unresponsive to ultrafast excitations above Tc.

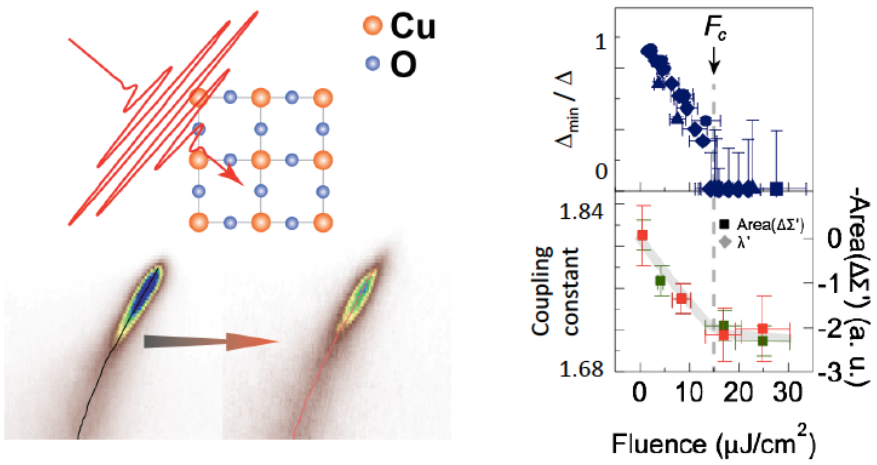


Figure 2 – Dynamics of electron-boson interaction and superconducting gap in optimally doped Bi2212 superconductor by tr-ARPES [Zha14]. A synchronous softening of the el-boson interaction and superconducting gap is observed.

In the study of materials with strong spin orbit coupling, our main focus has been on the topological insulators and specifically to understand how the spin texture is preserved when the system is excited away from equilibrium and Floquet type of states are induced above EF. By taking advantage of our unique tr-ARPES system we have mapped the spin texture for both the occupied and unoccupied states. In line with previous work [Joz13], we observe a strong dependence of the spin texture from polarization and we can discern two well defined time scales associated with different states.

Future Plans: In the near term we plan to investigate quasiparticle interactions and the relationship between different low-temperature phases in high-T_C superconductors [Hin13]. In these experiments, these properties can be tracked across all of momentum space via HHG trARPES, particularly at the antinodal point in the case of cuprates. Time-resolved optical and ultrabroadband THz studies will provide complementary insight into the low-energy collective modes and their timescales. Such studies promise powerful new insight into the physics of phase competition and superconductivity by helping determine the momentum-space signatures of the interactions and their energy spectral functions. Systems of interest include Bi-2212, LSCO, and Hg-based compounds, as well as iron-based superconductors.

In a second area of focus, the physics of materials with strong spin-orbit coupling will be investigated. We will study the interplay between spin-orbit and Coulomb interactions, and the possibility to optically control momentum and spin of the electrons quasiparticles. The concept of tailored excitations can be initially tested using THz/mid-IR excitations combined with optical probes and – in the longer view – applied in time-resolved ARPES studies with the aim of control of structural and electronic order in complex materials.

References

[Cos13] G. Coslovich, B. Huber, W.-S. Lee, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H. A. Bechtel, M.C. Martin, Z. X. Shen, R.W. Schoenlein, and R. A. Kaindl, *Ultrafast Charge Localization in a Stripe-Phase Nickelate*, Nature Comm. **4**, 2643 (2013).

[Hin13] J. P. Hinton, J. D. Koralek, Y. M. Lu, A. Vishwanath, J. Orenstein, D. A. Bonn, W. N. Hardy, and Ruixing Liang, *New collective mode in YBa_2Cu3O_{6+x} observed by time-domain reflectometry*, Phys. Rev. B **88**, 060508(R) (2013).

[Zha14] W. Zhang, C. Hwang, C. L. Smallwood, T. L. Miller, G. Affeldt, K. Kurashima, C. Jozwiak, H. Eisaki, T. Adachi, Y. Koike, D. H. Lee, A. Lanzara, *Ultrafast quenching of electron-boson interaction and superconducting gap in a cuprate superconductor*, Nature Comm. **5**, 4959 (2014).

[Wan14a] H. Wang, et al. *High Repetition-Rate Setup for Time- and Angle-Resolved Photoemission Spectroscopy with Extreme-Ultraviolet Pulses*, in preparation (2014).

[Wan14b] , Y. Xu, P. Ranitovic, J. S. Robinson, and R. A. Kaindl, *Bright high repetition rate source of narrowband extreme-ultraviolet harmonics beyond 22eV*, submitted (2014); arXiv:1408.6827.

[Joz13] C. Jozwiak, et al. *Photoelectron spin-flipping and Texture Manipulation in a Topological Insulator*. Nature Physics **9** 293-298 (2013)

Publications (2013-2014)

1. J. P. Hinton, J. D. Koralek, G. Yu, E. M. Motoyama, Y. M. Lu, A. Vishwanath, M. Greven, and J. Orenstein
   Time-Resolved Optical Reflectivity of the Electron-Doped $Nd_{2-x}Ce_xCuO_{4+\delta}$ Cuprate Superconductor: Evidence for an Interplay between Competing Orders
   Phys. Rev. Lett. **110**, 217002 (2013).

2. J. P. Hinton, J. D. Koralek, Y. M. Lu, A. Vishwanath, J. Orenstein, D. A. Bonn, W. N. Hardy, and Ruixing Liang
   New collective mode in YBa_2Cu3O_{6+x} observed by time-domain reflectometry
   Phys. Rev. B **88**, 060508(R) (2013).

3. G. Coslovich, B. Huber, W.-S. Lee, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H. A. Bechtel, M.C. Martin, Z. X. Shen, R.W. Schoenlein, and R. A. Kaindl
   Ultrafast Charge Localization in a Stripe-Phase Nickelate
   Nature Communications, **4**, 2643 (2013).

4. P. M. Nagel, J. S. Robinson, B. D. Harteneck, T. Pfeifer, M. J. Abel, J. S. Prell, D. M. Neumark,
   R. A. Kaindl, and S. R. Leone
   Surface Plasmon Assisted Electron Acceleration in Photoemission from Gold Nanopillars
   Chemical Physics **414**, 106–111 (2013).

5. G. Coslovich, B. Huber, W.-S. Lee, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H. A. Bechtel, M. C. Martin, R. W. Schoenlein, Z.-X. Shen, and R. A. Kaindl
   Ultrafast mid-infrared spectroscopy of the charge- and spin-ordered nickelates
   Proc. SPIE **8623**, 862308 (2013).

6. Y. D. Chuang, W. S. Lee, Y. F. Kung, A. P. Sorini, B. Moritz, R. G. Moore, L. Patthey, M. Trigo, D. H. Lu, P. S. Kirchmann, M. Yi, O. Krupin, M. Langner, Y. Zhu, S. Y. Zhou, D. A. Reis, N. Huse, J. S. Robinson, R. A. Kaindl, R.W. Schoenlein, S. L. Johnson, M. Först, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, T. Sasagawa, Z. Hussain, Z. X. Shen, and T. P. Devereaux
   Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered $La_{1.75}Sr_{0.25}NiO4$ Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction
   Phys. Rev. Lett. **110**, 127404 (2013).

7. G. Coslovich, B. Huber, W.-S. Lee, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H. A. Bechtel, M. C. Martin, R. W. Schoenlein, Z.-X. Shen, and R. A. Kaindl

Ultrafast Mid-infrared Spectroscopy of the Charge- and Spin-Ordered Nickelate $La_{1.75}Sr_{0.25}NiO_4$
Ultrafast Phenomena XVIIIth, EPJ Web of Conf. **41**, 03016 (2013).

8. A. Shavorskiy, S. Neppl, D. S. Slaughter, J. P. Cryan, K. R. Siefermann, F. Weise, M.-F. Lin, C. Bacellar, M. P. Ziemkiewicz, I. Zegkinoglou, M.W. Fraund, C. Khurmi, M. P. Hertlein, T. W. Wright, N. Huse, R. W. Schoenlein, T. Tyliszczak, G. Coslovich, J. Robinson, R. A. Kaindl, B. S. Rude, A. Ölsner, S. Mähl, H. Bluhm, and O. Gessner
Sub-nanosecond time-resolved ambient-pressure X-ray photoelectron spectroscopy setup for pulsed and constant wave X-ray light sources
Rev. Sci. Instrum. **85**, 093102 (2014)

9. S. Y. Zhou, M. C. Langner, Y. Zhu, Y.-D. Chuang, M. Rini, T. E. Glover, M. P. Hertlein, A. G. Cruz Gonzalez, N. Tahir, Y. Tomioka, Y. Tokura, Z. Hussain, R. W. Schoenlein
Glass-like recovery of antiferromagnetic spin ordering in a photo-excited manganite $Pr_{0.7}Ca_{0.3}MnO_3$
Scientific Reports **4**, 4050 (2014).

10. M. C. Langner, S. Roy, S. K. Mishra, J. C. T. Lee, X. W. Shi, M. A. Hossain, Y.-D. Chuang, S. Seki, Y. Tokura, S. D. Kevan, and R. W. Schoenlein
Coupled Skyrmion Sublattices in Cu2OSeO3
Phys. Rev. Letters **112**, 167202 (2014).

11. W. Zhang, C. Hwang, C. L. Smallwood, T. L. Miller, G. Affeldt, K. Kurashima, C. Jozwiak, H. Eisaki, T. Adachi, Y. Koike, D. H. Lee, A. Lanzara
Ultrafast quenching of electron-boson interaction and superconducting gap in a cuprate superconductor
Nature Communications **5**, 4959 (2014).

Submitted:

12. H. Wang, Y. Xu, P. Ranitovic, J. S. Robinson, and R. A. Kaindl
Bright high repetition-rate source of narrowband extreme-ultraviolet harmonics beyond 22eV
in review, arXiv:1408.6827 (2014).

13. M.C. Langner, S. Roy, A. F. Kemper, Y.-D. Chuang, S. K. Mishra, R. B. Versteeg, Y. Zhu, M.P. Hertlein, T.E. Glover, K. Dumesnil, R. W. Schoenlein
Transient Exchange Interaction in a Helical Antiferromagnet
in review, arXiv:1409.3614 (2014).

Collective Dynamics in Strongly Correlated Materials

Wei-Sheng Lee, SIMES, SLAC National Accelerator Laboratory

Program Scope

This program (PIs: W. S. Lee, Y. D. Chuang, Z. X. Shen, Z. Hussain, and T. P. Devereaux) is a subtask of "Time-resolved Soft X-ray Materials Science at the LCLS and ALS (FWP 10017)" led by T. P. Devereaux. In this subtask, our goal is to understand the emergent phenomenon in strongly correlated materials by measuring elementary excitations at various energy, length (i.e. momentum), and time scales. Our work is focused on the new capabilities offered at the Linac Coherent Light Source to study novel x-ray spectroscopies in both the time and frequency domains, in equilibrium and in response to tailored light pulse stimuli. We combined that work with other x-ray and optical based activities at other light sources and local laboratories, and utilize DOE tier I computational facilities to carry out numerical investigations. The techniques developed are important to the fundamental understanding of non-equilibrium physical processes and the origin of emergence but also open the ability to control novel properties in materials for energy and other technology applications.

Recent Progress

- Asymmetry of collective excitations in electron- and hole-doped cuprates [1]. We performed high-resolution momentum-resolved RIXS measurements on electron-doped high temperature superconducting cuprates. Surprisingly, upon electron doping, the energy scale of magnetic excitations increases. Furthermore, an unexpected branch of collective modes was also observed. Temperature and doping dependence of these modes indicate the existence of a distinct quantum phase. These behaviors are notably different from those in hole-doped compounds [2, 3]. Nevertheless, despite their differences, the persistence of magnetic excitations well beyond the antiferromagnetic phase boundary and the existence of a distinct quantum state appear to be universal for both hole- and electron-doped cuprates.

- Lattice-driven dynamics in a striped nickelate $La_{1.75}Sr_{0.25}NiO_4$. To elucidate the relation between the lattice and stripe state, we used tailored mid-IR laser pulses to resonantly excite bond-stretching phonons and track the dynamics of both spin and charge orders using femtosecond time-resolved resonant x-ray diffraction at LCLS. Surprisingly, spin order is found to response more dramatically than the charge order. In addition, the relaxation dynamics is different from the dynamics induced by optical-excitations [4, 5]. Our results imply an intriguing collective coupling between the lattice and stripes. Theoretical investigation is now in progress.

- Direct structural characterization of photo-induced coherent phonon oscillations in $BaFe_2As_2$. Upon the excitation of ultrafast optical pulse, the Fe-AS-Fe bond angle, which plays an important role in determining low energy electronic structures, can coherently oscillate. Time-resolved electronic probes have demonstrated that this coherent transient state can be a new

pathway to manipulate the band structure [6], or even the emergence of the spin-density wave state [7]. However, a direct structural characterization is still missing. Our work provides this missing information by performing femtosecond time-resolved x-ray diffraction at LCLS to track the time-evolution of Fe-As-Fe bond angle. Upon photo-excitation the Fe-As-Fe bond angle first decreases and then oscillates with the amplitude of approximately half of the maximal displacement. This information is crucial for theoretical estimations of the associated transient electronic structures. Next experiment at LCLS to further investigate the temperature and doping dependence of this coherent transient state will be conducted in March, 2015.

Future Plans

Using the unique capability of LCLS, we will continue to explore how to use light-matter interaction to manipulate collective dynamics in the strongly correlated materials. Photo-excitations using tailored light pulses, such as terahertz and mid-IR, will be further explored to achieve a better control on the photo-induced non-equilibrium state. In parallel, riding on the tide of RIXS's rapid development, we plan to continue investigating low energy elementary excitations in the energy-momentum space using state-of-the-art RIXS instruments. We plan to map out elementary excitations for the entire cuprate phase diagram; meanwhile other novel materials will also be explored. We anticipate some of these activities will be conducted using the q-RIXS endstation funded via this program, which will be completed before year 2015.

References

1. W. S. Lee *et al.*, Asymmetry of collective excitations in electron- and hole-doped cuprate superconductor. *To appear in Nature Physics.*
2. M. Le Tacon *et al.*, Intense paramagnon excitations in a large family of high-temperature superconductor. *Nature Phys.* **7**, 725 (2011).
3. M. P. M. Dean *et al.*, Persistence of magnetic excitations in $La_{2-x}Sr_xCuO_4$ from the undoped insulator to the heavily overdoped non-superconducting metal. *Nature Mater.* **12,** 1019 (2013).
4. W. S. Lee *et al.*, Phase fluctuations and the absence of topological defects in photo-excited charge ordered nickelate. *Nature Communications* **3**, 838 (2012).
5. Y. D. Chunag *et al.*, Real-time manifestation of strongly coupled spin and charge order Parameters in stripe-ordered $La_{1.75}Sr_{0.25}NiO_4$ nickelate crystals using time-resolved resonant x-ray diffraction. *Phys. Rev. Lett.* **110**, 127404 (2013).
6. Yang *et al.*, Ultrafast Modulation of the chemical potential in $BaFe_2As_2$ by Coherent Phonons. *Phys. Rev. Lett.* **112**, 207001.
7. Kim *et al.*, Ultrafast transient generation of spin-density-wave order in the normal state of $BaFe_2As_2$ driven by coherent lattice vibrations, *Nature Mater.* **11**, 497 (2012).

Publications

1. **W. S. Lee**, J. J. Lee, E. A. Nowadnick, S. Gerber, W. Tabis, S. W. Huang, V. N. Strocov, E. M. Motoyama, G. Yu, B. Moritz, H. Y. Huang, R. P. Wang, Y. B. Huang, W. B. Wu, C. T. Chen, D. J. Huang, M. Greven, T. Schmitt, Z. X. Shen, and T. P. Devereaux. *Asymmetry of collective excitations in electron and hole doped cuprate superconductors.* To appear in Nature Physics.

2. M. Hashimoto: G. Ghiringhelli, **W.-S. Lee**, G. Dellea, A. Amorese, C. Mazzoli, K. Kummer, N. B. Brookes, B. Moritz, Y. Yoshida, H. Eisaki, Z. Hussain, T. P. Devereaux, Z.-X. Shen, and L. Braicovich. *Direct observation of bulk charge modulations in optimally doped* $Bi_{1.5}Pb_{0.6}Sr_{1.54}CaCu_2O_{8+d}$. Phys. Rev. B **89**, 220511(R) (2014).

3. T. Kubacka, J.A. Johnson, M.C. Hoffmann, C. Vicario, S. de Jong, P. Beaud, S. Grübel, S-W. Huang, L. Huber, L. Patthey, Y-D. Chuang, J.J. Turner, G.L. Dakovski, **W-S. Lee,** W. Schlotter, R. G. Moore, C. Hauri, S.M. Koohpayeh, V. Scagnoli, G. Ingold, S.L. Johnson, U. Staub. *Large-Amplitude Spin Dynamics Driven by a THz Pulse in Resonance with an Electromagnon.* Science **343**, 1333 (2014).

4. J. J. Lee, B. Moritz, **W. S. Lee,** M. Yi, C. J. Jia, A. P. Sorini, K. Kudo, Y. Koike, K. J. Zhou, C. Monney, V. Strocov, L. Patthey, T. Schmitt, T. P. Devereaux, and Z. X. Shen. *Charge-orbital-lattice coupling effects in the dd excitation profile of one-dimensional cuprates.* Phys. Rev. B **89**, 041104(R) (2014).

5. M. Först, R. I. Tobey, H. Bromberger, S. B. Wilkins, V. Khanna, A. D. Caviglia, Y.-D. Chuang, **W. S. Lee**, W. F. Schlotter, J. J. Turner, M. P. Minitti, O. Krupin, Z. J. Xu, J. S. Wen, G. D. Gu, S. S. Dhesi, A. Cavalleri, and J. P. Hill. *Melting of Charge Stripes in Vibrationally Driven La1.875Ba0.125CuO4: Assessing the Respective Roles of Electronic and Lattice Order in Frustrated Superconductors.* Phys. Rev. Lett. **112**, 157002 (2014)

6. U. Staub, R.A. de Souza, P. Beaud, E. Möhr-Vorobeva, G. Ingold, A. Caviezel, V. Scagnoli, B. Delley, 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, A.T. Boothroyd, S.L. Johnson. *Persistence of magnetic order in a highly excited* Cu^{2+} *state in CuO*. Phys. Rev. B **89**, 220401(R)

7. A. D. Caviglia, M. Först, R. Scherwitzl, V. Khanna, H. Bromberger, R. Mankowsky, R. Singla, Y.-D. Chuang, **W. S. Lee**, O. Krupin, W. F. Schlotter, J. J. Turner, G. L. Dakovski, M. P. Minitti, J. Robinson, V. Scagnoli, S. B. Wilkins, S. A. Cavill,*, M. Gibert, S. Gariglio, P. Zubko, J.-M. Triscone, J. P. Hill, S. S. Dhesi, and A. Cavalleri. *Photoinduced melting of magnetic order in the correlated electron insulator* $NdNiO_3$. Phys. Rev. B **88**, 220401 (2013).

8. G. Coslovich, B. Huber, **W. S. Lee**, Y.-D. Chuang, Y. Zhu, T. Sasagawa, Z. Hussain, H.A. Bechtel, M.C. Martin, Z.-X. Shen, R.W. Schoenlein and R.A. Kaindl. *Ultrafast charge localization in a stripe-phase nickelate.* Nature Communications **4**, 3643 (2013).

9. Y. F. Kung, **W. S. Lee**, C. C. Chen, A. F. Kemper, A. P. Sorini, B. Moritz, and T. P. Devereaux. *Time-dependence charge-order and spin-order recovery in striped systems.* Phys. Rev. B **88**, 125114 (2013).

10. S. de Jong, R. Kukreja, C. Trabant, N. Pontius, C. F. Chang, T. Kachel, M. Beye, F. Sorgenfrei, C. H. Back, B. Brauer, W. F. Schlotter, J. J. Turner, O. Krupin, M. Doehler, D. Zhu, M. A. Hossain, A. O. Scherz, D. Fausti, F. Novelli, M. Esposito, **W. S. Lee**, Y. D. Chuang, D. H. Lu, R. G. Moore, M. Yi, M. Trigo, P. Kirchmann, L. Pathey, M. S. Golden, M. Buchholz, P. Metcalf, F. Parmigiani, W. Wurth, A. Fohlisch, C. Schussler-Langegeine, and H. A. Durr. *Speed Limit of the insulator-metal transition in magnetite.* Nature Materials **12**, 882 (2013).

11. **W. S. Lee,** S. Johnston, B. Moritz, J. Lee, M. Yi, K. J. Zhou, T. Schmitt, K. Kudo, Y. Koike, J. van den Brink, T. P. Devereaux, and Z. X. Shen. *The Role of Lattice Coupling in Establishing Electronic and Magnetic Properties in Quasi-One-Dimensional Cuprates.* Phys. Rev. Lett. **110**, 265502 (2013).

12. Y. D. Chuang, **W. S. Lee**, R. G. Moore, Y. Zhu, L. Patthey, M. Trigo, D. H. Lu, P. S. Kirchmann, O. Krupin, M. Yi,M. Langner, N. Huse, J. S. Robinson, Y. Chen, S. Y. Zhou, D. A. Reis, R. A. Kaindl, R. W. Schoenlein, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, S. L. Johnson, M. Först, T. Sasagawa, Y. F. Kung, A. P. Sorini, A. F. Kemper, B. Moritz, T. P. Devereaux, D.-H. Lee, Z. X. Shen, and Z. Hussain. *Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered $La_{1.75}Sr_{0.25}NiO_4$ Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction.* Phys. Rev. Lett. **110**, 127404 (2013).

13. **W. S. Lee**, Y. D. Chuang, R. G. Moore, Y. Zhu, L. Patthey, M. Trigo, D. H. Lu, P. S. Kirchmann, O. Krupin, M. Yi,M. Langner, N. Huse, J. S. Robinson, Y. Chen, S. Y. Zhou, G. Coslovich, B. Huber, D. A. Reis, R. A. Kaindl, R. W. Schoenlein, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, S. L. Johnson, M. Först, T. Sasagawa, Y. F. Kung, A. P. Sorini, A. F. Kemper, B. Moritz, T. P. Devereaux, D.-H. Lee, Z. X. Shen, and Z. Hussain. *Phase fluctuations and the absence of topological defects in photo-excited charge ordered nickelate.* Nature Communications **3**, 838 (2012).

14. **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).

15. R. I. Tobey, S. Wall, M. Forst, H. bromberger, V. Khanna, J. Turner, W. Schlotter, M. Trigo, O. Krupin, **W. S. Lee,** Y. D. Chuang, R. Moore, A. L. Vavalieri, S. B. Wilkins, H. Zheng, J. F. Mitchell, S. S. Dhesi, A. Cavalleri, and J. P. Hill. *Evolution of three-dimensional correlations during the photo-induced melting of antiferromagnetic order in* $La_{0.5}Sr_{1.5}MnO_{4.}$ Phys. Rev. B **86**, 064425 (2012).

16. 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**, 11396-11406 (2012).

17. W.F. Schlotter, J.J. Turner, M. Rowen, P. Heimann, M. Holmes, O. Krupin,M. Messerschmidt, S. Moeller, J. Krzywinski, R. Soufli, M. Fern´andez-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. L¨uning, 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).

18. M. Beye, O. Krupin, G. Hays, A.H. Reid, D. Rupp, S. de Jong, S. Lee, **W.-S. Lee,** Y.-D. Chuang, R. Coffee, J.P. Cryan, J.M. Glownia, A. Fohlisch, M.R. Holmes, A.R. Fry, W.E. White, C. Bostedt, A.O. Scherz, H.A. Durr, and W.F. Schlotter. *X-ray pulse Preserving Single-Shot Optical Cross-Correlation Method for Improved Experimental Temporal Resolution.* Appl. Phys. Lett. **100**, 121108 (2012).

19. S. L. Johnson, R. A. de Souza, U. Staub, P. Beaud, E. Möhr-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, A. T. Boothroyd. *Femtosecond Dynamics of the Collinear-to-Spiral Antifferomagnetic Phase Transition in CuO.* Phys. Rev. Lett. **108**, 037203 (2012).

20. S. K. Mo, **W. S. Lee**, F. Schmitt, Y. L. Chen, D. H. Lu, C. Capan, D. J. Kim, Z. Fisk, C.-Q Zhang, Z. Hussain, and Z. X. Shen. *Emerging coherence with unified energy, temperature and lifetime scale in heavy fermion* $YbRh_2Si_2$. Phys. Rev. B **85**, 241103 (2012).

21. S. Johnston, I. M. Vishik, **W. S. Lee**, F. Schmitt, S. Uchida, K. Fujita, N. Nagaosa, Z. X. Shen, T. P. Devereaux. *Evidence for the importance of extended coulomb interaction and forward scattering in Cuprates superconductor.* Phys. Rev. Lett. **108**, 166404 (2012).

Ultrafast Studies of Nanoscale Structural Dynamics (part of FWP: Time-resolved Soft X-ray Materials Science at the LCLS & ALS)

Aaron Lindenberg (Stanford University / SLAC National Accelerator Laboratory)

Program Scope

In this sub-task, we are interested in resolving the first atomic-scale steps in how materials transform and exploring means of manipulating specific degrees of freedom with respect to elucidating their functionality. Techniques spanning the range from x-ray scattering and spectroscopy to far-infrared terahertz spectroscopy are applied with focus on understanding the dynamics of thin film ferroelectric and multiferroic oxides, phase-change materials and related chalcogenides, and solid-solid structural phase transitions in semiconductor nanocrystals.

Recent Progress

Femtosecond x-ray scattering studies at the LCLS have enabled the first snapshots of a previously predicted but not experimentally observed intermediate phase associated with pressure-induced structural transformations in semiconductor nanocrystals (CdS and CdSe), related to a class of martensitic phase transformations. A stress-dependent transition path is observed with evidence for a transient five-coordinated intermediate structure observed on ten's of picosecond time-scales, consistent with first principles modeling (Publication 9). Additional x-ray studies have recorded anisotropic strains, morphological changes, and breathing mode responses in the same materials corresponding to percent level strains, occurring simultaneously with the melting transition on hundreds of femtosecond time-scales (*submitted*). Femtosecond soft x-ray spectroscopy studies have been used to investigate the first steps in superionic phase transitions in nanoscale Cu_2S, an important material for electrochemical energy storage exhibiting fast ionic transport of the Cu cation through a fixed anion sublattice. Measurements show

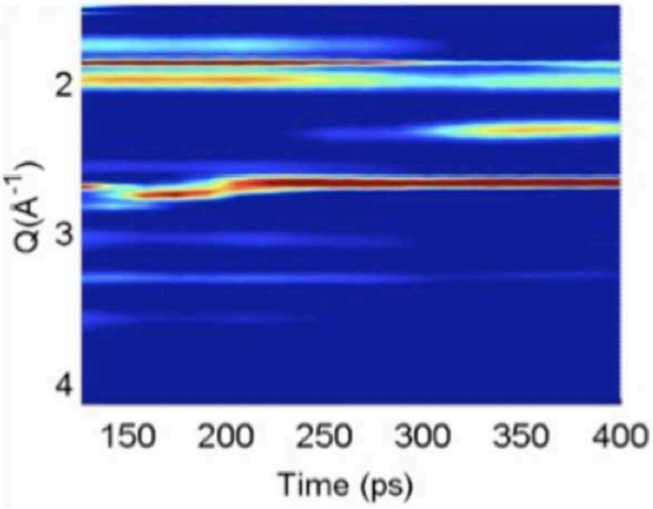


Fig. 1. Time-resolved x-ray diffraction data showing emergence of new structural phase in CdS nanorods driven by picosecond shock waves. Previously forbidden diffraction peak turns on at t~250 ps. Aluminum diffraction peak at Q~2.8 allows for extraction of magnitude of pressure.

that the time for the phase transition to occur is determined by the ionic hopping time (Publication 14). Additional ongoing experiments have measured THz-driven responses in phase-change materials, revealing the first steps in the electric-field-driven switching between amorphous and crystalline structural phases (Publications 7, 12, submitted). Recent x-ray scattering experiments at the LCLS and the APS have revealed novel THz-driven structural responses in ferroelectric $BaTiO_3$ thin films associated with both long-lived strains and ultrafast modulations in the unit cell structure factor, scaling quadratically with the applied THz field. Related experiments in multiferroic $BiFeO_3$ show first evidence for the generation of large amplitude changes in the ferroelectric polarization on ultrafast time-scales and dramatically enhanced responses near a morphotropic phase boundary, enabling giant THz-driven modulations in the nonlinear optical properties.

Future Plans

Recent work has shown preliminary evidence for THz-driven crystallization in phase-change materials and we are carrying out THz pump / mid-IR, THz, and x-ray probe studies of these responses. These studies have the potential to answer long-standing questions regarding the mechanism for threshold switching in these materials. Ongoing work in collaboration with other members of the FWP is focused on the dynamical structural response of PbTe and related materials (with Reis, Trigo et al), and on the dynamical structural and electronic response of 2D materials. Preliminary work in MoS2 monolayers (Publication 1) using the second order nonlinear optical susceptibility as a structural probe have shown evidence for unexpected increases in the second harmonic under extreme non-equilibrium excitation conditions (corresponding to of order 1 electron-hole pair per unit cell) opening up new possibilities for reversible all-optical modulation and control of the opto-electronic properties of two-dimensional transition metal dichalcogenide materials.

Publications (2013-2014)

1. "Ultrafast electronic and structural response of monolayer MoS_2 under intense photoexcitation conditions," E.M. Mannebach et al., *ACS Nano*, (2014). DOI: 10.1021/nn5044542.
2. "Room Temperature Stabilization of Nanoscale Superionic Ag_2Se", T. Hu et al., *Nanotechnology*, 25, 415705 (2014)
3. "Reversible optical switching of infrared antenna resonances with ultrathin phase-change layers using femtosecond laser pulses", Ann-Katrin U. Michel et al., *ACS Photonics*, 1, 833 (2014)
4. "Ultrafast polarization response of an optically-trapped single ferroelectric nanowire", S. Nah et al., *Nano Lett.*, 14, 4322 (2014)
5. "Picosecond carrier recombination dynamics in chalcogen-hyperdoped silicon", M. Sher et al.,

Appl. Phys. Lett. 105, 053905 (2014)
6. "Below gap optical absorption in GaAs driven by intense, single-cycle coherent transition radiation", J. Goodfellow et al., *Opt. Express* 22, 17423 (2014)
7. "Ultrafast terahertz-induced response of GeSbTe phase-change materials", M. Shu et al., *Appl. Phys. Lett.* 104, 251907 (2014)
8. "Measurement of transient atomic displacements in thin films with picosecond and femtometer resolution", M. Kozina et al.,*Struct. Dyn.* 1, 034301 (2014)
9. "Real-time visualization of nanocrystal solid-solid transformation pathways", J.S. Wittenberg et al., *Nano Lett.*, 14, 1995 (2014).
10. "Fourier-transform inelastic X-ray scattering from time and momentum dependent phonon-phonon correlations", M. Trigo et al.,*Nat. Phys.* 9, 790 (2013)
11. "High-pressure Raman spectroscopy of phase change materials", W. Hsieh et al., *Appl. Phys. Lett.* 103, 191108 (2013)
12. "Ultrafast sub-threshold photo-induced response in crystalline and amorphous GeSbTe thin films", M. J. Shu et al., *Appl. Phys. Lett.* 102, 201903 (2013)
13. "Intense THz pulses from SLAC electron beams using coherent transition radiation", Z. Wu, et al., Rev. Sci. Instrum. 84, 022701 (2013)
14. "The mechanism of ultrafast structural switching in superionic copper (I) sulfide nanocrystals", T.A. Miller et al., *Nat. Commun.* 4:1369 (2013)

Fundamental Mechanisms of Roughening During Thin Film Deposition

Karl F. Ludwig, Boston University

Randall L. Headrick, University of Vermont

Program Scope

The Scope of our current research program is the study of thin film growth mechanisms, particularly related to surface roughening and strain relaxation during growth. In-situ time resolved growth studies utilizing Grazing Incidence x-ray Diffraction (GID) and Grazing Incidence Small Angle Scattering (GISXAXS) are emphasized, and the studies include several physical vapor deposition methods and materials systems ranging from epitaxial complex oxides to amorphous metal thin films.

Recent Progress

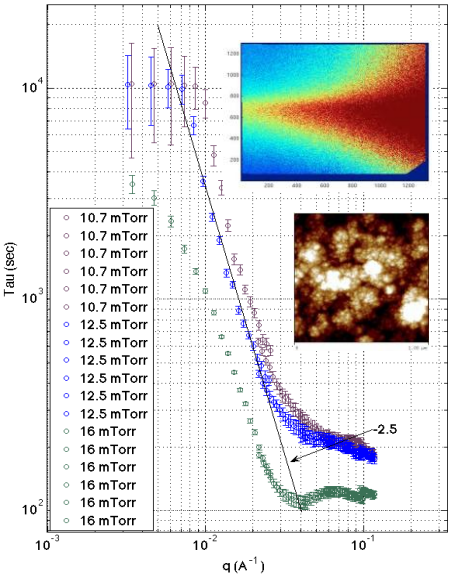


Figure 1. Coherent GISAXS data for sputter deposition of WSi_2 thin films at various Ar pressures showing the q-dependence of the time constant of the surface dynamics. The upper inset shows a single frame of GISAXS data with speckle, and the lower inset shows an AFM image of the final rough surface.

In this collaboration between Headrick and Ludwig, we are developing time-resolved Coherent GISAXS (CoGISAXS) techniques to study hard condensed matter systems, particularly the dynamics of surfaces and thin films evolving during deposition or processing. In an initial round of experiments, we have performed coherent hard x-ray studies of the temporal correlations of surfaces during sputter deposition of amorphous WSi_2 and Si thin films. A vacuum deposition system with the capability to perform time-resolved Coherent Grazing Incidence Small Angle X-ray Scattering (CoGISAXS) during the deposition process was developed and utilized for these measurements. During film deposition, the average statistical properties of the surface saturate in the steady-state regime. We have demonstrated that X-ray Photon Correlation Spectroscopy (XPCS) temporal correlations derived from CoGISAXS data yield information about fluctuations around the mean surface profile. This demonstration of the use of XPCS to study growing surfaces can be extended to additional materials systems, and additional phenomena that may include both steady-state and heterogeneous dynamics.

Time constants for fluctuating surface roughness during growth of WSi_2 are shown in Fig. 1. These time constants are derived from fitting the time-averaged temporal correlation functions from X-ray Photon Correlation Spectroscopy (XPCS) analysis of time-resolved co-GISAXS data. A two order of magnitude variation in the time constant of the fluctuations is observed as a function of the in-plane length scale. The time constant exhibits a power-law behavior over a narrow range, as we expect from kinetic roughening theory, but does not drop below a certain level.

The saturation behavior observed at large q in Fig. 1 is evidently due to background from the bulk of the film. We have discovered striking effect that is unique to coherent x-ray scattering that occurs when scattering from the bulk of the film interferes with scattering from the surface during thin film growth. The effect can be observed in time-correlation plots as a function of time delay. Fig. 2 shows an example, where the signals beat against each other temporally, a phenomenon known as heterodyning.[1, 2] The frequency of the oscillations is determined by the growth velocity and the component of the scattering q vector perpendicular to the surface as $\omega = v\, q_z$.

The lower panel in Fig. 2 is from the same series of data, but at a lower exit angle where the escape depth of x-rays is limited to a few nm. In this case the signal from the bulk is significantly attenuated, and the interference effect disappears almost completely, confirming that the reference wave is from the bulk of the film. This effect may be of use to monitor film growth in many thin film systems since it is very common to have a source of bulk scattering from defects even for crystalline materials.

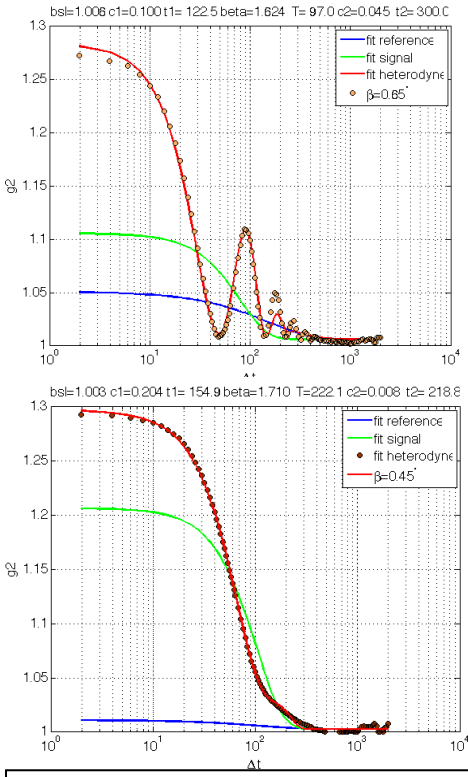


Figure 2. Heterodyne effect observed during sputter deposition of a WSi_2 thin film. The top panel shows the g2 temporal correlation versus time delay. The effect is clearly observed, and it can be modeled as the interference between the GISAXS signal from the surface of the film interfereing with a reference wave. The lower panel is from the same series of data, but at a lower exit angle at the critical angle of the surface, which extinguishes the effect.

We have also made significant progress on the interpretation of coherent GISAXS data of evolving surfaces. We have found that CoGISAXS directly measures the dynamic roughening exponent from dynamic scaling theory.[3] In particular, the dynamic roughening exponent can be extracted from measurement of the q-dependence of the fluctuation time constant (Fig. 1). This suggests the applicability of XPCS techniques more broadly in studies of the evolution of surfaces. We have also made significant progress in simulation of surface dynamics from

continuum equations and have found that simulations of the noisy Kuramoto-Sivashinsky equation reproduce previous computational results,[4] and exhibit features that correspond to our recent experiments.

Future Plans

These initial results point the way toward future development in this area that we will continue to explore. In the near future we will extend our experimental capabilities to perform coherent x-ray experiments during pattern formation by ion erosion of surfaces, during growth of clusters from a thermal source, and epitaxial growth during off-axis sputter deposition. This will enable us to study a broader range of phenomena. Ion erosion of surfaces produces patterns of ripples or dots, which saturate at late times but continue to fluctuate locally. This is a natural extension of our work on sputter deposited thin films. Another area is droplet nanoclusters on surfaces, which may exhibit heterogeneous dynamics.

References

1. de Jeu, W.H., et al., *Heterodyne and homodyne detection in fluctuating smectic membranes by photon correlation spectroscopy at X-ray and visible wavelengths.* Physica B-Condensed Matter, 2005. **357**(1-2): p. 39-44.

2. Sutton, M., *A review of X-ray intensity fluctuation spectroscopy.* Comptes Rendus Physique, 2008. **9**(5-6): p. 657-667.

3. Sneppen, K., et al., *Dynamic Scaling and Crossover Analysis for the Kuramoto-Sivashinsky Equation.* Physical Review A, 1992. **46**(12): p. R7351-R7354.

4. Nicoli, M., E. Vivo, and R. Cuerno, *Kardar-Parisi-Zhang asymptotics for the two-dimensional noisy Kuramoto-Sivashinsky equation.* Physical Review E, 2010. **82**(4).

Publications

"Transition from laminar to three-dimensional growth mode in pulsed laser deposited $BiFeO_3$ film on (001) $SrTiO_3$", P.V. Chinta, S.J. Callori, M. Dawber, A. Ashrafi, and R.L. Headrick. *Appl. Phys. Lett.* **101**, 201602 (2012).

"Origin of stress and enhanced carrier transport in solution-cast organic semiconductor films ", Cour, P.V. Chinta, C.M. Schlepütz, Y. Yang, R. Clarke, R. Pindak, and R.L. Headrick. *J. Appl. Phys.* **114**, 093501 (2013).

"In-situ x-ray diffraction study of the growth of highly strained epitaxial $BaTiO_3$ thin films ", J. Sinsheimer, S.J. Callori, B. Ziegler, B. Bein, P.V. Chinta, A. Ashrafi, R.L. Headrick, and M. Dawber. *Appl. Phys. Lett.* **103** 242904 (2013).

"Bimodal island size distribution in heteroepitaxial growth ", P. V. Chinta and R. L. Headrick. *Phys. Rev. Lett.* **112(7)** 075503 (2014).

"Spatial mapping of morphology and electronic properties of air-printed pentacene films ", S. Biswas, N. Geva, M. Shtein, Y. Yang, R. Clarke, M. Schlepütz, R.L. Headrick, R. Pindak. *Adv. Func. Mater.* **24** 3907 (2014).

"Real-Time X-ray Studies of Indium Island Growth Kinetics", A. DeMasi, M. Rainville and K.F. Ludwig, submitted to *Applied Surface Science*.

"In-Situ Synchrotron Based X-ray Techniques as Monitoring Tools for Atomic Layer Deposition – A Review", K. Devloo-Casier, K.F. Ludwig, C. Detavernier and J. Dendooven, *J. Vac. Sci Technol. A* 32, 010801 (2014).

"Atomic Layer Deposition of TiO_2 on Surface Modified Nanoporous Low-k Films", E. Levrau, K. Devloo-Casier, J. Dendooven, K. Ludwig, P. Verdonck, J. Meersschaut, M. Baklanov and C. Detavernier, *Langmuir* **29**, 12284 (2013).

"High Contrast X-ray Speckle from Atomic-Scale Order in Liquids and Glasses", S. Hruszkewycz, M. Sutton, P. Fuoss, B. Adams, S. Rosenkranz, K.F. Ludwig, W. Roseker, D. Fritz, M. Cammarata, D. Zhu, S. Lee, H. Lemke, C. Gutt, A. Robert, G. Gruebel and G.B. Stephenson, *Phys. Rev. Lett.* **109**, 185502 (2012).

"Evidence for Family-Meakin Dynamical Scaling in Island Growth and Coalescence during Vapor Phase Deposition", Leyla Çolakerol Arslan, Christopher Sanborn, Eitan Anzenberg and Karl F. Ludwig, Jr., *Phys. Rev. Lett.* **109**, 106102 (2012).

"Composition Dependent Bilayer Atomic Ordering in Al_xGa_{1-x} Films Examined by Polarization-Dependent Extended X-ray Absorption Fine Structure", J.C. Woicik, K.F. Ludwig, Jr. and T.D. Moustakas, *Appl. Phys. Lett.***100**, 162105 (2012).

"X-ray Photon Correlation Spectroscopy in Systems without Long-Range Order: Existence of an Intermediate-Field Regime", K. Ludwig, *J. Synchrotron Rad.* **19**, 66 (2012).

"Tuning the Pore Size of Ink-Bottle Mesopores by Atomic Layer Deposition", J. Dendooven, B. Goris, K. Devloo-Casier, E. Levrau, E. Biermans, M. Baklanov, K. Ludwig, P. Van Der Voort, S. Bals and C. Detavernier, *Chemistry of Materials* **24**, 1992 (2012).

HPCAT – Pressure-induced phenomena in elements, compounds and nanomaterials

Ho-kwang Mao, Guoyin Shen, & Viktor Struzhkin, Carnegie Institution of Washington

Program Scope

Our programmatic mission is to advance the high-pressure materials sciences using synchrotron radiations. The HPCAT beamline facility provides a comprehensive platform with x-ray diffraction, spectroscopy and imaging capabilities optimized for high-pressure research, that enable us to explore novel high-pressure phenomena in many directions as summarized in a group of three companion abstracts. The present abstract focuses on highlights of elements, compounds and nanoscience under pressures.

Recent Progress

Complexity of simple elements and compounds under pressures: Our experiments have shown that under pressure the simple metal Li behaves in a manner that is rather complex (*1*). Above 40 GPa, not only does Li melt at room temperature, but then remains molten down to 190 K, below which it crystallizes into a range of highly complex structures. Plasmon excitations of the next alkali metal, Na, (*2*) were measured up to 97 GPa using the momentum-dependent inelastic x-ray scattering technique. The results, however, showed that even under multiple fold densification, the solid Na of both bcc and fcc symmetry can still be regarded as simple metals. Our experiments show that Ca-III, the first known superconducting Ca phase under pressure is not exactly sc as previously thought, but sustains the sc-like, primitive unit by a rhombohedral distortion at 300 K, a monoclinic distortion below 30 K and β-tin structure (*3*) at 35 GPa in a small temperature range below 10K. The experimental observation establishes a new phase diagram for calcium up to 110 GPa and 5-300 K. By focusing ultrafast laser to induce confined micro-explosion inside a sapphire, we created a high *P-T* plasma, drove away the oxygen, and reduced the sapphire to Al which has been confirmed with x-ray micro-diffraction at HPCAT as the superdense bcc phase (*4*)

We showed that at pressures above 40 GPa, the arrangement of the bonds between the C atoms in the glassy carbon had completely shifted from sp^2 to sp^3 representing a new superhard carbon allotrope (*5*). Our experiments show that a precursor lattice of the high-pressure β-phase of Si appeared at pressures far below the transition pressure around 13GPa (*6*), providing a new mechanism for the α–β Si phase transition. Our results show that under a pressure of 66 GPa, elemental Ge undergoes a structural change from a metallic white tin structure to an orthorhombic Imma structure. It then undergoes another change under pressure of 90 GPa to the simple hexagonal structure (*7*).

Even the common salt NaCl can be changed to cubic and orthorhombic $NaCl_3$ and two-dimensional metallic tetragonal Na_3Cl at high pressures (*8*). These experiments establish that compounds violating chemical intuition can be thermodynamically stable even in simple systems. Around 32.5 GPa at 300 K, we observed a novel pressure-induced corundum-to-monoclinic transition between two metallic phases of V_2O_3, showing that the structural phase transition can be decoupled from the metal-insulator transition (*9*).

High-pressure nanoscience: When solvated C_{60} buckyballs were subjected to high compression, individual buckbulls were crushed into disordered clusters, while the clusters were still arranged in an ordered crystal structure (*10*). This discovery creates a new category of material with a long-range ordered structure formed by clusters of short-range disordered carbon atoms.

Knowledge on the size limit of dislocation grain rotation is fundamental for understanding the strength and plastic deformation of nanomaterials. We observed significant texturing in 3 nm nickel when compressed above 18.5 GPa. The observations of pressure-promoted texturing indicate that under high external pressures, dislocation activities can be extended down to a few-nanometer length scale. Hence, the strength of even small nanocrystals may be limited by dislocation activity (*11*). Meanwhile, active grain rotations are observed in very small nickel nanocrystals down to 3 nm size (*12*).

Ding *et al* (*13*) developed a novel high-*P* technique by integrating the DAC with a nanoscale XRD contrast-imaging probe which has been successfully employed for mapping antiferromagnetic domains in wüstite during high-*P* transition. Yang *et al* (*14*) successfully de-convoluted the 3D internal strain distribution of a 400 nm gold single crystal in a diamond anvil cell from the mixed Bragg coherent diffraction imaging. The 3D morphologies and strain evolutions of the same particle at different pressures up to 6.4 GPa were obtained with better than 20 nm spatial resolution.

Pressure induced amorphization in Ta_2O_5 nanowires. The resultant amorphous Ta_2O_5 nanowires show significant improvement in electrical conductivity compared to that in the traditional amorphous compound (*15*). Likewise pressure enhances electron transport in Nb-doped TiO_2 nanoparticles. The pressure-induced conductivity evolution provides direct evidence for rationalizing the correlation of packing factors with electron transport in semiconductors (*16*).

Future Plans

We plan to address the most fundamental problems in high-pressure physics related to alkali metal-insulation transition and phase relations of the first column elements.

1. We plan to develop maximum pressure capabilities beyond the current limit of 400 GPa, by improving the miniature designs of diamond anvils and testing the designs with x-ray microprobes with nanoscale resolutions.
2. We plan to solve the novel high-pressure crystallography of hydrogen and alkali metals with our recently developed multigrain crystallography method (*17, 18*)
3. We plan to studied the hydrogen bandgap and follow its pressure-induced changes up to metallization with the x-ray inelastic scattering capabilities at HPCAT.
4. We plan to extend the monitoring of Na plasmon and K-edge IXS spectroscopy beyond 100 GPa to enter the exciting regime of metal-insulator transition.
5. We plan to use the IXS instrument at HPCAT to study the lithium plasmon dynamics, and lithium *K* edge dipolar to monopolar excitations through the series of high-pressure phase transitions.

Publications

1. C. L. Guillaume, E. Gregoryanz, O. Degtyareva, M. I. McMahon, S. Evans, M. Hanfland, M. Guthrie, S. V. Sinogeikin, H. K. Mao, Cold melting and solid structures of dense lithium. *Nature Phys.* **7**, 211-214 (2011).
2. H. K. Mao, Y. Ding, Y. Xiao, P. Chow, J. Shu, S. Lebègue, A. Lazicki, R. Ahuja, Electronic dynamics and plasmons of sodium under compression. *Proc. Nat. Acad. Sci. USA* **108**, 20434-20437 (2011).
3. B. Li, Y. Ding, W. Yang, L. Wang, B. Zou, J. Shu, S. Sinogeikin, C. Park, G. Zou, H. K. Mao, Calcium with the β-tin structure at high pressure and low temperature. *Proc. Natl. Acad. Sci. USA* **109**, 16459-16462 (2012).
4. A. Vailionis, E. G. Gamaly, V. Mizeikis, W. Yang, A. V. Rode, S. Juodkazis, Evidence of superdense aluminium synthesized by ultrafast microexplosion. *Nature Commun.*, DOI: 10.1038/ncomms1449 (2011).
5. Y. Lin, L. Zhang, H.-k. Mao, P. Chow, Y. Xiao, M. Baldini, J. Shu, W. L. Mao, Amorphous diamond: A high-pressure superhard carbon allotrope. *Phys. Rev. Lett.* **107**, 175504 (2011).
6. G. Shen, D. Ikuta, S. Sinogeikin, Q. Li, Y. Zhang, C. Chen, Direct observation of a pressure-induced precursor lattice in silicon. *Phys. Rev. Lett.* **109**, 205503 (2012).
7. X.-J. Chen, C. Zhang, M. Yue, R.-Q. Zhang, Hai-Qing Lin, V. V. Struzhkin, H. K. Mao, β-tin→Imma→sh phase transitions of germanium. *Phys. Rev. Lett.* **106**, 135502 (2011).
8. W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka, Z. Konôpková, Unexpected stable stoichiometries of sodium chlorides. *Science* **342**, 1502-1505 (2013).
9. Y. Ding, C.-C. Chen, Q. Zeng, H.-S. Kim, M. J. Han, M. Balasubramanian, R. Gordon, F. Li, L. Bai, D. Popov, S. M. Heald, T. Gog, H.-k. Mao, M. van Veenendaal, Novel high-pressure monoclinic metallic phase of V_2O_3. *Phys. Rev. Lett.* **112**, 056401 (2014).
10. L. Wang, B. Liu, H. Li, W. Yang, Y. Ding, S. V. Sinogeikin, Y. Meng, Z. Liu, X. C. Zeng, W. L. Mao, Long-range ordered carbon clusters: A crystalline material with amorphous building blocks. *Science* **337**, 825-828 (2012).
11. B. Chen, K. Lutker, S. V. Raju, J. Yan, W. Kanitpanyacharoen, J. Lei, S. Yang, H.-R. Wenk, H. K. Mao, Q. Williams, Texture of nanocrystalline nickel: Probing the lower size limit of dislocation activity. *Science* **338**, 1448-1451 (2012).
12. B. Chen, K. Lutker, J. Lei, J. Yan, S. Yang, H. K. Mao, Detecting grain rotation at the nanoscale. *Proc. Natl. Acad. Sci. U.S.A.* **111**, 3350-3353 (2014).
13. Y. Ding, J. Fernandez-Rodriguez, J. Kim, F. Li, D. Casa, M. Upton, T. Gog, H. K. Mao, M. van Veenendaal, Spin-ordering mediated orbital hybridization in CoO at high pressures. *Phys. Rev. B* **86**, 094107 (2012).
14. W. Yang, X. Huang, R. Harder, J. N. Clark, I. K. Robinson, H. K. Mao, Coherent diffraction imaging of nanoscale strain evolution in a single crystal under high pressure. *Nature Commun.* **4**, DOI: 10.1038/ncomms2661 (2013).
15. X. Lv, Q. Hu, W. Yang, L. Bai, H. Sheng, L. Wang, F. Huang, J. Wen, D. J. Miller, Y. Zhao, Pressure-induced amorphization in single crystal Ta_2O_5

nanowires: A kinetic mechanism and improved electricalcConductivity. *J. Am. Chem. Soc.* **135**, 13947−13953 (2013).

16. X. Lv, W. Yang, Z. Quan, T. Lin, L. Bai, L. Wang, F. Huang, Y. Zhao, Enhanced electron transport in Nb-doped TiO_2 nanoparticles via pressure-induced phase transitions. *J. Am. Chem. Soc.* **136**, 419-426 (2014).
17. L. Zhang, Y. Meng, W. Yang, L. Wang, W. L. Mao, Q.-S. Zeng, J. S. Jeong, A. J. Wagner, K. A. Mkhoyan, W. Liu, R. Xu, H. K. Mao, Disproportionation of $(Mg,Fe)SiO_3$ perovskite in Earth's deep lower mantle. *Science* **344**, 877-882 (2014).
18. L. Zhang, Y. Meng, P. Dera, W. Yang, W. L. Mao, H. K. Mao, Single-crystal structure determination of $(Mg,Fe)SiO_3$ postperovskite. *Proc. Natl. Acad. Sci. U.S.A.* **110**, 6292–6295 (2013).

X-ray scattering studies of energy materials at extreme conditions

Wendy L. Mao

Photon Science, SLAC National Accelerator Laboratory

Geological and Environmental Sciences, Stanford University

Program Scope

Extreme environments broaden the arena in which to search for materials with desirable properties. Emergent phenomena observed in strongly correlated electron systems (e.g., colossal magnetoresistance (CMR) and superconductivity) may play a crucial role in future energy applications and next-generation electronic and spintronic devices. Understanding and harnessing these phenomena remains a challenge because of the complex coupling between lattice, orbital, electronic, and spin degrees of freedom. High pressure has proven to be an effective variable for decoupling these interactions and revealing the mechanisms behind the macroscopic properties of these compounds. Our program seeks to use both static and dynamic compression methods coupled with a suite of in-situ characterization tools to improve our understanding the changes wrought by high pressure which in turn illuminates the underlying physics and chemistry. Such insights are critical for controlling desired properties, which in turn enables the design of dramatically improved materials.

Recent Progress

Ultrafast optical and X-ray pulses are powerful tools to study various dynamic processes. We have been 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 (Hsieh *et al., APL* 2013), and also working to develop THz experiments in a diamond anvil cell (DAC). We are also performing high-pressure ultrafast pump-probe differential reflectivity measurements with the hope of helping understand phase transition physics in other strongly correlated systems and discovered a novel, transient metallic state in VO_2 (Hsieh *et al., APL* 2014).

My group has been involved in a number of experiments at the Matter at Extreme Conditions (MEC) end station of LCLS. We have investigated the kinetics of laser-shock induced phase transitions in metals SiO_2 (Gleason *et al*, in review), and we also have preliminary results from MEC on laser-shocked ice and water. This temporal approach has yielded new information on the structural dynamics of plastic yielding and nucleation and growth during phase transitions with ns resolution.

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 systems out of equilibrium. We continue to look at a wide range of

strongly correlated systems including mixed valence compounds (Wang *et al., PRB* 2013), high Tc superconductors like Hg cuprates (Wang *et al, PRB* 2014), binary chalcogenides (Zhao *et al, PRB* 2014; Zhao *et al, PRB* 2013), post-spinel manganese and cobalt oxides (Hirai *et al, PRB* 2013; Hirai *et al., APL* 2013a), and more exotic materials like the ferromagnetic Kondo lattice system CeRuPO (Hirai *et al., APL* 2013b). We have also studied the high pressure behavior of nanostructured Si for use as high capacity anode materials (Zeng *et al., J. Power Sources* 2013). For all of these studies we are working closely with various theory groups to interpret our high pressure synchrotron x-ray results.

My group has also been continuing to collaborate with researchers at SLAC and APS to develop high pressure nanoscale x-ray computed tomography (nanoXCT). Using this powerful, in-situ 3D imaging tool, we have also demonstrated the potential for nanoXCT to determine the equation of state of amorphous phases (Lin *et al., APL* 2013; Zeng *et al, PRL* 2014) with an accuracy rivaling XRD.

Future Plans

We plan to continue our work on ultrafast optical and x-ray measurements coupled with static and dynamic compression techniques on strongly correlated systems and on technique development related to nanoXCT. For all of these studies we will work closely with various theory groups to interpret our high pressure experimental results. In addition to the large number of synchrotron x-ray projects, we have submitted proposals to MEC to look at laser-shocked H_2O at high pressure conditions as well as at the dynamic strength of materials.

Publications

Bandgap closure and reopening in $CsAuI_3$ at high pressure, S. Wang, M. Baldini, M. Shapiro, S. Riggs, A. F. Kemper, Z. Zhao, Z. Liu, T. P. Devereaux, T. Geballe, I. R. Fisher, W. L. Mao, *Phys. Rev. B* **89**, 245109 (2014).

Universal Fractional Non-Cubic Power Law for Density of Metallic Glasses, Q. Zeng, Y. Kono, Y. Lin, Z. Zeng, J. Wang, S. V. Sinogeikin, C. Y. Park, Y. Meng, W. Yang, H.-k. Mao, and W. L. Mao, *Phys. Rev. Lett.* **112**, 185502 (2014).

Tuning the crystal structure and electronic states of Ag_2Se: Structural transitions and metallization under pressure, Z. Zhao, S. Wang, A. Oganov, P. Chen, Z. Liu, W. L. Mao, *Phys. Rev. B* **89**, 180102(R) (2014).

Pressure induced second-order structural and electronic transition in $Sr_3Ir_2O_7$, Z. Zhao, S. Wang, T. F. Qi, Q. S. Zeng, S. Hirai, P. P. Kong, L. Li, C. Park, S. J. Yuan, C. Q. Jin, G. Cao, W. L. Mao, *J. Phys.: Condens. Matter* **26**, 215402 (2014).

High pressure Raman and X-ray diffraction study of [121] Tetramantane, F. Yang, Y. Lin, J. E. P. Dahl, R. M. K. Carlson, W. L. Mao, *J. Phys. Chem. C*, doi:10.1021/jp500431 (2014).

Novel photo-induced monoclinic metallic VO_2 under high pressure, W. P. Hsieh, M. Trigo, D. A. Reis, G. A. Artioli, L. Malavasi, and W. L. Mao, *Appl. Phys. Lett*. **104**, 021917 (2014).

Strain derivatives of Tc in $HgBa_2CuO_{4+\delta}$: The CuO_2 plane alone is not enough, S. Wang, J. Zhang, J. Yan, X-J Chen, V. V. Struzhkin, W. Tabis, N. Barisic, M. Chan, C. Dorow, X. Zhao, M. Greven, W. L. Mao, T. Geballe, *Phys. Rev. B* **89**, 024515 (2014).

Densification process of GeO_2 glass: High pressure transmission x-ray microscopy study, Y. Lin, Q. S. Zeng, W. Yang, and W. L. Mao, *Appl. Phys. Lett.* **103**, 261909 (2013).

High-pressure Raman spectroscopy of phase change materials, W. P. Hsieh, P. Zalden, M. Wuttig, A. M. Lindenberg, and W. L. Mao, *Appl. Phys. Lett.* **103**, 191908 (2013).

Pressure induced structural transitions and metallization in Ag_2Te, Z. Zhao, S. Wang, H. Zhang, and W. L. Mao, *Phys. Rev. B* **88,** 024120 (2013).

The effect of composition on pressure-induced devitrification in metallic glasses, Q.S. Zeng, W. L. Mao, H. Sheng, Z. Zeng, Q. Hu, Y. Meng, H. Lou, F. Peng, W. Yang, S. V. Sinogeikin and J. Z. Jiang, *Appl. Phys. Lett.* **102**, 171905 (2013).

Pressure-induced tetragonal-orthorhombic phase transitions in CeRuPO, S. Hirai, Y. Kamihara, A. Wakatsuki, M. Matoba, and W. L. Mao, *Appl. Phys. Lett.* **102**, 051917 (2013b).

Novel pressure-induced transitions in Co_3O_4, S. Hirai and W. L. Mao, *Appl. Phys. Lett.* **102**, 041912 (2013a).

Giant displacement at a magnetic transition in metastable Mn_3O_4, S. Hirai, A. M. dos Santos, M. Shapiro, J. J. Molaison, N. Pradhan, M. Guthrie, C. A. Tulk, I. R. Fisher, W. L. Mao, *Phys. Rev. B* **87**, 014417 (2013).

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures, DE-SC-0012375

Ultrafast infrared nano-spectroscopy and nano-imaging of unconventional superconductivity in high-Tc systems " DE-SC0012592

Surface and Interface Physics of Correlated Electron Systems, DE-ER-046169

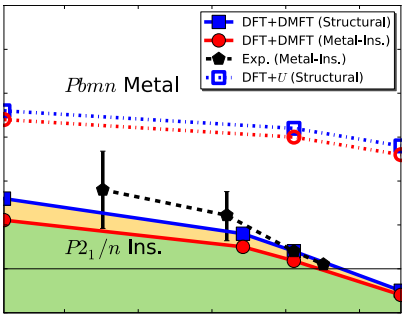
Andrew Millis, Department of Physics, Columbia University

Program Scope:

Dynamic processes in materials underpin many facets of energy science such as efficient energy conversion and transport. This project supports an interdisciplinary team including experts in new generations of ultrafast/ultrabright light sources in terahertz, infrared and hard X-ray frequencies, nano-diffractio and ultrafast infrared near-field nanospectroscopy to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales as well as theory. Fundamental research goals are to: (a) Establish materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions.

Recent Progress

The interesting electronic phenomena in transition metal oxides are often described using intuitively appealing terms such as ``charge order'', and modeled with simple models such as the Hubbard model, the real physics is typically richer and involves lattice degrees of freedom in an essential way. The Millis DOE research program develops the methods needed to address this physics and applying them to new situations. Progress relevant to the current (ultrafast) project includes (numbers refer to DOE supported publications): determination of the origin of the metal-insulator transition in rare earth nickelates [1] , elucidation of the conditions for magnetism in oxide superlattices [4] , establishment of the fundamental importance of the double counting correction and construction of a realistic theory of the metal-insulator transition in oxides [2,9], studies of the charge transfer in oxide superlattices [3], demonstration of how surface termination controls the phase behavior of oxide superlattices [5] and implemention of realistic total energy calculations in DFT+DMFT [10], showing quantitative

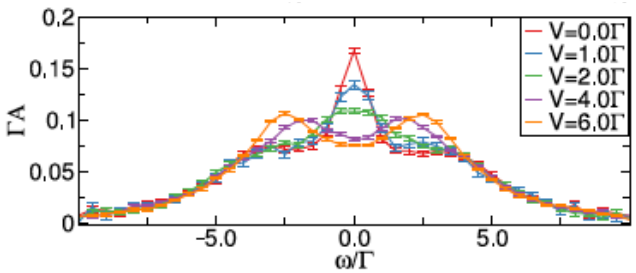


Calculated [10] structural and metal-insulator phase diagram of rare earth nickelates as function of rare earth ion (expressed as tolerance factor) and unit cell volume ;compared to data (black symbols) and DFT+U (dashed lines).

agreement with the structural and metal-insulator phase diagram of the rare earth nickelates

Future Plans

A key open issue in theory of ultrafast experiments is the development of methods that provide access to the long-time behavior of pumped correlated systems. By combining Keldysh-contous diagrammatic Monte Carlo [A], bold-line resummations [B] and memory function methods we are now becoming able to compute Greens functions [C] enabling us to fully solve the equations of nonequilibrium dynamical mean field theory [D] beyond the short time [A,B] or perturbative [E} limits. The power of our methods is demonstrated by our ability to resolve the current-induced peak splitting in the nonequilibrium Anderson model (see Fig.). We plan to build on these methodological developments to implement a full nonequilibrium dynamical mean field theory of pumped correlated systems. Simulataneously,and in close communication with experimental groups, we will use phenomenologoical and time-dependent hartree methods building on the real-materials work described above, to obtain a phenomenological description of phonon-pumping experiments for controlling charge and orbital order in correlated materials.



Calculated [D] electron spectral function (many-body density of states as function of frequency for voltage-biassed Anderson model demonstrativing current-induced splitting of central peak.

References

[A] "Diagrammatic Monte Carlo simulation of non-equilibrium systems", Philipp Werner, Takashi Oka, Andrew J. Millis, Phys. Rev. **B79**, 035320 (2009).

[B] ``Bold-line diagrammatic Monte Carlo method: General formulation and application to expansion around the noncrossing approximation'', Emanuel Gull, David R. Reichman, and Andrew J. Millis, Phys. Rev. **B82**, 075109 (2010).

[C] ``Green's functions from real-time bold-line Monte Carlo", Guy Cohen, David R. Reichman, Andrew J. Millis, Emanuel GullPhys. Rev. **B89,**115139 (2014).

[D] Nonequilibrium dynamical mean-field theory and its applications'', H. Aoki, N. Tsuji, M. Eckstein, M. Kollar, T. Oka, P. Werner, Rev. Mod. Phys. **86**, 779 (2014)

[E] `` Long-lived nonequilibrium states in the Hubbard model with an electric field'',Alexander V. Joura, J. K. Freericks, Alexander I. Lichtenstein , arXiv:1401.4089 (2014)

Recent Publications supported by DOE BES

[1] *Site-Selective Mott Transition in Rare-Earth-Element Nickelates*, Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, Phys. Rev. Lett. **109**, 156402 (2012).

[2] *Covalency, double-counting, and the metal-insulator phase diagram in transition metal oxides*, Xin Wang, M. J. Han, Luca de' Medici, Hyowon Park, C. A. Marianetti and Andrew J. Millis, Physical Review **B86**, 195136 (2012).

[3] Engineering Correlation Effects via Artificially Designed Oxide Superlattices,Hanghui Chen, Andrew J. Millis, and Chris A. Marianetti, Phys. Rev. Lett. **111**, 116403 (2013).

[4] Designing ferromagnetism in vanadium oxide based superlattices, H. T. Dang and A. J. Millis, Phys. Rev. **B87** 184434 (2013).

[5] *Theory of the magnetic and metal-insulator transitions in RNiO 3 bulk and layered structures*, Bayo Lau and A. J. Millis, Phys. Rev. Lett. Phys. Rev. Lett. **110**, 126404 (2013).

[6] *Theory of ferromagnetism in vanadium-oxide based perovskites*, Hung T. Dang and Andrew J. Millis, Phys. Rev. **B87**, 155127 (2013).

[7] Charge density distribution and optical response of the $LaAlO_3/SrTiO_3$ interface'', Seyoung Park and A. J. Millis, Phys. Rev. **B87** 205145 (2013).

[8] Quantum confinement in Oxide Quantum Wells (invited review), S. Stemmer and A. J. Millis, MRS Bulletin **38** 1032-39 (2013).

[9] *Covalency and the metal-insulator transition in titanate and vanadate perovskites*, Hung T. Dang, Andrew J. Millis and Chris A. Marianetti, Phys. Rev. **B89** 161113 (2014).

[10] Total energy calculations using DFT+DMFT: computing the pressure phase diagram of the rare earth nickelates, Hyowon Park, Andrew J. Millis, Chris A. Marianetti, Phys. Rev. **B89**, 245133 (2014).

[11] *Failure of DFT-based computations for a stepped-substrate-supported correlated Co wire*, Nader Zaki, Hyowon Park, Richard M. Osgood, Andrew J. Millis, and Chris A. Marianetti, Phys. Rev. **B89** 205472 (2014).

[12] *Visualization of Electron Nematicity and Unidirectional Antiferroic Fluctuations at High Temperatures in NaFeAs*, E. P. Rosenthal, E. F. Andrade, C. J. Arguello, R. M. Fernandes, L. Y. Xing, X. C. Wang, C. Q. Jin, A. J. Millis, A. N. Pasupathy, Nature Physics **10** 228 (2014).

[13] *Emergent properties hidden in plane view: Strong electronic correlations at oxide interfaces*, Jak Chakhalian, John W. Freeland, A. J. Millis, C. Panagopolous and James M. Rondinelli, Rev. Mod Phys. (Colloquium) **86** 1189 (2014).

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

Margaret Murnane, Henry Kapteyn and Thomas Silva

University of Colorado Boulder and NIST

Program Scope

A detailed understanding of nanoscale magnetization dynamics for 3d metals has become critical for spintronics-based memories as a low-power, non-volatile, ultrafast replacement for DRAM and SRAM in ubiquitous computing applications. However, we only have a crude understanding of magnetization dynamics of the transition metals because a comprehensive, self-consistent, microscopic model for metals that rigorously includes the spin, electronic, photonic and phonon-degrees of freedom and their interactions does not yet exist. While the fundamental length- and time-scales for magnetic phenomena are nanometers (exchange length) and femtoseconds (exchange splitting), tools that enable the exploration of dynamics at these scales have only recently become available. Our joint JILA-NIST program is exploring the fastest and smallest dynamics in magnetic materials by use of high harmonic generation (HHG) sources.

Recent Progress

Using HHG sources, we made several advances in uncovering new understanding of spin dynamics on the fastest timescales.[1-9] First, we uncovered evidence of quasi-ballistic, laser-generated spin-currents in magnetic multilayers that are generated during laser-driven ultrafast demagnetization.[3-5] Such pure spin-currents are of great interest for technological applications, where the information is encoded in the form of angular momentum rather than charge. By exciting a magnetic multilayer (Fe/Ru/Ni) with a ultrafast laser pulse, and then probing the magnetization of individual Ni and Fe layers using EUV tuned to the magnetically sensitive 3p-3d transitions, we found that optically-induced demagnetization of Ni causes the buried Fe layer to undergo a surprising transient *enhancement* of magnetization. We explain this as the result of an intense, majority spin-current that propagates from the Ni top-layer into the buried Fe layer at near-ballistic velocities. The data are consistent with the notion that the exchange-splitting of the Fe bands is enhanced by longitudinal spin-currents, thereby stabilizing the increased magnetization against fluctuations. *This suggests that the far-from-equilibrium spin dynamics can result in novel magnetic states that cannot be accessed by conventional means*.[1-5,8,9]

In a related vein, we solved a controversy regarding the microscopic mechanisms contributing to ultrafast demagnetization.[5] Two theoretical mechanisms had been proposed to explain ultrafast laser-induced magnetization dynamics: non-local quasi-ballistic spin-currents and local spin-flip scattering. Spin-currents would remove spin angular momentum from a given layer, whereas local spin-flip scattering results in a direct transfer of angular momentum between

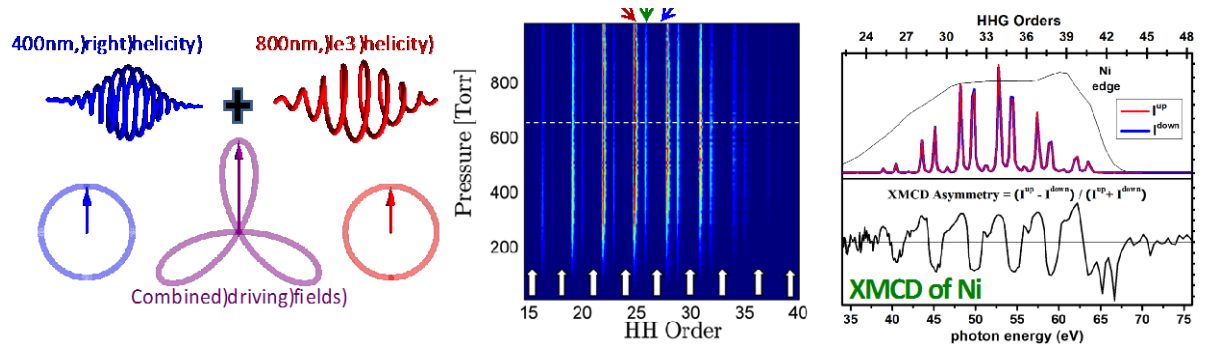


Fig. 1 First demonstration of bright circularly-polarized HHG. (left) The combined field of counter rotating red and blue lasers is a three-fold cloverleaf shape (purple). This gives rise to circularly polarized HHG where orders $q=3m+1$ rotate right, while $q=3m-1$ rotate left. (center) HHG from Ne where each successive order has opposite circular polarization and every 3rd harmonic is missing. (right) Transmission- and XMCD-spectra for Ni.

spins and lattice. Our data conclusively showed that *both* spin-currents and spin-flip scattering contribute with similar efficiency to ultrafast demagnetization in these multilayers.

Finally, in work in collaboration with Oren Cohen's group at Technion, we demonstrated the first bright, phase-matched, extreme UV circularly-polarized HHG and used this new light source for magnetic circular dichroism (MCD) measurements at the *M*-shell absorption edges of Ni (see Fig. 1). For decades it was assumed that HHG from atoms was brightest when both the driving laser and HHG fields were linearly polarized. While the use of passive optical components can convert from linear- to circular-polarization, these are far too inefficient to be practical. Using combined blue and red driving lasers with opposite polarity, we showed that phase matching of circularly-polarized HHG is unique and robust, producing a photon flux comparable to the linearly polarized high harmonic sources that we have successfully used for ultrafast, element-selective, magneto-optic experiments.[6] This work thus represents a critical advance that makes possible element-specific imaging and spectroscopy of multiple elements simultaneously in magnetic and chiral media with high spatial and temporal resolution, using tabletop setups. To date this capability was available only at large-scale X-ray facilities.

Future Plans

We are exploring how the electronic configuration is modified in laser-induced demagnetization on fs timescales.[8] In particular, there is strong disagreement in the field as to whether electron-electron scattering mediates the spin-flip process during ultrafast demagnetization, or whether only spin-phonon scattering dominates. We are also studying the correlation of the charge- and spin-dynamics after ultrafast laser transient, non-equilibrium, heating of a magnetic material. We are investigating magnetization dynamics in a variety of ferro- and anti-ferromagnetic multilayer systems and, in particular, coupled charge-spin-phonon transport. We also started collaborations with Frances Hellman, Peter Fischer, Jeff Kortright and Hermann Durr from LBNL and SLAC.

References

See publication list below.

Publications

1. C. La-O-Vorakiat, E. Turgut, C.A. Teale, HC. Kapteyn, M. Murnane, Stefan Mathias, M. Aeschlimann, C.M. Schneider, J.M. Shaw, H. Nembach, T.J. Silva, "Ultrafast Demagnetization Measurements using Extreme Ultraviolet Light: Comparison of Electronic and Magnetic Contributions", Physical Review X **2**, 011005 (2012).
   ** See also associated Physics Viewpoint Highlight "Spin Sensitive Optics" by Jean-Yves Bigot in Physics **5**, 11 (2012).*

2. S. Mathias, C. La-O-Vorakiat, P. Grychtol, J.M. Shaw, R. Adam, H.T. Nembach, M. Siemens, S. Eich, C.M. Schneider, T.J. Silva, M. Aeschlimann, H.C. Kapteyn, M.M. Murnane, "Probing the timescale of the exchange interaction in a ferromagnetic alloy", PNAS **109**, 4792 (2012).
   ** See also associated highlights in http://www.physicstoday.org/ titled "Fast times in ferromagnetic alloys".*
   ** Physics Focus: Analyse auf dem Tisch by U. Bovensiepen in Physik Journal **11**, 26 (2012).*

3. D. Rudolf, C. La-O-Vorakiat, M. Battiato, R. Adam, J.M. Shaw, E. Turgut, P. Maldonado, S. Mathias, P. Grychtol, H.T. Nembach, T.J. Silva, M. Aeschlimann, H.C. Kapteyn, M.M. Murnane, C.M. Schneider, P.M. Oppeneer, "Ultrafast magnetization enhancement in metallic multilayers driven by superdiffusive spin current", Nature Communications **3**, 1037 (2012).

4. Stefan Mathias, Chan La-o-vorakiat, Justin M. Shaw, Emrah Turgut, Patrik Grychtol, Roman Adam, Dennis Rudolf, Hans T. Nembach, Thomas J. Silva, Martin Aeschlimann, Claus M. Schneider, Henry C. Kapteyn, Margaret M. Murnane, "Ultrafast element-specific magnetization dynamics of complex magnetic materials on a table-top", invited review paper, Journal of Electron Spectroscopy and Related Phenomena **189**, 164 (2013). DOI: 10.1016/j.elspec.2012.11.013

5. E. Turgut, C. La-o-vorakiat, J. Shaw, P. Grychtol, H. Nembach, D. Rudolf, R. Adam, S. Mathias, M. Aeschlimann, C. Schneider, T.J. Silva, H.C. Kapteyn, M.M. Murnane, "Controlling the Competition between Spin Transport and Optically Induced Demagnetization in Magnetic Multilayers," Physical Review Letters **110**, 197201 (2013).

6. Ofer Kfir, Patrik Grychtol, Emrah Turgut, Ronny Knut Dmitriy Zusin, Dimitar Popmintchev, Tenio Popmintchev, Hans Nembach, Justin M. Shaw, Avner Fleicher, Henry Kapteyn, Margaret Murnane and Oren Cohen, "Generation of bright circularly-polarized extreme ultraviolet high harmonics for magnetic circular dichroism spectroscopy", *in press*, Nature Photonics (2014). arXiv:1401.4101

7. D. Nardi, E. Turgut, K. Hoogeboom-Pot, J. Shaw, H. Nembach, T.J. Silva, H.C. Kapteyn, M.M. Murnane, "Probing Materials Properties with sub-Angstrom Precision in Magnetic Multilayers," in preparation (2014).

8. Emrah Turgut, Patrik Grychtol, Justin Shaw, Ronny Knut, Dmitry Zusin, Hans Nembach, Stefan Mathias, Martin Aeschlimann, Thomas J. Silva, Margaret M. Murnane and Henry C. Kapteyn, “Access to the electronic structure of a demagnetizing ferromagnet”, in preparation (2014).

9. Emrah Turgut, Mingsu Si, Patrik Grychtol, Justin Shaw, Ronny Knut, Dmitry Zusin, Hans Nembach, Stefan Mathias, Martin Aeschlimann, Thomas J. Silva, Guo P. Zhang, Henry C. Kapteyn, Margaret M. Murnane, “Charge and spin dynamics during ultrafast demagnetization in Co”, in preparation (2014).

Low coordination of extreme oxide melts.

John B. Parise & Lawrie B. Skinner

Mineral Physics Inst. Stony Brook University, Stony Brook, NY 11794, USA.

Program Scope

The Current program is to investigate liquid, glassy and disordered crystalline materials at extreme conditions, high temperatures and/or pressures (T~3000K P~GPa), and metastable conditions (supercooled or supersaturated).

Recent Progress

This year we have produced high impact publications in Physical Review letters, PNAS, and Nature communications, all concerning oxide melt structure. Understanding and controlling oxide melts is important to natural phenomena such as magmas, and technologies where materials are processed *via* the liquid phase. High temperature ceramics, glass displays and lenses, laser garnets, and the fiber optic cables which connect countries, are a few technologies which stand to benefit from the improved knowledge provided.

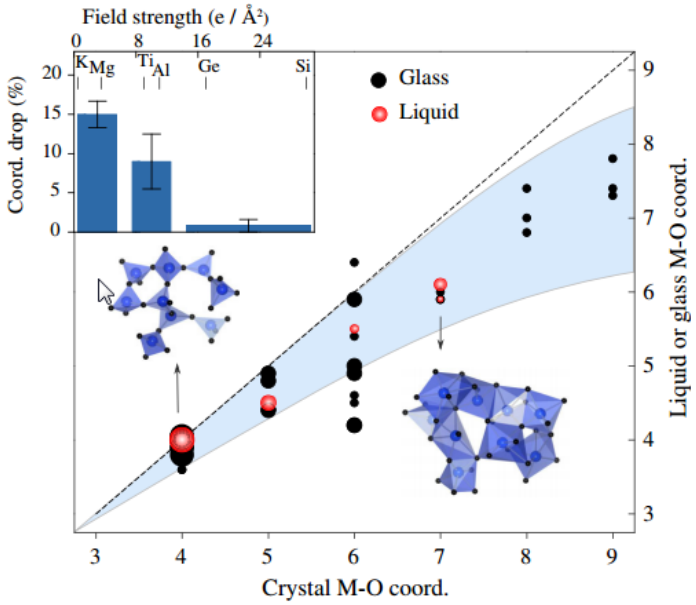


Fig. 1. The M-O coordination of the liquid (red) or glass (black) compared to their crystalline phases (M=Al, Si, Te, Ge, Ga, Ti, La ,Y, Mg, Ca ,Sr Ba, Pb, Na, K). Inset is the coordination drop divided into three groups of differing cation field strength.

Our PRL publication reveals a general trend that oxide melts and glasses have lower coordination than their crystalline counterparts [5]. This coordination drop (Fig. 1.) has important consequences for the behavior and properties of these melts. Melts with low cation field strength, such as ZrO_2, and UO_2 are found to have a particularly large coordination drop on melting. Highlights discussing our work can be found here [1-3].

Our PNAS paper provides a Pressure-Temperature map for predicting the density and pressure where coordination increase occurs in oxide glasses and melts [6]. Highlighted here [4].

Our Nature communications paper provides a structural explanation for the viscosity minimum in silicates melts [7]. This unusual behavior, where silicates initially become less viscous (thin) under pressure, is relevant to processes within Earth's mantle.

We also collaborated on a recent Nature paper studying liquid water at extremely low temperatures (-40 ºC) [8]. This is relevant to the debates about the amorphous and liquid phase transitions in water at these conditions, relevant to conditions in clouds and the behavior of water in interstellar space, which is expected to be amorphous.

Future Plans

We are currently working on high impact work where we measured the structure of molten UO_2 for the first time (this draft is currently under review for publication in Science). UO_2 is important technologically and to anthropological climate change since it is the fuel used in most nuclear power reactors, yet relatively little is known about the melt due to the very high temperatures (3200 K) and radiation controls required. Alongside this we have collected data on iron oxides and iron silicate melts, combined with control of the oxidation state. Understanding these melts is relvant to the deep Earth, steel production and slag waste.

In the next 3 months we will perform studies on water under negative pressure (under tension). This work will improve our understanding of water at these conditions. In nature, these negative pressure conditions occur in plants such as tall trees as the liquid drawn up the xylem, and inside minerals such as quartz, where fixed-volume water pockets are formed at high temperatures. Also control of cavitation, which occurs when liquids are momentarily stretched past their tensile limit, is critical to the design of turbines, propellers, and coolant lines in combustion engines.

Longer term we aim to extend our studies of high temperature, high pressure, melts beyond simple oxides, into carbides, nitrides and oxynitrides, New oxynitride glasses could be made with continuously tunable refractive indices between there oxide and nitride values. While carbides and nitrides such as TiN, and B_4C are used as cutting tools, radiation shielding, and semiconductor devices. Hence turbine engines, glass lenses, and the fiber optic cables, are just a few technologies that would directly benefit from improved knowledge of these materials around their melting point.

Many of the measurements we will perform are difficult, with complex sample environments that can potentially compromise data. We are working closely with the XPD beamline team at NSLS-II to apply modulation Enhanced Diffraction (MED) to our systems. As part of a BNL LDRD project we are applying MED, which requires a periodic perturbation applied in real time and observation of systems' diffraction response, we are applying the technique to gas separation materials [16-19]. We will expand these measurements to truly challenging H-isotope separations and melt studies as well.

References

[1] Argonne Highlight (http://www.anl.gov/articles/neutrons-and-x-rays-reveal-structure-high-temperature-liquid-metal-oxides).

[2] Oakridge highlight (http://www.ornl.gov/ornl/news/features/2014/neutrons-and-x-rays-reveal-structure-of-high-temperature-liquid-metal-oxides)

[3] ACerS highlight (http://americanceramicsociety.org/bulletin/2014/aug14/#/16/)

[4] Phys.org highlight (http://phys.org/news/2014-07-analysis-oxide-glass-formation-planetary.html)

Publications 2013-2014

[5] LB Skinner, CJ Benmore, JKR Weber, J Du, J Neuefeind, SK Tumber JB Parise. *Low cation coordination in oxide melts.* Phys. Rev. Lett. 112, 157801 (2014).

[6] Y Wang, T Sakamaki, LB Skinner *et al. Atomistic insight into viscosity and density of silicate melts under pressure.* Nature Communications **5**, 3241 (2014).

[7] A Zeidler, PS Salmon, LB Skinner. *Packing and the structural transformations in liquid and amorphous oxides from ambient to extreme conditions.* Proc. Nat. Acad. Sci. **111**, 10045 (2014).

[8] JA Sellberg *et al. Ultrafast X-ray probing of water structure below the homogeneous ice nucleation temperature.* Nature 510, 381-384 (2014).

[9] OLG Alderman, LB Skinner *et al. Structure of molten titanium dioxide.* Phys. Rev. B 90, 094204 (2014).

[10] P Kidkhunthod, LB Skinner *et al. Structure of Ba-Ti-Al-O glasses produced by aerodynamic levitation and laser heating.* Phys. Rev. B 90, 094206 (2014).

[11] JKR Weber, CJ Benmore, LB Skinner *et al. Measurements of liquid and glass structures using aerodynamic levitation and in-situ high energy x-ray and neutron scattering.* J. Non Cryst. Sol. 1**5**, 8566-8572 (2013).

[12] LB Skinner, CJ Benmore, JKR Weber, MC Wilding, SK Tumber *et al. A time resolved high energy x-ray diffraction study of cooling liquid SiO_2.* Phy. Chem. Chem. Phys. **15**, 8566-8572 (2013).

[13] LB Skinner, AC Barnes, PS Salmon, L Hennet, *et al. The structure of liquid alumina: a joint diffraction and modeling approach.* Phys. Rev. B **87**, 024201 (2013).

[14] Y Xiang, J Du , LB Skinner , CJ Benmore, AW Wren, DJ Boyd, *et al. Structure & diffusion of ZnO-SrO-CaO-Na_2O-SiO_2 bioactive glasses: A combined x-ray diffraction and molecular dynamics simulation study.* RSC Adv. **3**, 5966-5978 (2013).

[15] LB Skinner, C Huang, D Schlesinger, LGM Pettersson, A Nilsson, CJ Benmore. *Benchmark oxygen-oxygen pair-distribution function of ambient water from x-ray diffraction measurements with a wide Q-range.* J. Chem. Phys. **138**, 074506 (2013).

[16] AM Plonka, D Banerjee, WR Woerner, ZJ Zhang, J Li, JB Parise. *Effect of ligand geometry on selective gas-adsorption: the case of a microporous cadmium metal organic framework with a V-shaped linker*. Chem. Comm., **49**, 7055 (2013).

[17] D Banerjee, AM Plonka, SJ Kim, WQ Xu, JB Parise. *Synthesis, structural characterization and high pressure phase transitions of monolithium hydronium sulfate*. J Solid State Chem, **197**, 181 (2013).

[18] XY Chen, AM Plonka, D Banerjee, D, JB Parise, *Synthesis, Structures and Photoluminescence Properties of a Series of Alkaline Earth Metal-Based Coordination Networks Synthesized Using Thiophene-Based Linkers*. Cryst Growth Des, **13**, 326 (2013).

[19]. AM Plonka, D Banerjee, WR Woerner, ZJ Zhang, N Nijem, YJ Chabal, J Li, JB Parise, *Mechanism of Carbon Dioxide Adsorption in a Highly Selective Coordination Network Supported by Direct Structural Evidence*. Angew Chem-Int Edit, **52**, 1692 (2013).

Atomic Structure of Nanoalloy Catalysts in As-Synthesized and Active State

V. Petkov, Dept. Physics, Central Michigan University, Mt. Pleasant, MI 48859
C.-J. Zhong, Dept. Chemistry, SUNY at Binghamton, Binghamton, NY 13902

Program Scope

The project aims at ***i)*** synthesizing a series of technologically important binary and ternary nanoalloy catalysts, ***ii)*** determining their atomic-scale structure and how it evolves under realistic reaction conditions by high-energy x-ray diffraction (XRD), including element specific resonant XRD, coupled to atomic pair distribution functions (PDF)s analysis and 3D structure modeling, ***ii)*** revealing synthesis – atomic structure – catalytic properties relationships in the nanoalloys and ***iii)*** using the unique knowledge obtained as a feedback loop for streamlining their synthesis thus drafting a roadmap to nanoalloy catalysts by rational design. Work on the project will push forward high-energy synchrotron XRD and atomic PDFs analysis, in particular resonant XRD, provide new hardware for in-situ high-energy XRD studies of catalytic reactions and perfect 3D computer modeling of nanometer-size materials, such as nanoalloy catalysts, of DOE interest.

Recent Progress

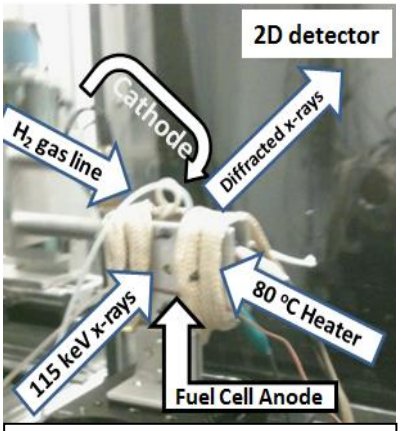


Figure 1. PEMFC cell as used at beamline 11-ID-C, Argonne.

In the last two years we carried out a series of ex- [1,3,5,6,8,11] and in-situ [4,7,12] high-energy XRD experiments on 3-7 nm NM-TM alloy catalysts, where NM = Au, Pt, Ir, Rh, Pd, Ag and TM= Fe, Co, Ni, Cu, V, Sn. In situ experiments involved mostly catalytic reactions under reactive gas (H_2, O_2 and CO) atmosphere. Atomic PDFs analysis and 3D structure modeling guided by the experimental data shed much-needed extra light on the gas-phase reaction mechanisms at atomic level opening up new avenues for optimizing nanoalloy catalysts with respect to their activity, selectivity and stability. Recently we extended our in-situ studies toward Proton Exchange Membrane Fuel Cell (PEMFC) applications. We designed a fully functional PEMF reaction cell (see Fig. 1). The cell was used to study the structural evolution of $Pt_{45}Ni_{33}Co_{22}$, $Pt_{62}Co_{38}$ and $Pd_{26}Ni_{74}$ PEMFC cathode catalysts upon prolonged (~12 h), heavy duty usage (~3000 cycles) of the cell. Experimental PDF data (see Fig. 2) indicated that nanoalloy atomic structure changes significantly with PEMFC usage time. Structure changes were found to go hand in hand with changes in the nanoalloy chemical composition, due to "leaching" of TM species, and nanoalloy activity for Oxygen Reduction Reaction (ORR) taking place at the PEMFC cathode. Findings hint a strategy for optimizing PEMFC cathode catalysts and so improving PEMFC viability.

Also, in the last two years we put a lot of effort into developing [2,10] computational procedures for generating realistic 3D models of nanoalloy catalysts, in particular into the so-called hybrid reverse Monte Carlo (RMC) simulations. RMC-based models proved [3,4,5,6,8,9, 12] very useful in assessing how structural characteristics of nanoalloys, in particular those of nanoalloy surface, relate to their catalytic properties.

Furthermore, we kept demonstrating the great potential of resonant high-energy XRD. A study on Au-Cu and Au-Ag nanoalloy catalysts [9] revealed that Cu and Ag atoms change in size

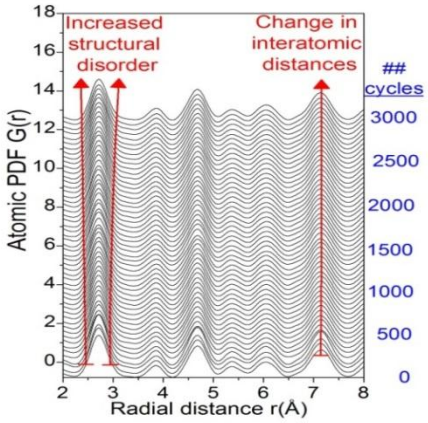


Figure 2. Experimental PDFs for $Pt_{45}Ni_{33}Co_{22}$ nanoalloy catalyst used at the cathode of PEMFC cell of Fig. 1. Vertical lines (in red) emphasize increased structural disorder and change in interatomic distances with PEMFC usage time given in terms of number of cycles (in blue).

substantially when alloyed with Au atoms at the nanoscale and so do Cu- and Ag-Au atom bond lengths and strengths. As a result, oxygen inactive Au and oxygen very active Cu and Ag species form nanoalloys exhibiting greatly enhanced activity for low temperature CO oxidation.

Very recently we conducted resonant high-energy XRD studies on ~ 5 nm in size Ru core-Pt shell type catalysts explored for energy conversion applications based on electrolytic oxidation of ethanol and methanol. Special attention was paid to characterizing Ru core-Pt shell interface in terms of structural coherence and inter-diffusion of Pt and Ru species since those had been found to have a dramatic effect on the rate of ethanol and methanol oxidation reactions. 3D models based on differential and partial atomic PDFs extracted from the resonant XRD data proved very useful in quantifying the structural and chemical "uniformity" of Ru core-Pt shell interface (see Fig. 3) opening the door to using resonant high-energy XRD for characterizing "buried" interfaces in nanomaterials.

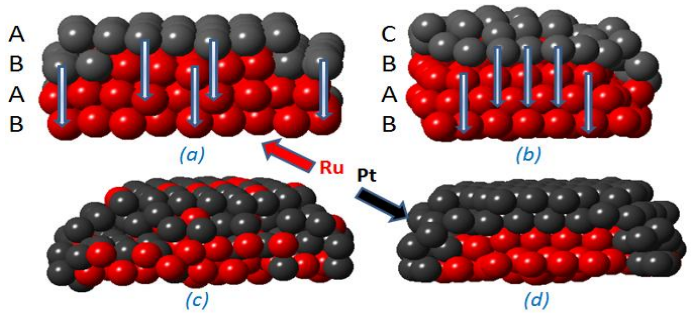


Figure 3. Core-shell interface in RMC models of ~ 5 nm in size Ru core-Pt shell catalysts. First neighbor Ru and Pt layers can be packed hcp- (a) or fcc-like (b) rendering Ru core and Pt shell structurally incoherent and coherent, respectively. Note bulk Ru is hcp- and bulk Pt - fcc-type metal. Also, neighboring Ru and Pt atoms may inter-diffuse forming "nanoalloy-type" interface (c) or (d) segregate.

Future Plans

We are planning on studying a variety of so far largely unexplored binary and ternary nanoalloys such as, for example, Pd-(Cu/Ni), PtCo(V/Fe), PtIrSn, and others, aiming at reducing the amount of scarce Pt as much as possible. Also, we are planning on studying the effect of nanoalloy support (e.g. Carbon vs TiO_2 vs SiO_2 vs Al_2O_3 vs CeO_2) on the atomic structure of usually supported nanoalloys and, hence, on their catalytic properties. Both ex-situ and in-situ high-energy XRD experiments will be carried out. The latter will concentrate on electrolytic reactions. For the purpose we will be using designed by us PEMF (H_2-based) reaction cell. Also, we are planning on designing and testing a reaction cell for in-situ studies of nanoalloy catalysts for direct ethanol oxidation (DEF). Yet nanoalloy catalysts for gas-phase reactions, mostly involving CO oxidation, will be subjected to in-situ studies as well. For the purpose we will be using the gas-phase reaction cell available at the beamline 11-ID-B, Argonne. The increased complexity of envisioned nanoalloys will require experimental PDF data with increased element specificity. For the purpose we applied for and have been given beamtime for resonant high-energy XRD experiments at Sectors 1 and 6, Argonne. Instrumentation at the former will allow us probe K edges of Au, Pt and Ir while that at the latter – K edges of Rh, Pd, Ag and Sn. We will continue upgrading our software for hybrid RMC.

Publications (last two years) of work supported by DOE-BES Grant DE-SC0006877:

[1] R. Loukrakpam, Q. Yuan, V. Petkov, L. Gan, S. Rudi, R. Yang, Y. Huang, S. R. Brankovic and P. Strasser "Efficient C–C bond splitting on Pt monolayer and sub-monolayer catalysts during ethanol electrooxidation: Pt layer strain and morphology effects" **16** *Phys. Chem. Chem. Phys.* (2014) 18866.

[2] V. Petkov, B. Prasai,Y. Ren, S. Shan, J. Luo, P. Joseph and Ch.-J. Zhong "Solving the nanostructure problem: exemplified on metallic alloy nanoparticles" **6** *Nanoscale* (2014) 10048.

[3] N. Erini, R. Loukrakpam, V. Petkov, E. A. Baranova, R.Yang, D. Teschner, Y. Huang, S. R. Brankovic, and P. Strasser "Ethanol Electro-Oxidation on Ternary Platinum−Rhodium-Tin Nanocatalysts: Insights in the Atomic 3D Structure of the Active Catalytic Phase" *ACS Catalysis* **4** (2014) 1859.

[4] S. Shan, V. Petkov, L.Yang ,J. Luo, H. Joseph, D. Mayzel, B. Prasai, L. Wang, M. Engelhard and Ch.-J. Zhong " Atomic-structural synergy for catalytic oxidation of CO over Pd-Ni nanoalloys" *J. Am. Chem. Soc.* **136** (2014) 7140. **(Editor's Choice/Journal Spotlight Story).**

[5] Xian-Yang Quek, Ivo A. W. Filot, Robert Pestman, Rutger A. van Santen,Valeri Petkov and Emiel J. M. Hensen "Correlating Fischer–Tropsch activity to Ru nanoparticle surface structure as probed by high-energy X-ray diffraction" *ChemComm*. **50** (2014) 6005.

[6] V. Petkov, Y. Ren, S. Shan, J. Luo and Ch. J. Zhong "A distinct atomic structure–catalytic activity relationship in 3–10 nm supported Au particles" *Nanoscale* **6** (2014) 532.

[7] S. Shan, V. Petkov, L.Yang, D. Mott, B.N. Wanjala, F. Cai, B. H. Chen, J. Luo and Ch.-J. Zhong "Oxophilicity and Structural Integrity in Maneuvering Surface Oxygenated Species on Nanoalloys for CO Oxidation" *ACS Catalysis* **13** (2013) 3075.

[8] R. Loukrakpam, Sh. Shan, V. Petkov, L.Yang, J. Luo and C. J. Zhong "Atomic Ordering Enhanced Electrocatalytic Activity of Nanoalloys for Oxygen Reduction Reaction" *J. Phys. Chem. C* **117** (2013) 20715.

[9] V. Petkov, S. Shastri, Sh. Shan, Ph. Joseph, J. Luo, C. J. Zhong, T. Nakamura, Y. Herbani and Sh. Sato "Resolving Atomic Ordering Differences in Group 11 Nanosized Metals and Binary Alloy Catalysts by Resonant High-Energy X‑ray Diffraction and Computer Simulations" *J. Phys. Chem. C* **117** (2013) 22131.

[10] O. Gereben and V. Petkov "Reverse Monte Carlo study of spherical sample under non-periodic boundary conditions: the structure of Ru nanoparticles based on x-ray diffraction data" *J. Phys.: Condens. Matter* **25** (2013) 454211 **(Journal Cover Story).**

[11] X. Tuaev, S. Rudi, V. Petkov, A. Hoell and P. Strasser “In Situ Study of Atomic Structure Transformations of Pt-Ni Nanoparticle Catalysts during Electrochemical Potential Cycling” *ACS Nano* **7** (2013) 5766.

[12] V. Petkov, S. Shan, P. Chupas, J. Yin, L. Yang, J.Luo and C.J. Zhong "Noble-transition metal nanoparticle breathing in a reactive gas atmosphere" *Nanoscale* **5** (2013) 7379.

Femtosecond Nano-Magnetism

Alex Reid, Joachim Stöhr, Hermann Dürr
SLAC National Accelerator Laboratory, Stanford University

Program Scope

Magnetism is virtually unexplored at its fundamental few-nm length and few-fs time scales as set by the exchange interaction since the spatial resolution of conventional fs optical [Kirilyuk2010] and VUV laser [Mathias2012] sources are limited by their respective wavelengths. Yet a deeper understanding of magnetism at this level is becoming essential as future magnetic recording aims at exactly this regime: Tbit densities switched at THz rates. We employ the unique x-ray capabilities at SLAC to access these sub-10 nm lengthscale on the complementary fs timescales. The next generation of magnetic data storage devices is thought to be heat assisted magnetic recording where the high magnetic anisotropy of recording media has to be overcome by a laser integrated into the read/write head. This technology is being implemented now. The generation after this could be all-optical switching if we can figure out now how it works. We propose to use the unique x-ray capabilities available at SLAC to study all-optical magnetic switching in novel metallic alloys and synthetic magnetic structures to develop a fundamental understanding of the ultrafast manipulation of the exchange coupling. This knowledge base will ultimately be used to tailor future generations of data storage devices.

Recent Progress

We have made fundamental progress in understanding the flow of angular momentum and energy in the all-optical switching process in GdFeCo. Using the fs time and nm spatial resolution of resonant x-ray scattering, we have been able to extract the signature of nanoscale angular momentum transfer between distinct chemical regions of the magnetic alloy. This study was the first to show the existence of chemical segregation within this metal alloy, and further highlight its importance to the light induced switching of magnetization. Figure 1 shows the measured local reversal of the Gd moments within the Gd-enriched regions 1 ps after excitation. This reversal is driven by a net spin current into these enriched regions. This first-of-its-kind study, points to new ways of engineering materials at a nanoscale level to add new dynamic functionality.

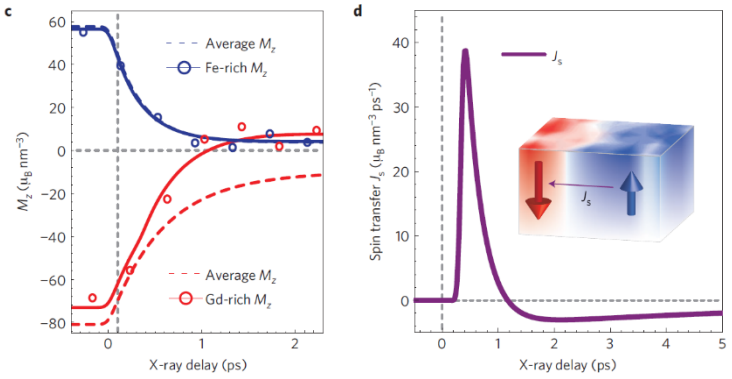


Fig. 1: (left) Element resolved dynamics of magnetization in GdFeCo follow laser excitation. (right) Time resolved spin transfer into Gd-enriched regions in GdFeCo. [Graves2013]

We have further studied the ability of light to switch nanoscale domains by using near-field optical confinement. By using plasmonic antennas deposited directly onto the magnet film we can selectively excite a nanoscale region of the film above the energy threshold for all-optical switching to occur. Our results demonstrate this as a proof of concept all-optical recording, and further show that the process is reversible. Analysis of the switching shows that in film properties are fundamental in determining the size of switched regions which cannot be explained by the near-field enhancement alone.

Future Plans

Our understanding of the important of spin and energy transfer on short length has been illuminated by the currently progress in our program. However, there is still not a full understanding of how spin-reversal nucleated at a nanoscale evolves into a switched domain. This is highlighted by the unexpected inhomogeneity in TbFeCo. We propose to try and determine how the first ps dynamics links to the final state we observed.

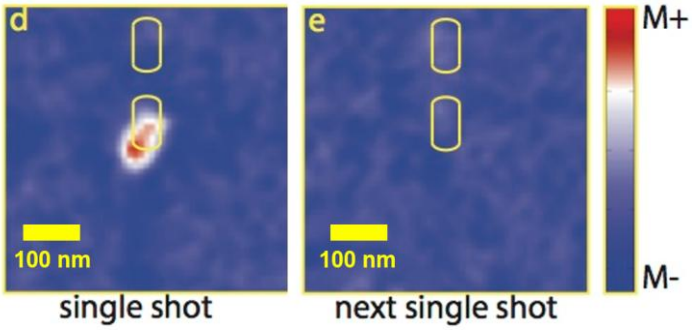


Fig. 2: Resonant x-ray holographic reconstructions of magnetization in TbFeCo. (left) A reversed magnetic domain of <1nm in size is written below the gold antenna structure, outlined in gold. (right) A further laser shot erases the magnetic domain. [Liu2014]

The recent discovery of all-optical switching in the technologically important system of granular FePt [Lambert2014] has raised questions about how the process can occur in ferromagnet. We are undertaking to explore this system and understand if the process is radically different.

References

[Kirilyuk2010] A.Kirilyuk, A. Kimel and Th. Rasing, "*Ultrafast optical manipulation of magnetic order", Rev. Mod. Phys.* **82**, 2731 (2010).

[Mathias2012] S. Mathias, *et al.*, "*Probing the timescale of the exchange interaction in a ferromagnetic alloy", PNAS* **109**, 4792 (2012).

[Graves2013] C. E. Graves, et al. Nanoscale spin reversal by non-local angular momentum transfer following ultrafast laser excitation in ferrimagnetic GdFeCo *Nature Materials*, **12,** 293 (2013).

[Liu2014] T. Liu, *et al. "Nanoscale confinement of all-optical switching in TbFeCo using plasmonic antennas"* http://arxiv.org/abs/1409.1280, submitted (2014).

[Lambert2014] C-H. Lambert, *et al.* All-optical control of ferromagnetic thin films and nanostructures. *Science* DOI:10.1126/science.1253493 (2014).

Publications (see submission by H. Dürr)

Nonequilibrium Phonon Dynamics (part of FWP: Time-resolved Soft X-ray Materials Science at the LCLS & ALS)

David Reis[1,2] and Mariano Trigo[1]
[1]SLAC National Accelerator Laboratory
[2]Stanford University

Program Scope

The goal of the nonequilibrum phonon dynamics subtask is to understand the complex dynamics of advanced materials at the level of atomic-scale interactions of phonons and other collective modes with photons, electrons, and other phonons. Under DOE support, we are developing and applying novel ultrafast optical and x-ray scattering techniques that are necessary to resolve these interactions both near and far from equilibrium on their natural time and length scales. In particular we make use of the bright femtosecond bursts of x rays from LCLS and SACLA to make high-resolution measurements of phonon dispersion and non-equilibrium phonon populations in photo-excited materials. This program is responsive to the grand challenge problems of "emergence", non-equilibrium dynamics, and to probe model systems for deep insights on materials for energy conversion, transport and efficiency.

Recent Progress

We have made substantial progress in using optical and x-ray scattering from non-equilibrium coherent and squeezed phonons for studying materials dynamics in several prototypical materials including VO2, Bi, Sb, and other materials (see publication list). Of particular relevance to the goals of this FWP, we have published the first results on our Fourier transform x-ray inelastic scattering (FT-IXS) method [Trigo et al., *Nat. Phys.* **9,** 790, 2013]. The experiments made use of the hard x-ray beamline at LCLS to achieve sub-meV resolution of collective modes in photoexcited germanium spanning a large portion of the Brillouin zone. In these experiments, an ultrafast light pulse couples to pairs of phonons with equal and opposite momentum and produces temporal coherences in the mean square displacements at a given momentum transfer. The subsequent evolution of the coherent atomic motion is read off as a function of time by femtosecond x-ray scattering using a massively parallel detection. While these experiments can easily measure low energy excitations, the results were limited by the timing jitter of the XFEL to modes with frequencies below a couple THz (<8meV). By resorting the data based on arrival time, we have been able to beat the jitter-limited resolution and can resolve acoustic phonons spanning the full Brillouin zone. We have used this technique to study anharmonic phonon interactions in the incipient ferroelectric PbTe on both LCLS and SACLA. Some of our results are shown in Fig. 1. In this case, the material response includes two-phonon coherences involving mixed modes that can be connected to a differential change in the dynamical matrix involving forces between like and unlike atoms. These results can then be used to compare with first principle calculations from our colleauges at Tyndall to help elucidate the nature of the anharmonicity and stability of the paraelectric phase.

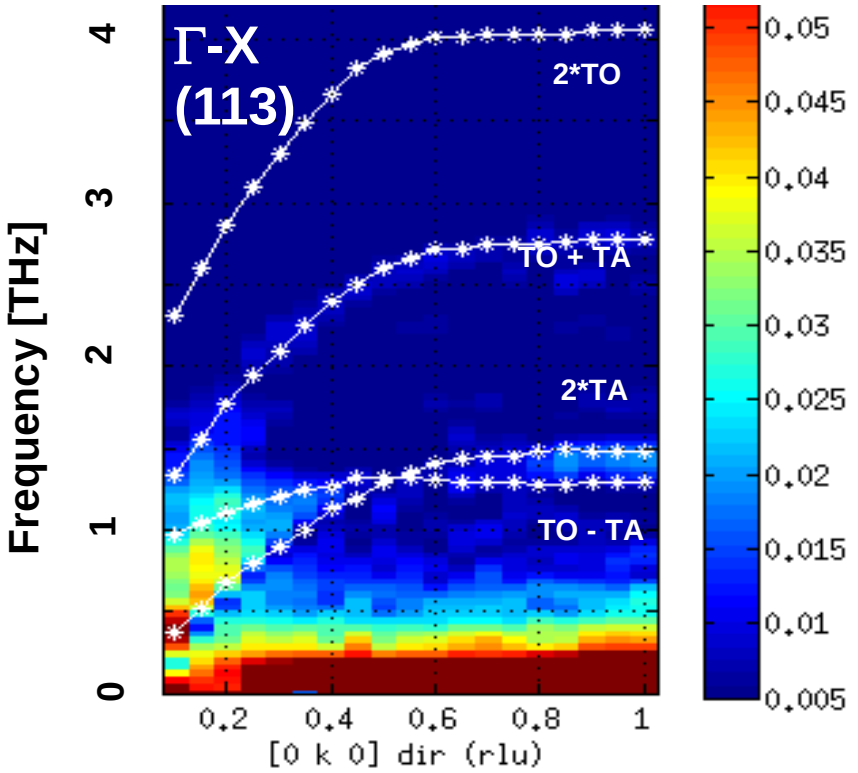


Fig. 1. FT-IXS spectrum of transverse two-phonon excitations in PbTe along Γ-X following near band-gap excitation which increases the stability of the paraelectric rock-salt structure. The spectrum is obtained via Fourier transform of the time-domain inelastic x-ray scattering signal using LCLS. The white lines show assignments based on various combinations of phonon branches from published inelastic neutron scattering data of Cochran *et al., Proc. R. Soc. Lond. A 293: 433 (1966).*

Future Plans

We have shown that non-resonant time-domain inelastic x-ray scattering can measure near-equilibrium dynamics with extreme resolution in both highly harmonic and anharmonic systems. This paves the way to studying not only more complex materials where macroscopic properties "emerge" due to strong electron-phonon and phonon-phonon interactions, but also functional materials for energy conversion and transport applications, since they operate far from equilibrium in modern devices. In the near term, we plan to submit the results from the jitter-corrected FT-IXS data, the results on anharmonicity in PbTe, as well experiments on coherent acoustic phonons and demagnetization in thin Fe films (in collaboration with Hermann Dürr). We have two upcoming beamtimes scheduled on LCLS: the first is to study the mechanism for generation of two-phonon coherences, so that we can understand under what conditions we expect the FT-IXS technique to be operable; in the second we will study charge density wave (CDW) dynamics (amplitude and phase modes) in the rare-earth tri-telluride system with the goal of resolving: (i) how the anisotropy in the electron-phonon coupling determines the CDW wavevector and (ii) the relationship between the Fermi surface structure and the two CDW orderings (1D and 2D) observed in the system. We also continue to work with Mao and Lindenberg groups on dynamics of materials near phase transitions.

Publications (2013-2014)

[1] M. Kozina, T. Hu, J. S. Wittenberg, E. Szilagyi, M. Trigo, T. A. Miller, C. Uher, A. Damodaran, L. Martin, A. Mehta, J. Corbett, J. Safranek, D. A. Reis, and A. M. Lindenberg. Measurement of transient atomic displacements in thin films with picosecond and femtometer resolution. ***Structural Dynamics*****,** 1(3):–, 2014.

[2] W.-P. Hsieh, M. Trigo, D. A. Reis, G. Andrea Artioli, L. Malavasi, and W. L. Mao. Evidence for photo-induced monoclinic metallic VO_2 under high pressure. ***Applied Physics Letters***, 104(2):–, 2014.

[3] M. Trigo, M. Fuchs, J. Chen, M. P. Jiang, M. Cammarata, S. Fahy, D. M. Fritz, K. Gaffney, S. Ghimire, A. Higginbotham, S. L. Johnson, M. E. Kozina, J. Larsson, H. Lemke, A. M. Lindenberg, G. Ndabashimiye, F. Quirin, K. Sokolowski-Tinten, C. Uher, G. Wang, J. S. Wark, D. Zhu, and D. A. Reis. Fourier-transform inelastic x-ray scattering from time- and momentum-dependent phonon-phonon correlations. ***Nature Physics***, 9(12):790–794, 12 2013.

[4] S. de Jong, R. Kukreja, C. Trabant, N. Pontius, C. F. Chang, T. Kachel, M. Beye, F. Sorgenfrei, C. H. Back, B. Bräuer, W. F. Schlotter, J. J. Turner, O. Krupin, M. Doehler, D. Zhu, M. A. Hossain, A. O. Scherz, D. Fausti, F. Novelli, M. Esposito, W. S. Lee, Y. D. Chuang, D. H. Lu, R. G. Moore, M. Yi, M. Trigo, P. Kirchmann, L. Pathey, M. S. Golden, M. Buchholz, P. Metcalf, F. Parmigiani, W. Wurth, A. Föhlisch, C. Schüßler-Langeheine and H. A. Dürr, Speed limit of the insulator-metal transition in magnetite. ***Nature Materials*** **12**, 882 (2013).

[5] J. Chen, M. Trigo, S. Fahy, E. D. Murray, Y. M. Sheu, T. Graber, R. Henning, Y. J. Chien, C. Uher, and D. A. Reis. Time- and momentum-resolved probe of heat transport in photo-excited bismuth. ***Applied Physics Letters***, 102(18):181903, 2013.

[6] Y. D. Chuang, W. S. Lee, Y. F. Kung, A. P. Sorini, B. Moritz, R. G. Moore, L. Patthey, M. Trigo, D. H. Lu, P. S. Kirchmann, M. Yi, O. Krupin, M. Langner, Y. Zhu, S. Y. Zhou, D. A. Reis, N. Huse, J. S. Robinson, R. A. Kaindl, R. W. Schoenlein, S. L. Johnson, M. Först, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, T. Sasagawa, Z. Hussain, Z. X. Shen, and T. P. Devereaux. Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered $La_{1.75}Sr_{0.25}NiO_4$ Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction. ***Physical Review Letters***, 110:127404, 2013.

[7] J. J. Li, J. Chen, D. A. Reis, S. Fahy, and R. Merlin. Optical probing of ultrafast electronic decay in Bi and Sb with slow phonons. ***Phyical Review Letters***, 110:047401, 2013.

[8] Y. M. Sheu, Y. J. Chien, C. Uher, S. Fahy, and D. A. Reis. Free-carrier relaxation and lattice heating in photoexcited bismuth. ***Phyical Review B***, 87:075429, 2013.

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures, DE-SC-0012375

Dynamical Materials Design Using Atomic Scale Anharmonic Interactions

James Rondinelli, Dept. of Materials Science and Engineering, Northwestern University

Program Scope

Dynamic processes in materials underpin many facets of energy science such as efficient energy conversion and transport. This project supports an interdisciplinary team including experts in new generations of ultrafast/ultrabright light sources in terahertz, infrared and hard X-ray frequencies, nano-diffractio and ultrafast infrared near-field nanospectroscopy to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales as well as theory. Fundamental research goals are to: (a) Establish materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions.

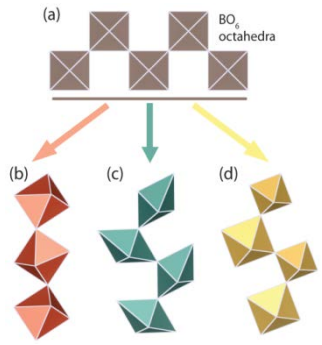


Figure 1. Common distortions to the ideal BO_6 octahedral framework of the perovskite aristotype (a). The physical distortions manifest as rotations (b), tetragonal distortions with 2-short and 4-long B–O bonds (c), or vice versa, and cooperative dilation and contraction (d) of the octahedra.

Recent Progress

Rondinelli has developed new theories for how competing electronic interactions may be controlled in bulk and thin film perovskites to produce new phases. The concept relies on leveraging the anharmonic interactions among lattice normal modes in ferroic and correlated oxides, which are characterized by various lattice instabilities (Figure 1). Progress relevant to the DOE program builds on prior support from ARO (W911NF-12-1-0133) and ONR (N00014-11-1-0664), includes discovery of novel ferr*i*electric phase transitions [1], polar conductors [2], emergent ferroelectricity in superlattices and layered oxides [3], and control of charge-ordered breathing distortions in materials exhibiting metal-insulator transitions [4]. Many of these studies were performed with the High Performance Compute (HPC) facilities at the Center for Nanoscale Materials (CNM, Argonne). Recently, Rondinelli was awarded a 220,000 hour HPC allocation (CNM 40077) for FY 2015 on “Dynamical Materials Design for Non-equilibrium Phase Discovery,” for studies planned in DE-SC-0012375.

Future Plans

Rondinelli will computationally explore the extent to which instabilities of the octahedral rotations in perovskite oxides may be used as a new structural “sand box” to design dynamic phases

of matter. Using group theoretical methods and density functional theory computations, he will identify key unit cell level features that give rise to large lattice anharmonicity between IR-active and Raman active modes (rotations, Jahn-Teller distortions, etc., that dictate functionality through the orbital degrees of freedom). It is hypothesized that through electron-lattice interactions, it will be possible to stabilize new non-equilibrium phases by mode-selective excitation of IR modes indirectly coupled to the Raman modes, through effective static ionic displacements.

The proposed calculations will first explore oxides in bulk close to metal-insulator or ferroic phase boundaries. Total energy surface calculations as a function of the amplitude of the IR/Raman modes will be performed on nickelate, manganite, and vanadate oxides synthesized by experimental team members, Chakhalian, Martin, and Engel-Hebert, respectively. Rondinelli will identify the nature and strength of the coupling between the various IR and Raman phonons. The electronic and magnetic properties will be determined as a function of IR-R coupling to construct "non-equilibrium" phase diagrams, forming the basis for advanced calculations with dynamical fluctuations by Millis. These results will guide the subsequent selection of material systems for growth in thin films/superlattices and guide targeted excitation of resonance frequencies in the THz range (or ranges accessible by the available optics) by Averitt, Gopalan, Freeland, Wen, and Basov. Together we will formulate design rules for light-induced transitions, and provide an understanding of how to extend the lifetime of the dynamical states in heterostructures.

References

[1] G. Gou, and J.M. Rondinelli, "Strain-induced isosymmetric ferri-to-ferroelectric transition with large piezoelectricity," *Adv. Mater. Interfaces*, **1** 1400042 (2014)

[2] D. Puggioni, and J.M. Rondinelli, "Designing a robustly metallic noncenstrosymmetric ruthenate oxide with large thermopower anisotropy," *Nat. Commun.*, **5** 3432 (2014)

[3] J. Young and J.M. Rondinelli, "Improper Ferroelectricity and Piezoelectric Responses in Rhombohedral $(A,A')B_2O_6$ Perovskite Oxides," *Phys. Rev. B*, **89** 174110 (2014); H. Akamatsu, et al., "Inversion symmetry breaking by oxygen octahedral rotations in the Ruddlesden-Popper Na*R*TiO_4 family," *Phys. Rev. Lett.*, **112** 187602 (2014); J.M. Rondinelli and C.J. Fennie, "Octahedral rotation-induced ferroelectricity in cation ordered perovskites," *Adv. Mater.*, **24** 1961 (2012).

[4] P.V. Balachandran and J.M. Rondinelli, "Interplay of octahedral rotations and breathing distortions in charge ordering perovskite oxides," *Phys. Rev. B*, **88** 054101 (2013); A. Cammarata and J.M. Rondinelli, "Octahedral engineering of orbital polarizations in charge transfer oxides," *Phys. Rev. B*, **87** 155135 (2013).

Publications

None.

HPCAT – Advances in High Pressure Melting and Polyamorphism in Liquids

Guoyin Shen, Ho-kwang Mao, and Viktor Struzhkin
Carnegie Institution of Washington

Program Scope

HPCAT's mission is to advance compression science in multidisciplinary fields using synchrotron radiation. HPCAT has played pioneering role in enabling many new capabilities and establishing new ways of conducting experiments. This abstract summarizes one development area on high pressure melting and polyamorphism in liquids.

Recent Progress

High pressure melting anchors the phase diagram of a material and is fundamental in thermodynamics. However, large controversial results, differing over thousands of degrees, still exist in recent literatures, due to the lack of reliable melting identification, large temperature gradients, and chemical reactions between the sample and the pressure media or anvils.

In the past two years, we have made considerable developments in establishing a robust method in determining the high-pressure melting curves of materials. Although x-ray diffraction promises to be the most robust to document the loss of long range order upon melting[1-3], observing diffuse scattering from molten areas has been experimentally challenging, largely because of small heating area, small x-ray probe, and their mutual alignment. The "tail" of the x-ray beam, which is 2-5 times larger than the size at FWHM, may scatter from relatively cold unmelted region. While the scatter from crystalline portion by the tail is weak in general, it could be comparable to the weak diffuse scattering from the central molten area, resulting in inconclusive mixed diffraction patterns. This important detail is often not described in the published literature, but is one major factor responsible for the large controversies. We have developed a new melting criterion using pulsed laser heating (Figure). When the peak power was adjusted to above melting temperatures followed by fast quenching, a continuous diffraction ring is observed arising from fine grains of the sample. Obviously, the nucleation process from liquid is fast enough relative to this quenching rate, but the grain growth is largely prevented, leaving a signature of the molten history. The advantages of this method include unambiguity in melting detection, only short heating duration needed, and strong diffraction signals from crystalline sample (rather than based on weak diffuse scattering). In addition, with the use of powerful lasers, large temperature gradients can be eliminated by having large hot spots (>80 μm in diameter) on the sample which effectively reduce the effect of chromatic aberration[4, 5] in temperature measurements. Our developments in encapsulated sample configuration clearly reduce unwanted chemical reactions.

The developed method is also applicable to study polyamorphism in liquids, a fundamentally important yet unresolved phenomenon[6]. One example is the simple alkali elements like Li and Na. Our previous results show that both Li and Na display melt-down and

complexity of crystal structures at high pressure[7, 8]. This is contrary to the conventional wisdom that the crystal structures at high pressure became simple arrays of closely packed balls. High pressure increases the interaction of the inner electrons, and atoms become irregularly-shaped and non-spherical, resulting in very complicated crystal structures, and very large unit cells[7-9]. Currently, their liquid counterparts are simply treated as a blank, randomly disordered void. With the new developments, we will address the role of increased interaction of the inner electrons at high pressure and possible polymorphism in these liquids.

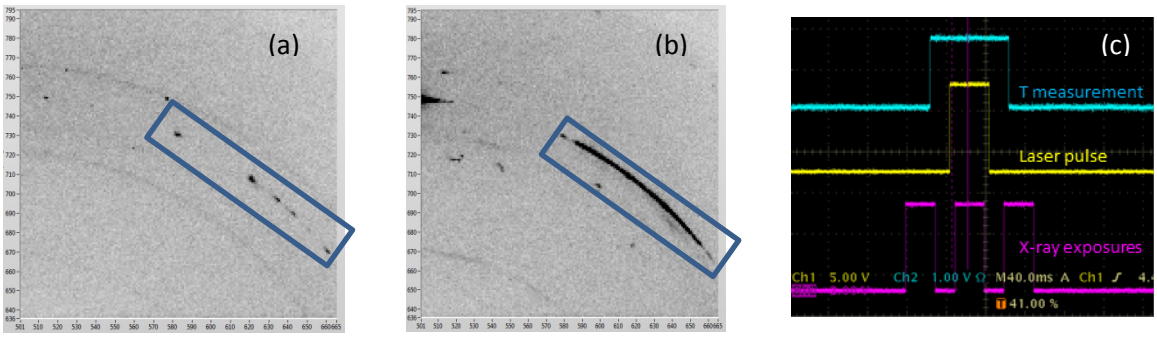


Figure. Abrupt changes of microstructure in Mo can be observed in samples which have been quenched from a molten state. a) (110) reflection from bcc-Mo quenched from a temperature below the melting point (seen in area bounded by the rectangle); b) (110) reflection from bcc-Mo quenched from a temperature above the melting point; c) timing in pulsed heating experiments.

Future Plans

The newly enabled methods will be applied to determine high pressure melting of transition metals of Fe, Mo, Ta, and W up to multi-Mbar pressures. In addition, we will study liquid-liquid transitions at high pressure using x-ray diffraction and x-ray inelastic scattering techniques to address the polyamorphism, both gradual and abrupt, in liquids.

References

1. G. Shen, V. B. Prakapenka, M. L. Rivers, et al, Phys. Rev. Lett. 92, 185701 (2004).
2. A. Dewaele, M. Mezouar, N. Guignot, et al., Phys. Rev. Lett. 104 (25), 255701 (2010).
3. S. Anzellini, A. Dewaele, M. Mezouar, et al., Science 340, 464 (2013).
4. G. Shen, M. L. Rivers, Y. Wang and S. J. Sutton, Rev. Sci. Instrum. 72, 1273 (2001).
5. R. Boehler, Rev. Geophysics 38, 221-245 (2000).
6. P. H. Poole, T. Grande, C. A. Angell and P. F. McMillan, Science 275, 322 (1997).
7. C. L. Guillaume, E. Gregoryanz, O. Degtyareva, et al., Nature Phys. 7, 211-214 (2011).
8. E. Gregoryanz, O. Degtyareva, M. Somayazulu, et al., Phys. Rev. Lett. 94, 185502, (2005).
9. W. Grochala, R. Hoffmann, J. Feng and N. W. Ashcroft, Ang. Chem. 46, 3620 (2007).

Publications since 2013

1. Yoshio Kono, Curtis Kenney-Benson, Changyong Park, Guoyin Shen, Yanbin Wang, Anomaly in the viscosity of liquid KCl at high pressures, Phys. Rev. B **87** (2), 024302 (2013)
2. Adam Cadien, Q.Y. Hu, Y. Meng, Y.Q. Cheng, M.W. Chen, J.F. Shu, H.K. Mao, H.W. Sheng, First-Order Liquid-Liquid Phase Transition in Cerium, Phys. Rev. Lett. **110** (12), 125503 (2013)
3. Bianca Haberl, Malcolm Guthrie, David J. Sprouster, Jim S. Williams, Jodie E. Bradby, New insight into pressure-induced phase transitions of amorphous silicon: the role of impurities, J. Appl. Crystallogr. **46** (3), 758 (2013)
4. Jackson, J. M., Sturhahn, W. , Lerche, M., Zhao, J., Toellner, T.S., Alp, E. E., Sinogeikin, S. V., Bass, J. D., Murphy, C. A., and Wicks, J.K. , Melting of compressed iron by monitoring atomic dynamics, *Earth Planet. Sci. Lett.* 362, 143-150 (2013)
5. M.J. Lipp, Y. Kono, Z.s. Jenei, H. Cynn, C. Aracne-Ruddle, C. Park, C. Kenney-Benson, W.J. Evans, Strength and Debye temperature measurements of cerium across the [gamma - alpha] volume collapse: the lattice contribution, J. Phys. Condens. Matter **25** (34), 345401 (2013)
6. Qiaoshi Zeng, Wendy L. Mao, Hongwei Sheng, Zhidan Zeng, Qingyang Hu, Yue Meng, Hongbo Lou, Fang Peng, Wenge Yang, Stanislav V. Sinogeikin, Jian-Zhong Jiang, The effect of composition on pressure-induced devitrification in metallic glasses", Appl. Phys. Lett. **102** (17), 171905 (2013)
7. Zhang, Li, Y. Meng, W. Yang, L. Wang, W. L. Mao, Q. Zeng, J. S. Jeong, A. J. Wagner, K. A. Mkhoyan, W. Liu, R. Xu, and H-k. Mao, Disproportionation of (Mg,Fe)SiO3 perovskite in Earth's deep lower mantle, *Science*, Vol 344, no. 6188 pp. 877 (2014)
8. Sanloup, C., J.W.E. Drewitt, C. Crépisson, Y. Kono, C. Park, C. McCammon, L. Hennet, S. Brassamin, and A. Bytchkov, Structure and density of molten fayalite at high pressure *Geochimica et Cosmochimica Acta*, 118, 118 (2013)
9. Shi, C.Y., L. Zhang, W. Yang, Y. Liu, J. Wang, Y. Meng, J. C. Andrews, and W. L. Mao, Formation of an interconnected network of iron melt at Earth's lower mantle conditions, *Nature Geoscience*, 6, 971 (2013)
10. Haberl, B., M. Guthrie, B. D. Malone, J. S. Smith, S. V. Sinogeikin, M. L. Cohen, J. S. Williams, G. Shen, and J. E. Bradby, Controlled formation of metastable germanium polymorphs, *Phys. Rev. B* 89, 144111 (2014)
11. Jing, Z-c., Y. Wang, Y. Kono, T. Yu, T. Sakamaki, C. Park, M.L. Rivers, S.R. Sutton, and G. Shen, Sound velocity of Fe–S liquids at high pressure: Implications for the Moon's molten outer core, *Earth Planet.Sci. Lett.*396, 78 (2014)
12. Kono, Y., C. Park, C. Kenney-Benson, G. Shen, and Y. Wang, Toward comprehensive studies of liquids at high pressures and high temperatures: Combined structure, elastic wave velocity, and viscosity measurements in the Paris–Edinburgh cell, *Phys. Earth Planet. In.*, 228, 269 (2014)
13. Lipp, M. J., M.J. Lipp, Zs. Jenei, D. Ruddle, C. Aracne-Ruddle, H. Cynn, W.J. Evans, Y. Kono, C. Kenney-Benson, and C. Park, Equation of state measurements by radiography

provide evidence for a liquid-liquid phase transition in cerium
J. Phys. Conf. Series 500 (3), 032011 (2014)
14. Liu, Lei; Yoshio Kono, C. Kenney-Benson, Wenge Yang, Yan Bi, and Guoyin Shen, Chain breakage in liquid sulfur at high pressures and high temperatures *Phys. Rev. B* 89, 174201 (2014)
15. Sakamaki, T., Y. Wang, C. Park, T. Yu, and G. Shen, Contrasting behavior of intermediate-range order structures in jadeite glass and melt, *Phys. Earth Planet. In.*,228, 281 (2014)
16. Sakamaki, T., Y. Kono, Y. Wang, C. Park, T. Yu, Z. Jing, and G. Shen, Contrasting sound velocity and intermediate-range structural order between polymerized and depolymerized silicate glasses under pressure, *Earth Plan. Sci. Lett.*, 391, 288 (2014)
17. Seoung, D., Y. Lee, H. Cynn, C. Park, K-Y. Choi, D. A. Blom, W. J. Evans, C.-C. Kao, T. Vogt, and Y. Lee, Irreversible xenon insertion into a small-pore zeolite at moderate pressures and temperatures, *Nat. Chem.* 6, 9, 835 (2014)
18. Wang,Yanbin, T. Sakamaki, L. B. Skinner, Z. Jing, T. Yu, Y. Kono, C. Park, G. Shen, M. L. Rivers, and S. R. Sutton, Atomistic insight into viscosity and density of silicate melts under pressure, *Nat. Commun.* 5, 3241 (2014)
19. Zeng, Qiaoshi; Y. Kono, Y. Lin, Z. Zeng, J. Wang, S. V. Sinogeikin, C. Park, Y. Meng, W. Yang, Ho-K. Mao, and W. L. Mao, Universal Fractional Noncubic Power Law for Density of Metallic Glasses, *Phys. Rev. Lett.* 112 (18), 185502 (2014)

Electronic and Magnetic Properties of Quantum Materials

Z.X. Shen, T.P. Devereaux, D.H. Lu, Rob Moore, Patrick Kirchmann, M. Hashimoto and B. Moritz
Stanford Institute for Materials and Energy Sciences
SLAC National Accelerator Laboratory and Stanford University

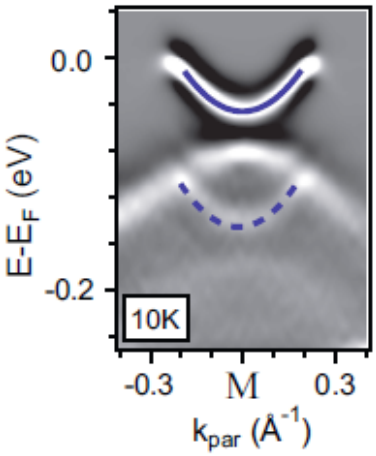
Program Scope

This FWP has its core activities in studying novel properties of quantum materials using angle resolved photoemission spectroscopy (ARPES) in various modes, and couple to in-situ materials synthesis. The materials of focus are novel superconductors (such as the cuprates and Fe-pnictides or iron chalcogenides) or materials with strong spin-orbit interactions (such as topological insulators or transition metal dichalcogenides). The main activity is synchrotron based ARPES, but modern methods such as laser-ARPES, time resolved ARPES, 2PPE ARPES and spin-ARPES are also been actively pursued.

Recent Progress

A few examples of recent progress are illustrated below:

A. Quantum systems in confined geometries have been a very rich ground for discoveries. We have made a number of breakthroughs in uncovering new physics at the atomically thin limit – such as monolayer superconductor FeSe and monolayer semiconductor MoSe2 [1-3]. We will focus on mono-unit-cell (UC) superconductor FeSe grown on SrTiO3, where the Cooper pairing temperature has been reported to have dramatically enhanced from its bulk value of 8K to ~ 60-70K. A challenge is to understand the cause of the enhanced pairing strength, and possibly increase superconducting T*c*. We show angle-resolved photoemission spectroscopy (ARPES) data that provide clear evidence (as the shadow band highlighted by the dash blue line in the figure) for strong cross-interface electron-phonon coupling in single UC limit, suggesting a likely pair enhancing mechanism [1]. This provides a pathway of “integrated functional components” approach to boost superconducting properties.

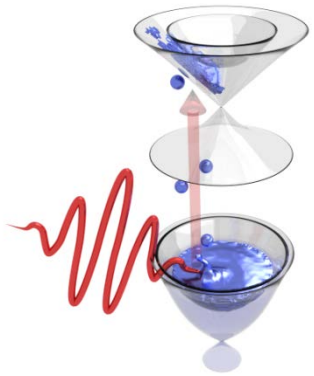


B. The unusual phase diagram containing the so-called pseudogap in cuprate superconductor remains a key puzzle in physics today. We have made substantial progress in understanding the electronic phase diagram and the relationship between the pseudogap and the superconducting gap [4-6], after the earlier progresses in showing distinct doping, temperature, and symmetry properties among them [7-10]. In particular, we show clear evidence that the pseudogap and superconducting gap has an intertwined but competing relationship [6, 10]. The long term and sustained support of BES enable a systematic and scholarly study that is necessary to make substantial progress on such a hard physics problem.

C. The Fe-pnictide superconductors offer a new window into the physics of strongly correlated electron system and its connection with superconductivity. The multi-orbital nature of the

materials reveals new physics that is absent in single orbital materials such as cuprates. At the same time, the highly metallic nature of the materials raises the question whether the correlation effect plays an important role in pnictides. We have systematically studied the physics of strong correlation as a function of material parameters [11-12]. In particular, we have uncovered orbital select Mott physics that reveals a new dimension of electron correlation effect not well appreciated before [11].

D. Combining modern ultrafast UV laser and state of the art ARPES system, we have embarked in the development of time resolved photoemission spectroscopy, and have uncovered a number of interesting new physics on topological superconductors [13-15]. In particular, we demonstrated an efficient method to elucidate empty band structure with unprecedented precision and efficiency. In it, we discovered a second non-tivial Dirac cone above the conventional topological Dirac cone, as illustrated in the figure. [14].



E. In parallel with experimental developments, we have performed Keldysh-Wigner time-domain simulations to explore the out-of-equilibrium dynamics of pump driven systems [16]. We have investigated how decay rates in electron-phonon coupled systems can be related to microscopically derived quantities [17] and continued to investigate the influence of driving fields on broken symmetry phases such as the “melting” of charge or spin density waves [18] and the emergence of collective modes in pump driven superconductors and other materials.

Future Plans

With the commissioning of the new beamline at SSRL, we should be able to perform better and more sophisticated experiments, including the utilization of circularly polarized beam, to address a number of open issues in novel superconductors. At the same time, we will be able to take advantage of the investments in the oxide MBE system that has received general support from BES. We also plan to expand our time resolved ARPES experiments into other materials systems, including charge density wave and superconducting materials. Leveraging the newly developed 11 eV laser and other tools, we will expand on our chalcogedide film success. We will also develop spin resolved ARPES experiments. The theory effort will proceed in parallel with experiments, but an additional component that involves theoretical tool development and conceptual issues derived from experiments.

References

1) JJ Lee, F.T. Schmitt, R.G. Moore, S. Johnston, Y.T. Cui, W. Li, M. Yi, Z.K. Liu, M. Hashimoto, Y. Zhang, D.H. Lu, T.P. Devereaux, D.H. Lee, and Z.X. Shen
Significant Tc Enhancement in FeSe Films on SrTiO3 Due to Interfacail Model Coupling
arXiv; 1312.2633, accepted for publication in Nature (2014)

2) Y. Zhang, T.R. Chang, B. Zhou, Y.T. Cui, H. Yan, Z.K. Liu, F. Schmitt, J.J. Lee, R.G. Moore, Y.L. Chen, H. Lin, H.T. Jeng, S-K Mo, Z. Hussain, A. Bansil, and Z.X. Shen
Direct observation of the transition from indirect to direct bandgap in atomically tin epitaxial MoSe2
Nature NanoTechnology, V9/2 (February 2014)

3) M. Ugeda, A.J. Bradley, S.F. Shi, F.H. da Jornada, Y. Zhang, D.Y. Qiu, S.K. Mo, Z. Hussain, Z.X. Shen, F. Wang, S.G. Louie, M.F. Crommie
Observation of Giant Bandgap Renormalization and Excitonic Effects in a Monolayer Transition Metal dichalcogenide Semiconductor
arXiv; 1404.2331, accepted for publication in Nature Materials (2014)

4) Vishik, IM; Hashimoto, M; He, RH; Leeb, WS; Schmitt, F; Lu, D; Moore, RG; Zhang, C; Meevasana, W; Sasagawa, T; Uchida, S; Fujita, K; Ishida, S; Ishikado, M; Yoshida, Y; Eisaki, H; Hussain, Z; Devereaux, TP; Shen, ZX
Phase competition in trisected superconducting dome
Proceedings of The National Academy of Sciences of the United States of America, 109/45, 18332-18337 (Nov. 6, 2012)

5) M. Hashimoto, I.M. Vishik, R.H. He, T.P. Devereaux, Z.X. Shen
Energy gaps in high-transition-temperature cuprate superconductors
Nature Physics 10, 483 (June 30 2014)

6) M. Hashimoto, I.M. Vishik, R.H. He, T.P. Devereaux, Z.X. Shen
Energy gaps in high-transition-temperature cuprate superconductors
Accepted for publication in Nature Materials

7) M. Hashimoto, R.H. He, K. Tanaka, J.P. Testaud, W. Meevasana, R.G. Moore, D.H. Lu, H.Yao, Y. Yoshida, H. Eisaki, Z. Hussain, and Z.-X. Shen
Particle-hole symmetry breaking in the pseudogap state of Bi2201
Nature Physics 6, 414-418 (2010)

8) Kiyohisa Tanaka, W.S. Lee, D.H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D.J. Scalapino, T.P. Devereaux, Z. Hussain, and Z.X. Shen
Distinct Fermi-momentum dependent energy gaps in deeply underdoped Bi2212
Science 314, 1910 (2006)

9) W.S. Lee, K. Tanaka, D.H. Lu, T. Sasagawa, N. Nagaosa, T.P. Devereaux, Z. Hussain, and Z.X. Shen
Abrupt Onset of Second Energy Gap at Superconducting Transition along the Fermi Arc of Underdoped Bi2212
Nature, 450, 81 (2007)

10) R.H. He, M. Hashimoto, H. Karapetyan, J.D. Koralek, J.P. Hinton, J.P. Testaud, V. Nathan, Y. Yoshida, Hong Yao, K. Tanaka, W. Meevasana, R.G. Moore, D.H. Lu, S.K. Mo, M. Ishikado, H. Eisaki, Z. Hussain, T.P. Devereaux, S.A. Kivelson, J. Orenstein, A. Kapitulnik, Z.-X. Shen
From a single band metal to a high-temperature superconductor via two thermal phase

transitions
Science, 331, 1579 (2011)
11) M. Yi, D. H. Lu, R. Yu, S. C. Riggs, J.-H. Chu, B. Lv, Z. K. Liu, M. Lu, Y.-T. Cui, M. Hashimoto, S.-K. Mo, Z. Hussain, C. W. Chu, I. R. Fisher, Q. Si, Z.-X. Shen
Observation of Temperature-Induced Crossover to an Orbital-Selective Mott Phase in AxFe2-ySe2 (A=K, Rb) Superconductors
Physical Review Letters, 110/6, 067003 (Feb. 5, 2013)
12) M. Yi, Y. Zhang, Z.K. Liu, X. Ding, J-H Chu, A.F. Kemper, N. Plonka, B. Moritz, M. Hashimoto, S-K Mo, Z. Hussain, T.P. Devereaux, I.R. Fisher, H.H. Wen, Z.X. Shen, D.H Lu
Dynamic competition between spin-density wave order and superconductivity in underdoped Ba1-xKxFe2As2.
Nature Communications, V5 (April 25, 2014)
13) J.A. Sobota, S. Yang, J.G. Analytis, Y.L. Chen, I.R. Fisher, P.S. Kirchmann, and Z.X. Shen
Ultrafast Optical Excitation of a Persistent Surface-State Population in the Topological Insulator Bi2Se3
Phys. Rev. Lett., 108, 117403 (2012)
14) J.A. Sobota, S.-L. Yang, A.F. Kemper, J.J. Lee, F.T. Schmitt, W. Li, R.G. Moore, J.G. Analytis, I.R. Fisher, P.S. Kirchmann, T.P. Devereaux, and Z.X. Shen
Direct Optical Coupling to an Unoccupied Dirac Surface State in the Topological Insulator Bi2Se3
Physical Review Letters, V111/13, 136802 (September 24, 2013)
15) J.A. Sobota, S.-L. Yang, D. Leuenberger, A.F. Kemper, J.G. Analytis, I.R. Fisher, P.S. Kirchmann, T.P. Devereaux, and Z.X. Shen
Distinguishing Bulk and Surface Electron-Phonon Coupling in the Topological Insualtor Bi2Se3 Using Time-Resolved Photoemission Spectrocopy
Physical Review Letters, V113, 157401 (October 10, 2014)
16) M. Sentef, M. Sentef, A. F. Kemper, B. Moritz, J. K. Freericks, Z.-X. Shen, and T. P. Devereaux
Examining Electron-Boson Coupling Using Time-Resolved Spectroscopy
Physical Review X, 41033 (2013)
17) A. F. Kemper, M. A. Sentef, B. Moritz, J. K. Freericks, and T. P. Devereaux
Effect of dynamical spectral weight redistribution on effective interactions in time-resolved spectroscopy
Physical Review B, 075126 (2014)
18) W. Shen, Y. Ge, A. Y. Liu, H. R. Krishnamurthy, T. P. Devereaux, and J. K. Freericks
Nonequilibrium "melting" of a charge density wave insulator via an ultrafast laser pulse
Physical Review Letters 112, 176404 (2014)

2013/2014 Publication List

1) Z. K. Liu, R.-H. He, D. H. Lu, M. Yi, Y. L. Chen, M. Hashimoto, R. G. Moore, S.-K. Mo, E. A. Nowadnick, J. Hu, T. J. Liu, Z. Q. Mao, T. P. Devereaux, Z. Hussain, and Z.-X. Shen
Measurement of Coherent Polarons in the Strongly Coupled Antiferromagnetically Ordered Iron-Chalcogenide Fe1.02Te using Angle-Resolved Photoemission Spectroscopy
Physical Review Letters, 110/3, 037003 (Jan. 18, 2013)

2) S.H. Yao; B. Zhou; M.H. Lu; Z.K. Liu; Y.B. Chen; J.G. Analytis; C. Brune; W.H. Dang; S.K Mo; Z.X. Shen; I.R. Fisher; L.W. Molenkamp; H.L. Peng; Z. Hussain; Y.L. Chen
Observing electronic structures on ex-situ grown topological insulator thin films
Physica Status Solidi-Rapid Research Letters, V7/1-2, SI (February 2013)

3) M. Yi, D. H. Lu, R. Yu, S. C. Riggs, J.-H. Chu, B. Lv, Z. K. Liu, M. Lu, Y.-T. Cui, M. Hashimoto, S.-K. Mo, Z. Hussain, C. W. Chu, I. R. Fisher, Q. Si, Z.-X. Shen
Observation of Temperature-Induced Crossover to an Orbital-Selective Mott Phase in AxFe2-ySe2 (A=K, Rb) Superconductors
Physical Review Letters, 110/6, 067003 (Feb. 5, 2013)

4) S.R. Park; T. Morinari; D.J. Song; C.S. Leem; C. Kim; S.K. Choi; K. Choi; J.H. Kim; F. Schmitt; S.K. Mo; D.H. Lu; Z.X. Shen; H. Eisaki; T. Tohyama; J.H. Han; C. Kim
Interaction of itinerant electrons and spin fluctuations in electron-doped cuprates
Physical Review B, V87/17, 174527 (May 31, 2013)

5) C.R. Rotundu; T. Cuk; R.L. Greene; Z.X. Shen; R.J. Hemley; V.V. Struzhkin
High-pressure resistivity technique for quasi-hydrostatic compression experiments
Review of Scientific Instruments, V84/6, 063903 (June 2013)

6) M.P. Allan, A. Tamai, E. Rozbicki, M.H. Fischer, J. Voss, P.D.C. King, W. Meevasana, S. Thirupathaiah, E. Rienks, J. Fink, D.A. Tennant, R.S. Perry, J.F. Mercure, M.A. Wang, Jinho Lee, C.J. Fennie, E-A. Kim, M.J. Lawler, K.M. Shen, A.P. Mackenzie, Z-X Shen, F. Baumberger
Formation of Heavy d-electron quasiparticles in Sr3Ru2O7
New Journal of Physics, 15, 063029 (June 20, 2013)

7) W. S. Lee, S. Johnston, B. Moritz, J. Lee, M. Yi, K. J. Zhou, T. Schmitt, L. Patthey, V. Strocov, K. Kudo, Y. Koike, J. van den Brink, T. P. Devereaux, and Z. X. Shen
Role of Lattice Coupling in Establishing Electronic and Magnetic Properties in Quasi-One-Dimensional Cuprates
Physical Review Letters, 110, 265502 (June 25, 2013)

8) A.F. Kemper; M. Sentef; B. Moritz; C.C. Kao; Z.X. Shen; J.K. Freericks; T.P. Devereaux
Mapping of unoccupied states and relevant bosonic modes via the time-dependent momentum distribution
Physical Review B, V87/23, UNSP 235139 (June 28, 2013)

9) Y.D. Chuang, W.S. Lee, Y.F. Kung, A.P. Sorini, B. Moritz, R.G. Moore, L. Patthey, M. Trigo, D.H. Lu, P.S. Kirchmann, M. Yi, O. Krupin, M. Langner, Y. Zhu, S .Y. Zhou, D.A. Reis, N. Huse, J.S. Robinson, R.A. Kaindl, R.W. Schoenlein, S.L. Johnson, M. Forst, D. Doering, P. Denes, W.F. Schlotter, J.J. Turner, T. Sasagawa, Z. Hussain, Z.X. Shen, T.P. Devereaux
Real-Time Manifestation of Strongly Coupled Spin and Charge Order Parameters in Stripe-Ordered La1.75Sr0.25NiO4 Nickelate Crystals Using Time-Resolved Resonant X-Ray Diffraction
Physical Review Letters, 110/12, 127404 (March 20, 2013)

10) H. Suzuki; T. Yoshida; S. Ideta; G. Shibata; K. Ishigami; T. Kadono; A. Fujimori; M. Hashimoto; D.H. Lu; Z.X. Shen; K. Ono; E. Sakai; H. Kumigashira; M. Matsuo; T. Sasagawa
Absence of superconductivity in the hole-doped Fe pnictide Ba(Fe1-xMnx)(2)As-2: Photoemission and x-ray absorption spectroscopy studies
Physical Review B, V88/10, 100501 (September 3, 2013)

11) J.A. Sobota; K. Kim; H. Takatsu; M. Hashimoto; S.K. Mo; Z. Hussain; T. Oguchi; T. Shishidou; Y. Maeno; B.I. Min; Z.X. Shen
Electronic structure of the metallic antiferromagnet PdCrO2 measured by angle-resolved photoemission spectroscopy
Physical Review B, V88/12, 125109 (September 5, 2013)

12) J.A. Sobota, S.-L. Yang, A.F. Kemper, J.J. Lee, F.T. Schmitt, W. Li, R.G. Moore, J.G. Analytis, I.R. Fisher, P.S. Kirchmann, T.P. Devereaux, and Z.X. Shen
Direct Optical Coupling to an Unoccupied Dirac Surface State in the Topological Insulator Bi2Se3
Physical Review Letters, V111/13, 136802 (September 24, 2013)

13) G. Coslovich; B. Huber; W.S. Lee; Y.D. Chuang; Y. Zhu; T. Sasagawa; Z. Hussain; H.A. Bechtel; M.C. Martin; Z.X. Shen; R.W. Schoenlein; R.A. Kaindl
Ultrafast charge localization in a stripe-phase nickelate
Nature Communications, V4, 2643 (October 2013)

14) Y.L. Chen, M. Kanou, Z.K. Liu, H.J. Zhang, J.A. Sobota, D. Leuenberger, S.K. Mo, B. Zhou, S.-L. Yang, P.S. Kirchmann, D.H. Lu, R.G. Moore, Z. Hussain, Z.X. Shen, X.L. Qi, and T. Sasagawa
Discovery of a Single Topological Dirac Fermion in the Strong Inversion Asymmetric Compound BiTeCl
Nature Physics, V9 /11 (November 2013)

15) M. Sentef; A.F. Kemper; B. Moritz; J.K. Freericks; Z.X. Shen; T.P. Devereaux
Examining Electron-Boson Coupling Using Time-Resolved Spectroscopy
Physical Review X, V3/4, 041033 (December 26, 2013)

16) N. Plonka, A. F. Kemper, S. Graser, A. P. Kampf, and T. P. Devereaux
Tunneling spectroscopy for probing orbital anisotropy in iron pnictides
Physical Review B 88, 174518 (2013)

17) B. Moritz, A. F. Kemper, M. Sentef, T. P. Devereaux, and J. K. Freericks

Electron-Mediated Relaxation Following Ultrafast Pumping of Strongly Correlated Materials: Model Evidence of a Correlation-Tuned Crossover between Thermal and Nonthermal States
Physical Review Letters 111, 077401 (2013)

18) S. Johnston, E. A. Nowadnick, Y. F. Kung, B. Moritz, R. T. Scalettar, and T. P. Devereaux
Determinant quantum Monte Carlo study of the two-dimensional single-band Hubbard-Holstein model
Physical Review B 87, 235133 (2013)

19) C.-C. Chen, M. Sentef, Y. F. Kung, C. J. Jia, R. Thomale, B. Moritz, A. P. Kampf, and T. P. Devereaux
Doping evolution of the oxygen K-edge x-ray absorption spectra of cuprate superconductors using a three-orbital Hubbard model
Physical Review B 87,165144 (2013)

20) A. F. Kemper, B. Moritz, J. K. Freericks, and T. P. Devereaux
Theoretical description of high-order harmonic generation in solids
New Journal of Physics 15,023003 (2013)

21) H.-M. Eiter, M. Lavagnini, R. Hackl, E. A. Nowadnick, A. F. Kemper, T. P. Devereaux, J.-H. Chu, J. G. Analytis, I. R. Fisher, and L. Degiorgi
Alternative route to charge density wave formation in multiband systems
Proceedings of the National Academy of Science 110,64 (2013)

22) A. F. Kemper, M. A. Sentef, B. Moritz, J. K. Freericks, and T. P. Devereaux
Effect of dynamical spectral weight redistribution on effective interactions in time-resolved spectroscopy
Physical Review B 90, 075126 (2014)

23) W. Shen, T. P. Devereaux, and J. K. Freericks
Exact solution for Bloch oscillations of a simple charge-density-wave insulator
Physical Review B 89, 235129 (2014)

24) W. Shen, Y. Ge, A. Y. Liu, H. R. Krishnamurthy, T. P. Devereaux, and J. K. Freericks
Nonequilibrium "melting" of a charge density wave insulator via an ultrafast laser pulse
Physical Review Letters 112, 176404 (2014)

25) C.J. Jia, E. A. Nowadnick, K. Wohlfeld, Y. F. Kung, C.-C. Chen, S. Johnston, T. Tohyama, B. Moritz, and T. P. Devereaux
Persistent spin excitations in doped antiferromagnets revealed by resonant inelastic light scattering
Nature Communications 5, 3314 (2014)

26) J.J. Lee, B. Moritz, W.S. Lee, M. Yi, C.J. Jia, A.P. Sorini, K. Kudo, Y. Koike, K.J. Zhou, C. Monney, V. Strocov, L. Patthey, T. Schmitt, T.P. Devereaux, Z.X. Shen
Charge-orbital-lattice coupling effects in the dd excitation profile of one-dimensional cuprates
Physical Review B, V89, 4 (January 9, 2014)

27) Y. Zhang, T.R. Chang, B. Zhou, Y.T. Cui, H. Yan, Z.K. Liu, F. Schmitt, J.J. Lee, R.G. Moore, Y.L. Chen, H. Lin, H.T. Jeng, S-K Mo, Z. Hussain, A. Bansil, and Z.X. Shen
Direct observation of the transition from indirect to direct bandgap in atomically tin epitaxial MoSe2
Nature NanoTechnology, V9/2 (February 2014)

28) Z.K. Liu, B. Zhou, Y. Zhang, ZJ Wang, HM Weng, D. Prabhakaran, S.K. Mo. Z.X. Shen, Z. Fang, X. Dai, Z. Hussain, Y.L. Chen
Discovery of a Three-Dimensional Topological Dirac Semimetal, Na3Bi
Science 343, 864 (February 21, 2014)

29) S.-L.Yang, J.A. Sobota, C.A. Howard, C.J. Pickard, M. Hashimoto, D.H. Lu, S.-K. Mo, P.S. Kirchmann, and Z.X. Shen
Superconducting graphene sheets in CaC6 enabled by phonon-mediated interband interactions
Nature Communications, 5, 2 (March 2014)

30) M. Yi, Y. Zhang, Z.K. Liu, X. Ding, J-H Chu, A.F. Kemper, N. Plonka, B. Moritz, M. Hashimoto, S-K Mo, Z. Hussain, T.P. Devereaux, I.R. Fisher, H.H. Wen, Z.X. Shen, D.H Lu
Dynamic competition between spin-density wave order and superconductivity in underdoped Ba1-xKxFe2As2.
Nature Communications, V5 (April 25, 2014)

31) S. Ideta, T. Yoshida, M. Nakajima, W. Malaeb, H. Kito, H. Eisaki, A. Iyo, Y. Tomioka, T. Ito, K. Kihou, C.H. Lee, Y. Kotani, K. Ono, S.K. Mo, Z. Hussain, Z.X. Shen, H. Harima, S. Uchida, A. Fujimori
Electronic structure of BaNi2P2 observed by angle-resolved photoemission spectroscopy
Physical Review B, V89, 19 (May 28, 2014)

32) I.M. Vishik, N. Barisic, M.K. Chan, Y. Li, D.D. Xia, G. Yu, X. Zhao, W.S. Lee, W. Meevasana, T.P Devereaux, M. Greven, Z.X. Shen
Angle-resolved photoemission spectroscopy study of HgBa2CuO4+delta
Physical Review B, V89, 19 (May 29, 2014)

33) H. Suzuki, T. Kobayashi, S. Miyasaka, T. Yoshida, K. Okazaki, L.C.C. Ambolode, II, S. Ideta, M. Yi, M. Hashimoto, D.H. Lu, Z.X. Shen, K. Ono, H. Kumigashira, S. Tajima, A. Fujimori
Strongly three-dimensional electronic structure and Fermi surfaces of SrFe2(As0.65P0.35)(2): Comparison with BaFe2(As1-xPx)(2)
Physical Review B, V89, 18 (May 30, 2014)

34) M. Hashimoto, G. Ghiringhelli, W.S. Lee,
G. Dellea, A. Amorese, C. Mazzoli, K. Kummer, N.B. Brookes, B. Moritz, Y. Yoshida, H. Eisaki, Z. Hussain, T.P. Devereaux, Z.X. Shen, L. Braicovich
Direct observation of bulk charge modulations in optimally doped Bi 1.5Pb 0.6Sr 1.54CaCu 2O 8+delta
Physical Review B, V89, 22 (June 1, 2014)

35) U. Staub, R.A. de Souza, P. Beaud, E. Moehr-Vorobeva, G. Ingold, A. Caviezel, V. Scagnoli, B.

Delley, 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, A.T. Boothroyd, S.L. Johnson
Persistence of magnetic order in a highly excited Cu2+ state in CuO
Physical Review B, V89, 22 (June 2, 2014)

36) M. Hashimoto, I.M. Vishik, R.H. He, T.P. Devereaux, Z.X. Shen
Energy gaps in high-transition-temperature cuprate superconductors
Nature Physics 10, 483 (June 30 2014)

37) Z.K. Liu, J. Jiang, B. Zhou, Z.J. Wang, Y. Zhang, H.M. Weng, D. Prabhakaran, S.-K. Mo, H. Peng, P. Dudin, T. Kim, M. Hoesch, Z. Fang, X. Dai, Z.X. Shen, D.L. Feng, Z. Hussain, and Y.L. Chen
A Stable Three-dimensional Topological Dirac Semimetal Cd3As2
Nature Materials, V13, 7 (July 2014)

38) S.-L. Yang, J.A. Sobota, P.S. Kirchmann, Z.X. Shen,
Electron propagation from a photo-excited surface: implications for time-resolved photoemission
Applied Physics A. Materials Science & Processing, V116, 1 (July 2014)

39) Z.A. Feng, F. El Gabaly, X. Ye, Z.X. Shen, W.C. Chueh
Fast vacancy-mediated oxygen ion incorporation across the ceria–gas electrochemical interface
Nature Communications, 5:4374 (July 9, 2014)

40) Y. Zhang, ZK Liu, B. Zhou, Y. Kim, Z. Hussain, ZX Shen, YL Chen, SK Mo
Molecular beam epitaxial growth of a three-dimensional topological Dirac semimetal Na3Bi
Applied Physics Letters, V105, 3 (July 21, 2014)

41) J.J. Lee, F.T. Schmitt, R.G. Moore, S. Johnston, Y.T. Cui, W. Li, M. Yi, Z.K. Liu, M. Hashimoto, Y. Zhang, D.H. Lu, T.P. Devereaux, D.H. Lee, and Z.X. Shen
Significant Tc Enhancement in FeSe Films on SrTiO3 Due to Interfacail Model Coupling
arXiv; 1312.2633, accepted for publication in Nature (2014)

42) M. Ugeda, A.J. Bradley, S.F. Shi, F.H. da Jornada, Y. Zhang, D.Y. Qiu, S.K. Mo, Z. Hussain, Z.X. Shen, F. Wang, S.G. Louie, M.F. Crommie
Observation of Giant Bandgap Renormalization and Excitonic Effects in a Monolayer Transition Metal dichalcogenide Semiconductor
arXiv; 1404.2331, accepted for publication in Nature Materials (2014)

In-operando imaging of strain, ionic diffusion and topological defects in Nanoscale Materials.

PI: Oleg G. Shpyrko, University of California San Diego

Program Scope

The current program scope is to develop and apply novel coherent x-ray imaging probes for studies of a variety of nanoscale phenomena. In particular, we have applied Coherent X-ray Diffractive Imaging and ptychography in Bragg geometry to image shape and strain distribution in metallic nanowires, nanoparticles, domain structure in magnetic thin films as well as lithium diffusion in operando battery materials

Recent Progress

Coherent x-ray diffraction imaging is used to map the local three dimensional strain inhomogeneity and electron density distribution of nanostructures, in particular metallic nanowires, nanoparticles as well as individual $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ cathode nanoparticles in both *ex-situ* and *in-situ* environments. We observed strain inhomogeneity due to multiple competing effects, such as shape, surface curvature, interactions with substrate, magnetostrictive effects etc. [1,2] In Li-ion cathode nanoparticles, we report direct observation of evolution of both stripe morphologies and coherency strain resulting from ionic diffusion. [3, 4, 5] Our results suggest the critical size for stripe formation is 50 nm. Surprisingly, the single nanoparticle elastic energy landscape, which we map with femtojoule precision, depends on charge versus discharge, indicating hysteresis at the single particle level. [4]

We also were able to observe a single edge dislocation under *operando* conditions in a Lithium ion battery via coherent x-ray diffractive imaging. [6] We were able to track single dislocation movement in response to applied current and observe it act as a nucleation

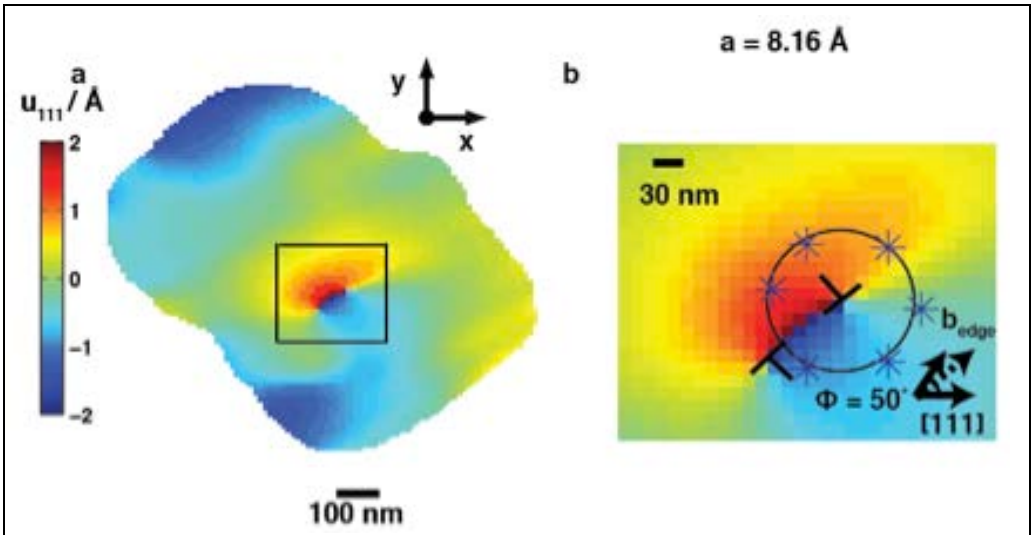


Figure: Edge dislocation pairs induced by repeated cycling in a single nanoparticle. Scalebar is displacement in Å and applies to all color images. Section (a) is a cross-section through the particle of the u_{111} displacement field in Å. (b) shows magnified region in (a) with Burgers vector orientation relative to [111] sketched. Edge dislocations are indicated by symbol "T". From Ref. [6]

point during the structural phase transformation.

Future Plans

We aim to continue application of Coherent X-ray Diffractive Imaging with specific focus on imaging of operating devices, as well as CXDI and ptychographic imaging in Bragg geometry. We recently demonstrated the ability to image not only total shape/electron density of nanostructures, but also 3D distribution of lattice strain, magnetic domain structure, ionic content, topological defects, phase transitions, etc. Our future plans involve more detailed investigation, of the coupling between these order parameters, including, for example, the role played by dislocations and other defects in ionic transport in operando battery materials, or magnetic domain dynamics. We would also like to explore the possibility of optimization of defect density or location in order to obtain desirable materials properties.

References

[1] E. Fohtung, et al., “Probing the three-dimensional strain inhomogeneity and equilibrium elastic properties of single crystal Ni nanowires” Appl. Phys. Lett. 101, 033107 (2012)
[2] J.-W. Kim et al., "Curvature-induced and thermal strain in polyhedral gold nanocrystals", Appl. Phys. Lett. (in press, 2014)
[3] A. Ulvestad, et al. "Nanoscale strain mapping in battery nanostructures." *Applied Physics Letters* 104.7 (2014): 073108.
[4] A. Ulvestad, et al. "Single particle nanomechanics in operando batteries via lensless strain mapping." *Nano Lett.*, 2014, *14* (9), pp 5123–5127
[5] A. Singer, et al. "Non-equilibrium structural dynamics of nanoparticles in LiNi1/2Mn3/2O4 cathode under operando conditions." *Nano Lett.*, 2014, *14* (9), pp 5295–5300
[6] A. Ulvestad et al., in press (2014)

Publications

O. G. Shpyrko, “X-ray photon correlation spectroscopy” *J. Synchrotron Rad.* **21**, 1057-1064 (2014).

J.-W. Kim et al., "Curvature-induced and thermal strain in polyhedral gold nanocrystals", Appl. Phys. Lett. (in press, 2014)

Andrew Ulvestad, Andrej Singer, Hyung-Man Cho, Jesse N. Clark, Ross Harder, Jorg Maser, Ying Shirley Meng, and Oleg G. Shpyrko "Single particle nanomechanics in operando batteries via lensless strain mapping." *Nano Lett.*, 2014, *14* (9), 5123 (2014)

Andrej Singer, Andrew Ulvestad, Hyung-Man Cho, Jong Woo Kim, Jörg Maser, Ross Harder, Ying Shirley Meng, and Oleg G. Shpyrko, "Non-equilibrium structural dynamics of

nanoparticles in LiNi1/2Mn3/2O4 cathode under operando conditions." *Nano Lett.*,, *14* (9), 5295 (2014)

S. H. Dietze, M. J. Marsh, Siming Wang, J.-G. Ramírez, Z.-H. Cai, J. R. Mohanty, Ivan K. Schuller, and O. G. Shpyrko "X-ray-induced persistent photoconductivity in vanadium dioxide" Phys. Rev. B 90, 165109 (2014)

J. Carnis, W. Cha, J. Wingert,J. Kang, Z. Jiang, S. Song, M. Sikorski, A. Robert, C. Gutt, S. Chen, Y. Dai, Y. Ma, H, Guo, L. Lurio, O. Shpyrko, S. Narayanan, M. Cui, I. Kosif, T. Emrick, T. Russell, H. Lee, C Yu, G. Grübel, S. Sinha and H. Kim, "Demonstration of Feasibility of X-Ray Free Electron Laser Studies of Dynamics of Nanoparticles in Entangled Polymer Melts", Scientific Reports, 4, (2014)

A. Ulvestad, H. M. Cho, R. Harder, J. W. Kim, S. H. Dietze, E. Fohtung, Y. S. Meng and O. G. Shpyrko, "Nanoscale strain mapping in battery nanostructures", Appl. Phys. Lett. 104, 073108 (2014)

A. Tripathi, I. McNulty, and O. G. Shpyrko, "Ptychographic overlap constraint errors and the limits of their numerical recovery using conjugate gradient descent methods", Optics Express, 2 (2), 1452 (2014)

H.C. Kim, J.M. Logan, O. G. Shpyrko, P.B. Littlewood and E. D. Isaacs , "Metastability and microscopic avalanche dynamics in charge-density waves of chromium", Phys. Rev. B 88, 140101(R) (2013)

J.-D. Su, A. R. Sandy, J. Mohanty, O. G. Shpyrko and M. Sutton, "Collective pinning dynamics of charge density waves in 1T-TaS2", Phys. Rev. B 86, 205105 (2012)

S. O. Hruszkewycz, M. V. Holt, C. E. Murray, J. Bruley, J. Holt, A. Tripathi, O. G. Shpyrko, I. McNulty, M. J. Highland, P. H. Fuoss, "Quantitative imaging of lattice distortions in epitaxial semiconductor heterostructures using x-ray Bragg ptychography", Nano Lett. 12, 5148 (2012)

E. Fohtung, J. W. Kim, Keith T. Chan, Ross Harder, Eric E. Fullerton, and O. G. Shpyrko, "Probing the 3D strain inhomogeneity and equilibrium elastic properties of single crystal Ni nanowires", Appl. Phys. Lett. 101, 033107 (2012)

J. M. Logan, H. C. Kim, D. Rosenmann, Z. Cai, R. Divan, O. G. Shpyrko and E. D. Isaacs, "Antiferromagnetic domain wall engineering in chromium films" Appl. Phys. Lett. 100, 192405 (2012)

Measurement of Transient Spin Accumulation in Copper by X-Ray Spectro-Microspopy

J. Stöhr, H. Dürr, and A. Reid

Stanford Institute for Materials & Energy Sciences, SLAC National Accelerator Laboratory, Stanford University

Program Scope

The results reported below were obtained under the umbrella of our larger program on investigating magnetic nanoscale phenomena with x-ray spectroscopy and microscopy. The results open up a completely new area and will form the basis for incorporating a new direction into our next FWP.

Recent Progress

It has increasingly become clear that transient spins can be generated and used in revolutionary new ways. Besides their use for reading information through the GMR effect, spin currents can also be used to write information by spin-torque switching of magnetic bits [1]. Through discovery of the spin-Hall effect [2], spin accumulation can now be generated even in non-magnetic materials consisting of heavy atoms such as Pt with a large spin-orbit coupling [3]. While the presence of spin transport and diffusion can often be sensed through its coupling to an adjacent ferromagnet, direct detection of the transient spins is extremely difficult due to the small size of the spin polarization, which is expected to be of the order of 10^{-4} of the large atomic moments. We have now accomplished the detection of transient spins in nanostructures by use of time resolved x-ray spectro-microscopy. This opens the door to the direct investigation of many spin-current related phenomena with x-rays.

In our experiment we used a nanopillar of 250 nm diameter that contained a perpendicularly magnetized Co layer (~10nm thick) and a non-magnetic Cu layer (~20 nm). A pulsed current supplied to the pillar by top and bottom leads (see Fig. 1), could be sent either from Co into Cu or vice versa. We used the new scanning transmission x-ray microscope at SSRL BL 13.1 and circularly polarized x-rays from an undulator to obtain images of the Co and Cu layers in the nanopillar by tuning to the Co (778 eV) and Cu (932 eV) L_3 edges (Fig. 1). We then recorded current-on/off magnetic images of the magnetization in both the Co and Cu layers. The difference images and the change in the magnetic contrast was then measured by scanning the photon energy through the L_3 edges.

On the right side of Fig. 1 we show the magnetic signal induced by the spin current in the Cu layer. The size of the signal can be converted into the spin-imbalance or magnetic moment per Cu atom in the presence of the current. For a current of 5 mA, we found a transient moment of $8\text{x}10^{-5}$ μ_B on the Cu atoms and $3\text{x}10^{-4}$ μ_B on the Co atoms, with both signals scaling linearly with current, as expected.

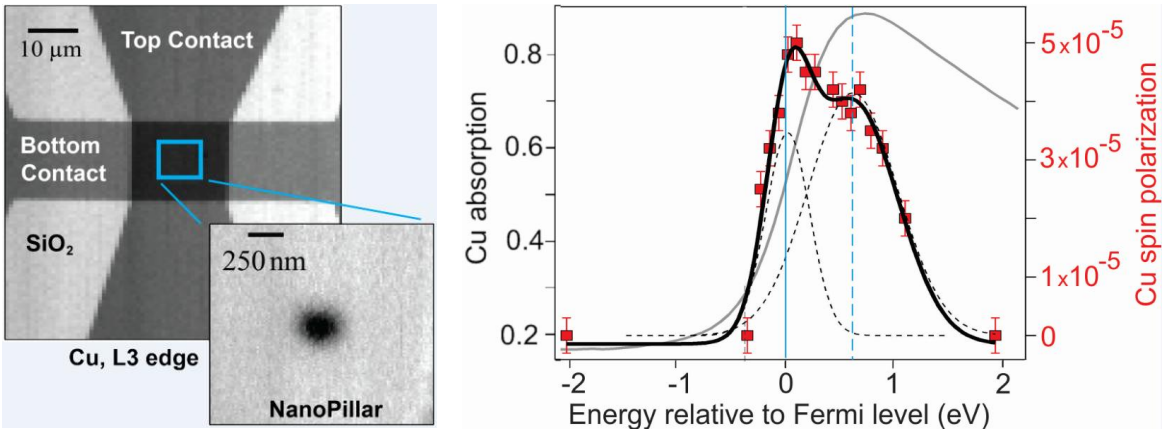


Figure 1: Left: X-ray microscopy image of the Au contacts and blown-up image of the nanopillar. Right: Spectroscopic x-ray magnetic circular dichroism signal of the transient spins in the Cu layer within the nanopillar , plotted as a function of energy relative to the Fermi level. Note the tiny value of the Cu spin polarization which is more than four orders of magnitude smaller than a typical magnetic moment in a ferromagnet.

The detected spin polarization is less than expected for a perfect interface and has a surprising energy dependence shown on the left of Fig. 1. When the photon energy scale is referenced to the Fermi level, we see a narrow peak (fits shown as dashed lines) with the intrinsic core hole line width centered around the Fermi level. This is the spin polarization of the itinerant electrons that flow at the Fermi level, as expected. A second broader peak is observed at an energy of about 0.7 eV above the Fermi level. Its position coincides with the peak in the Cu absorption spectrum shown as a solid gray line. We presently interpret the occurrence of two peaks as a spitting of the electronic states induced by the large exchange field of the transient spins.

Future Plans

We plan to extend our measurements of spin currents to laser-induced currents and spin accumulation in metals induced by the spin Hall effect. We also plan to investigate the use of the spin Hall effect for magnetic switching.

References

[1] J.C. Slonczewski, *J. Magn. Magn. Mater*. **159**, L1 (1996); L. Berger, *Phys. Rev*. **B 54**, 9353 (1996); Y. Acremann *et al*., *PRL* 96, 217202 (2006), *PRL* **100**, 247201 (2008).
[2] S. Murakami, N. Nagaosa, S.-C. Zhang, *Science* **301**, 1348 (2003); J. Sinova *et al*., *Phys. Rev. Lett.* **92**, 126603 (2004); Y. K. Kato, R. C. Myers, A. C. Gossard, D. D. Awschalom, *Science* **306**, 1910 (2004).
[3] I. M. Miron et al., *Nat. Mater.* **9**, 230 (2010).

Publications (see submission by H. Dürr)

HPCAT – Magnetic and Superconducting Materials at High Pressures

Viktor Struzhkin, Guoyin Shen, and Ho-kwang Mao
Carnegie Institution of Washington

Program Scope

HPCAT's mission is to advance compression science in multidisciplinary fields using synchrotron radiation. HPCAT has played pioneering role in enabling many new capabilities and establishing new ways of conducting experiments. This abstract summarizes developments in the new thrust area under HPCAT umbrella – exploratory science in the field of novel superconducting and magnetic materials.

Recent Progress

Alkali metals polyhydrides: Hydrogen rich polyhydrides of alkali metals and alkaline earth have been predicted to have high hydrogen content (1,2) and they hold promise for metallization and high-T_c superconductivity (3) at high pressures. We have studied formation of Li and Na polyhydrides in a diamond anvil cell at pressures up to 70 GPa assisted with laser heating to 2000K. These experiments are very demanding since hydrogen at high pressure-temperature conditions is a very chemically and physically aggressive pressure medium. However, we succeeded in producing Na polyhydrides, and characterized them with Raman and x-ray diffraction experiments (submitted). Raman measurements in the vibron region clearly indicate formation of a compound which contains H_2 structural units (Fig. 1). Future plans are to access higher pressure range and to combine sample synthesis with transport measurements. We are also planning to study recoverable polyhydrides at low pressure, low temperature conditions. This work is performed in close collaboration with our theory group.

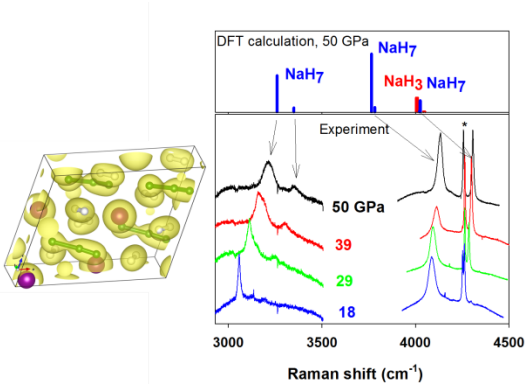


Fig. 1. Raman spectra of NaH_n sample, showing higher-frequency vibrons from H_2. The left panel shows the structure of NaH_7, which contains H_3 complexes. The top panel shows calculated Raman intensity for NaH_3 and NaH_7. Raman from pure H_2 vibron is indicated by asterisk.

Notably, these materials are predicted to exhibit high-temperature superconductivity at very high pressures (above 100 GPa) (3). We have developed a suite of techniques that will allow experimental tests of theoretically predicted high critical superconducting temperatures (3).

Superconductivity and magnetism in transition metals and compounds: A novel quantum critical point (QCP) has been discovered in $BaFe_2As_2$ superconductor. In this material, (NFL) and Fermi-liquid (FL) regimes have been determined by the exponent n in the formula of $\rho=\rho_0+AT^n$ with ρ_0 the residual resistivity. In Fig.2, the squares and circles represent the antiferromagnetic (AFM) and superconducting (SC) transition temperatures, respectively. The black dashed lines represent the crossover temperatures. The results indicate the presence of a

quantum critical point (QCP) at a pressure around 5.0 GPa. Synchrotron spectroscopic techniques will be used to probe structural and magnetic properties near the QCP (4).

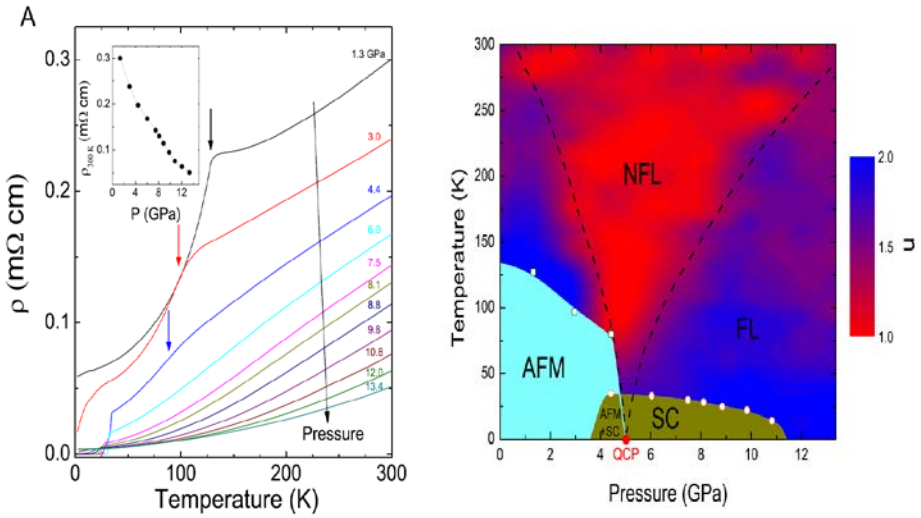


Fig. 2. Left panel – resistivity , right panel -phase diagram of $BaFe_2As_2$ under pressure. Red and blue colors represent non-Fermi liquid.

Future Plans

The new thrust area will focus on several high priority topics, e. g. insulator-metal transition and superconductivity in compressed hydrogen and hydrides, insulator-metal transitions in correlated materials and related superconducting properties of the metallic phases. We will study in detail magnetic and superconducting properties of transition metals and compounds (including high-Tc superconductors), that are potentially important for fundamental science and applications as high-temperature/high-critical parameter superconductors. Important part of the proposal is further improvement in the resistive and magnetic techniques based on Focused Ion Beam (FIB) technologies and photolithography tools, and implementation of the advanced sensing techniques with NV- cenetrs in diamond. The measurements will be performed at the static limit of the diamond anvil cell at high and very low temperatures, thus greatly expanding the horizon in the search for novel physical phenomena at ultrahigh pressures.

References

1. E. Zurek, R. Hoffmann, N. W. Ashcroft, A. R. Oganov, A. O. Lyakhov, A little bit of lithium does a lot for hydrogen. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17640 (2009).
2. P. Baettig, E. Zurek, Pressure-Stabilized Sodium Polyhydrides: NaH_n(n>1). *Phys. Rev. Lett.* **106**, 237002 (2011).
3. H. Wang, J. S. Tse, K. Tanaka, T. Iitaka, Y. Ma, Superconductive sodalite-like clathrate calcium hydride at high pressures. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 6463 (2012).
4. G. Giovannetti, et al. Proximity of iron pnictide superconductors to a quantum tricritical point. Nat Commun 2, 398 (2011).

Publications since 2013

1. Wang, Shibing, Jianbo Zhang, Jinyuan Yan, Xiao-Jia Chen, Viktor Struzhkin, Wojciech Tabis, Neven Barišić, Mun K Chan, Chelsey Dorow, Xudong Zhao, Martin Greven, Wendy L Mao, Ted Geballe, Strain derivatives of T c in $HgBa_2CuO_{4+\delta}$: The CuO2 plane alone is not enough, Physical Review B **89** , 024515 (2014).

2. Doherty, Marcus W, Viktor V Struzhkin, David A Simpson, Liam P McGuinness, Yufei Meng, Alastair Stacey, Timothy J Karle, Russell J Hemley, Neil B Manson, Lloyd CL Hollenberg, Steven Prawer, " Electronic Properties and Metrology Applications of the Diamond NV− Center under Pressure", *Phys. Rev. Lett.,* **112**, 047601 (2014).

3. Goncharov, A. F., J. S. Tse, Wang, Hui, Yang, Jianjun, Struzhkin, Viktor V., Howie, Ross T., Gregoryanz, Eugene, "Bonding, structures, and band gap closure of hydrogen at high pressures." *Physical Review B* **87**: 024101 (2013).

4. Rotundu, C. R., T. Ćuk, R. L. Greene, Z. -X. Shen, R. J. Hemley, and V. V. Struzhkin, High-pressure resistivity technique for quasi-hydrostatic compression experiments, Review Scientific Instruments **84**, 063903 (2013).

5. Gavriliuk, A. G., I. S. Lyubutin, S. S. Starchikov, A. A. Mironovich, S. G. Ovchinnikov, I. A. Trojan, Y. Xiao, P. Chow, S. V. Sinogeikin, V. V. Struzhkin, The magnetic PT phase diagram of langasite $Ba_3TaFe_3Si_2O_{14}$ at high hydrostatic pressures up to 38 GPa, Applied Physics Letters **103**, 162402 (2013).

6. Ranga P. Dias, Choong-Shik Yoo, Viktor V. Struzhkin, Minseob Kim,Takaki Muramatsu, T. Masuoka, Yasuo Ohishi, and Stainislav Sinogelkin, Superconductivity and Magnetic Ordering in Highly Disordered Carbon Disulfide Under Pressure, PNAS, **110**, 11720-4 (2013)

7. Yamanaka, T., A Kyono, Y Nakamoto, Y Meng, S Kharlamova, VV Struzhkin, H Mao,High-pressure phase transitions of Fe3–xTixO4 solid solution up to 60 GPa correlated with electronic spin transition, American Mineralogist 98 (4), 736-744 (2013).

8. Rotundu, C. R. and Struzhkin, V. V. and Somayazulu, M. S. and Sinogeikin, S. and Hemley, Russell J. and Greene, R. L, High-pressure effects on single crystals of electron-doped $Pr_{2-x}Ce_xCuO_4$, *Phys. Rev. B* **87**, 024506 [5], (2013).

9. Kurakevych, Oleksandr O., Timothy A. Strobel, Duck Young Kim, Takaki Muramatsu and Viktor V. Struzhkin, Na-Si Clathrates Are High-Pressure Phases: A Melt-Based Route to Control Stoichiometry and Properties, *Cryst. Growth Des*. **13**, 303–307 (2013).

10. Lyubutin, I. S., V.V. Struzhkin, A. A. Mironovich, A. G. Gavriliuk, P. G. Naumov, J. F. Lin, S. G. Ovchinnikov, S. Sinogeikin, P. Chow, Y. Xiao, Quantum critical point and spin

fluctuations in the lower-mantle ferropericlase, Proceedings of the National Academy of Sciences **110** , 7142-7147 (2013).

11. Derzsi, Mariana, Armand Budzianowski, Viktor V. Struzhkin, Przemysław J. Malinowski, Piotr J. Leszczyński, Zoran Mazej and Wojciech Grochala, Redetermination of crystal structure of Ag(II)SO_4 and its high pressure behavior up to 30 GPa, *CrystEngComm*, **15**, 192-198 (2013).

Toward Multimodal Spatiotemporally Resolved X-ray Imaging for Mesoscale Science

Haidan Wen, Advanced Photon Source, Argonne National Laboratory

Program Scope

Heterogeneity highlights the complexity of mesoscale materials science where the collective behavior and interaction of individual members prevail. Imaging heterogeneity in the time domain is the key to understanding and harnessing this aspect of real materials for their functionality. The program scope is to visualize the mesoscale dynamics that spans a hierarchy of time (10^{-10}-10^{-3} s), space (10^{-8} to 10^{-4} m) and energy (1-100 meV) scales by multimodal spatiotemporally resolved x-ray imaging. This program is at the proposal stage and will greatly benefit two newly funded proposals by DOE-BES (Grant No. DE-SC0012375 and DE-SC0012509).

Recent Progress

Two recent studies led by the PI demonstrated the importance of spatiotemporal resolved measurements. The first is a study of photoinduced structural phase transition in a VO_2 and the second is a study of near-field THz-driven lattice dynamics in $BaTiO_3$.

In the first example, we show that the structural phase transition of a VO_2 thin film (Fig.1a) upon a homogenous optical excitation occurs inhomogeneously. Upon 800 nm, 100 fs pulse excitation, the monoclinic and rutile Bragg intensity were simultaneously monitored by either an unfocused or focused hard x-ray probe (Fig.1b). The scanning probe by a 300 nm x-ray beam revealed two-dimensional (2D) intensity maps of the corresponding structural phases at each time delay (Fig. 1c). As marked by the red arrows in Fig. 1c, the region showing prominent increase of the rutile intensity were accompanied by a decrease of the monoclinic intensity. Since each point in the 2D maps was obtained by averaging 10000 pump-probe events, if the phase transition occurs at random nucleation sites for each pump-probe event, these inhomogeneous features would be washed out.

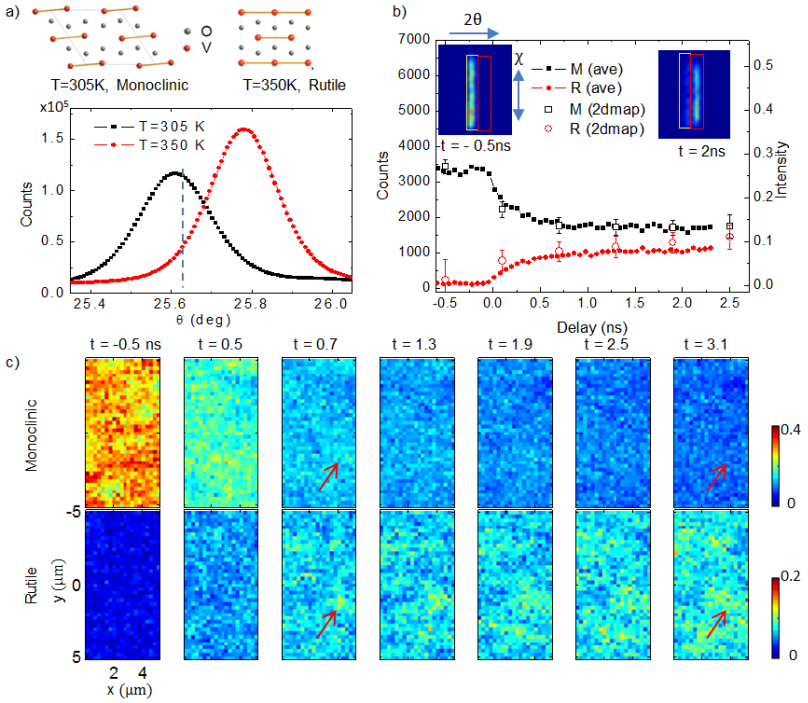


Fig. 1 a) The lattice structure of monoclinic and rutile phases of VO_2. The bottom plot shows the 002 Bragg peak of VO_2 below and above the transition temperature of T_c=340 K measured by x-ray diffraction probe of 10 keV at the APS; b) The Bragg intensity as a function of delay using unfocused (solid) and focused (open squares show integrated intensity of the 2D maps) x-ray probe at θ=25.61 degree. The inset shows the diffraction peak on an area detector where the monoclinic and rutile peaks are well separated along 2θ direction and can be simultaneously monitored. The yellow and red rectangles show the integration areas of monoclinic and rutile Bragg intensities respectively. The intensity spread along χ-direction is due to mosaicity of the film. c) The 2D Bragg intensity maps as a function of delay. The arrows point to one of the pinning sites.

The fact that we observed this inhomogeneous increase of Bragg intensity supports that the rutile phase developed at pinning sites during photoinduced phase transition. The on-going analysis will reveal the spatiotemporally resolved dynamics of the structural phase transition.

In the second example, we demonstrated that a localized THz excitation created an inhomogeneous structural profile that was mapped by a focused x-ray probe. A THz pulse, when coupled with metamaterials, can create a localized ultrafast and intense electric field. In this experiment, a THz pulse with a peak field of 100 kV/ cm was incident on a 100 nm-thick gold bowtie structure with a 400 nm-wide slit on top of a 90 nm $BaTiO_3$ film. Since the excitation volume is confined by the enhancement region across the slit, we employed a 12 keV x-ray pulse focused by a zone plate to 400 nm FWHM to probe the THz-induced structural change within the slit. The diffraction intensity at the low angle side of 002 Bragg peak was monitored by a gated area detector as a function of delay between the THz and x-ray pulses (Fig.2 a). The increase of diffraction intensity is a result of Bragg peak shift to the lower angle, corresponding to a lattice expansion. By scanning the sample across the x-ray probe, an enhanced THz-induced diffraction signal was observed across the slit (Fig.2b). The differential signal before and after excitation was normalized to the signal measured at a bare film without the gold slit and shows 13 folds enhancement of the structural change in the slit. The structural change is a result of localized THz field coupling to ferroelectric polarization in the film, paving a new way to manipulate material properties using confined ultrafast electric fields.

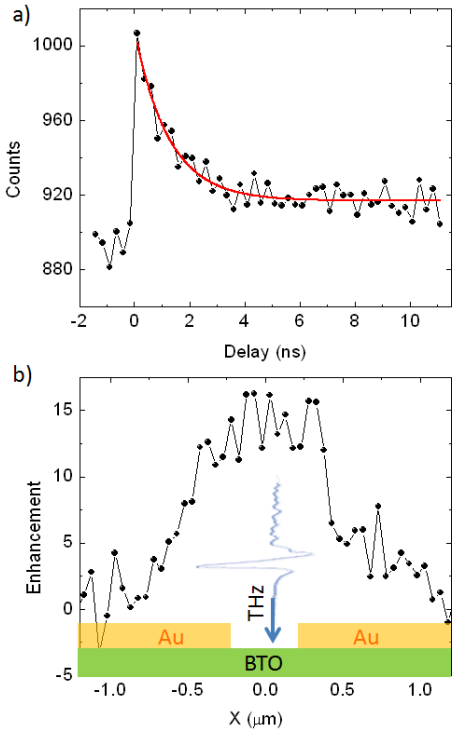


Fig. 2 a) The diffraction intensity at low angle (θ=14.825°) of 002 Bragg peak of the (BTO) film as a function of delay between THz pump and x-ray probe pulses. The red line is an exponential fit with a time constant of 1.2 ns. b) The THz enhancement factor measured by the structural response of the (BTO) film as a function of probe position across the slit. The inset shows the side view of THz near-field excitation enhanced by a 400 nm wide, 100 nm thick Au slit.

Future Plans

These initial efforts as supported by Argonne LDRD Grant 2013-036 provide essential methods and tools to two recently funded projects led by Dr. Gopalan (DE-SC0012375) and Dr. Xu (DE-SC0012509). For example, the time-resolved hard x-ray nanodiffraction will be used for ultrafast grazing incidence x-ray diffraction study of small WSe_2 flakes grown by Xu group. It also provides an ideal x-ray probe for localized near-field THz excitation with metamaterials designed by Averitt Group and ferroic thin films grown by Martin Group. The resulted structural dynamics can be correlated with the localized electronic properties measured by Basov group. The experiments will be guided by and corroborate the theoretical prediction provided by Millis, Rondinelli and Xiao. Besides these funded activities, the future plan is to combine time-resolved capabilities with state-of-the-art coherent x-ray imaging and in-situ near-field optical microscope together to enable multimodal simultaneous spatiotemporally resolved optical, THz and x-ray imaging for visualizing mesoscopic dynamics.

Theoretical Investigation of Valley Dynamics and Berry Phase Effect in 2D Materials

Di Xiao, Department of Physics, Carnegie Mellon University

Program Scope

In many crystals the Bloch bands have degenerate but inequivalent energy extrema in the momentum space, known as valleys. The valley pseudospin, which enumerates degenerate energy extrema, constitutes a well-defined discrete degree of freedom for low-energy carriers that may be used to encode and process information. The primary goal of this program is to theoretically investigate the valley dynamics in a family of novel two-dimensional (2D) materials–monolayers of transition metal dichalcogenides (TMDs), particularly phenomena pertaining to the Berry phase of Dirac electrons. This program is supported by the newly funded DOE-BES proposal (Grant No. DE-SC0012509).

Recent Progress

Although the investigation of valley pseudospin dates back to the late 1970's on 2D electron gases in silicon inversion layers, dynamic control of valley pseudospin has not been realized in solid-state systems because of a lack of intrinsic valley properties which can couple to external fields. In a recent breakthrough,[1] we predicted that in monolayer TMDs, due to the lack of an inversion center, the valley pseudospin can be associated with a number of valley-contrasting phenomena, such as the valley magnetic moment, the valley Hall effect, and the valley-dependent optical selection rule. The unique valley physics has its roots in the Berry phase theory of electron dynamics[2] developed by the PI and others–by breaking the inversion symmetry, the Bloch electrons in opposite valleys acquire opposite Berry phase, a quantity that also plays a central role in the theory of topological insulators. Soon after our prediction, the optical generation of valley polarization by circularly polarized light was experimentally verified in monolayer MoS2.[3-5] Working with PI-Xu, we have also demonstrated the ability to electrically control the degree of valley polarization in bilayer MoS2.[6] In the following we present two recent studies on the valley dynamics and Berry phase effect.

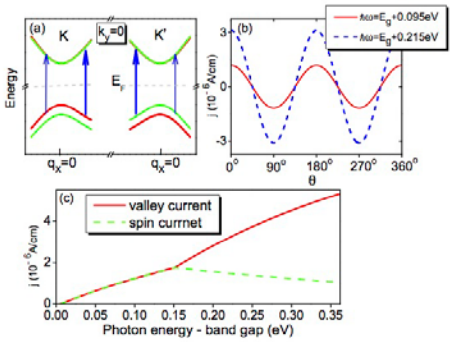


Figure 1 Linear valley and spin photogalvanic effect (PGE) of monolayer MoS_2. (a) Schematics of band dispersion around valley K(K') along the k_x axis. Red (green) curves denote states with spin up (down). Thick (thin) solid blue arrows depict strong (weak) optical transition rates in each valley. Fermi energy E_F = 0. (b) Angular dependence of valley current on the polarization angle θ along zigzag direction. (c) Valley and spin current as functions of photon energy.

In addition to valley polarization, an equally important quantity is valley current. So far only valley-polarized electric current has been reported. In analogy to spintronics, it would be desirable to generate a pure valley current, in which there is no net motion of charge; carriers in opposite valley move in opposite direction. Such a pure valley current would generate minimal Joule heating. Recently we proposed a new approach to the generation and detection of a pure valley current by optical means (Figure 1). Based on both symmetry analysis and an effective $k \cdot p$ Hamiltonian, we show that a pure valley current can be generated by linearly polarized light in

monolayer TMDs. The generating mechanism parallels that for spin current. However, the role of spin-orbit coupling is replaced by the trigonal warping in the band structure, which is entirely a lattice effect. Due to the unique spin-valley coupling in this system, the generated valley current is accompanied by a spin current. We also developed a theory for valley diffusion that takes into account the spin-valley coupling, and show that the pure valley current can be detected by either photoluminescence measurements or the ultrafast pump-probe technique. Our method, together with the previously demonstrated generation of valley polarization opens up the exciting possibility of ultrafast optical-only manipulation of the valley index.

The other unique feature of monolayer TMDs is the giant exciting binding energy (~ 0.5 eV), which offers us an ideal platform to investigate exciton physics. Recently, we studied the Berry phase effect on exciton formation and energy spectrum of massive Dirac fermions. We showed that the presence of the Berry phase generally leads to an energy splitting between valley exciton states with opposite angular momentum (Figure 2). This splitting is caused by the chiral nature of Dirac fermions. We also show that a gauge-invariant angular momentum quantum number should be used to correctly label the exciton states and to interpret theoretical calculations. The chiral nature of the Dirac fermions also leads to an unusual optical selection of the valley excitons. This study reveals the importance of Berry phase in exciton physics, and calls for a thorough investigation of its effect on many-body phenomena.

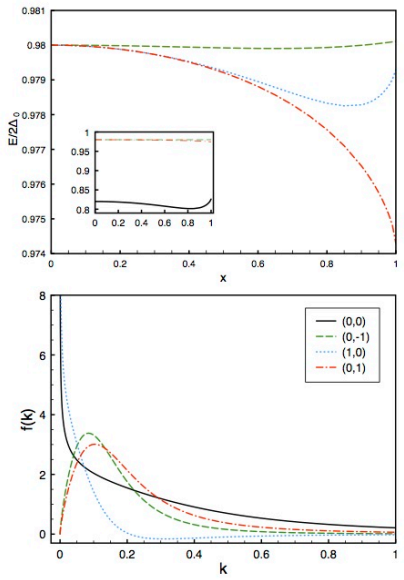


Figure 2 a) The top panel shows the evolution of exciton energy vs the band coupling parameter *x*. The bottom panel depicts their momentum space wave functions.

Future Plans

Rapid experimental and theoretical progress based on 2D quantum materials points to an outstanding new direction–investigation of valley quantum dynamics and Berry phases effect of composite particles such as bound electron-hole pairs. While early investigations of valley physics were led by theoretical predictions, recent experiments have brought out new challenges and opportunities. The original MX2 theory was developed based on the non-interacting electron model with an infinite valley lifetime. These assumptions are obviously too simplistic to describe real materials. Developing theories to take into account various factors that can affect the valley life time and many-body interactions will be the next step. We will also investigate the Berry phase effect on exciton dynamics.

1. D. Xiao, G.-B. Liu, W. Feng, X. Xu, W. Yao, Phys. Rev. Lett. **108**, 196802 (2012).
2. D. Xiao, M.-C. Chang, Q. Niu, Rev. Mod. Phys. **82**, 1959 (2010).
3. K. F. Mak, K. He, J. Shan, and T. F. Heinz, Nature Nanotechnol. **7**, 494 (2012)
4. H. Zeng, J. Dai, W. Yao, and X. Cui, Nature Nanotechnol. **7**, 490 (2012)
5. T. Cao et al, Nature Commun. **3**, 887 (2012)
6. S. Wu, Nature Phys. **9**, 149–153 (2013).

Photon-Electron Interactions in Dirac Quantum Materials

Xiaodong Xu, Department of Physics and Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195

Program Scope

The objective of this proposal is to understand and control electron, photon, and phonon interactions in new classes of Dirac quantum materials, such as graphene and atomically thin transition metal dichalcogenides (TMDs), for new energy harvesting technologies. These materials have unusual physical properties which allow us to probe unprecedented quantum phenomena otherwise not assessable in other material systems. Graphene is a gapless Dirac material with linear energy momentum dispersion for low energy carriers. It has unusual quantum Hall effects with large Landau level spacing, which enables us to investigate non-equilibrium carrier dynamics in the quantum Hall (QH) regime. Monolayer TMDs have a honeycomb lattice structure like graphene. This fact gives them analogous Dirac-like electronic valleys at the corners (K-points) of the hexagonal Brillouin zone. A key difference from graphene is that TMDs possess inversion asymmetry, which gives rise to direct band gaps in the visible regime and non-trivial Berry-phase related physics[3]. But more profoundly, $\pm K$ valleys have circularly polarized optical selection rules, providing the first solid state system for dynamic control of the valley degree of freedom. A second important difference, arising from the transition metal, is large spin-orbit coupling which spin-splits the valence band by 150 ~ 450 meV. Combined with the inversion-symmetry breaking, this truly two-dimensional (2D) semiconductor affords new possibilities for manipulating charge, layer (dipole), spin, and valley degrees of freedom to explore exotic physical phenomena[1].

Recent Progress

Non-equilibrium Quantum Hall Carrier Dynamics: The QH effect is probably the most famous and dramatic phenomenon in the physics of 2D systems. However, remarkably little is known about non-equilibrium carrier dynamics in the QH regime, either theoretically or experimentally. We have recently performed the first measurements of hot-carrier relaxation in graphene with fully quantized Landau levels. We found that carrier relaxation is dramatically different from the classical regime which is dominated by disorder assisted cooling. Further, by tuning the carrier density, we observed that the carrier relaxation time oscillates with the period of the Landau level spacing (Fig. 1a). This observation implies the tuning of carrier diffusion by controlling the longitudinal resistance.

Optoelectronic Control of Spin and Pseudospin Dynamics: A central theme in condensed matter physics is to study and understand the consequences of the interplay between distinct quantum degrees of freedom of electrons. In bilayer WSe_2, we discovered a new coupling effect between spin, valley, and layer pseudospins. Here, both spin and valley degrees of freedom are associated with magnetic moments. The layer degree of freedom is associated with electrical polarization, which corresponds to electrons either in the upper or lower layer. We both theoretically[2] and experimentally[3] demonstrated the strong coupling effects between spin and

layer pseudospin. Due to the strongly suppressed interlayer hopping, these strongly coupled indices lead to a long spin relaxation time. We were also able to show electrical control of spin Zeeman splitting without any applied magnetic fields (Fig. 1b).

Electroluminescence from Valley Excitons: How electronic energy can most efficiently be converted into light emission remains one of the DoE's greatest challenges. We address this by investigating electroluminescence at the single atomic layer limit. We identify light emission from the radiative recombination of valley excitons[4], i.e. excitons localized at the corners of the hexagonal Brillouin zone, which is important for further investigation of polarized light emission using unique spin-valley coupled physics in TMDs. By tuning the amplitude of the electrical current, we observe electroluminescence from impurity bound excitons, negatively charged excitons, positively charged excitons, and neutral excitons (Fig. 1c). Such rich excitonic electroluminescence arises from the strong Coulomb interaction between electrically injected electrons and holes.

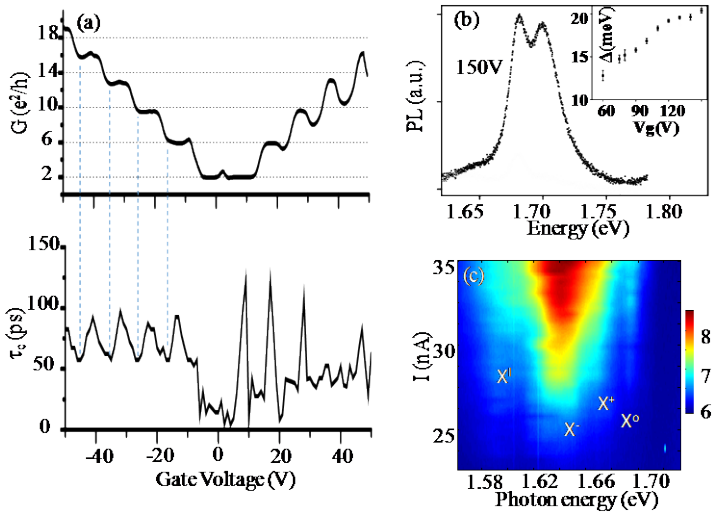


Figure 1. (a) Top: two-terminal conductance of graphene at B=7.5T. Bottom: Hot-carrier relaxation time constant as a function of gate voltage, showing oscillation. (b) Photoluminescence spectrum of bilayer WSe_2 at a gate voltage of 150 V. Inset: energy separation of the doublet as a function of gate voltage. (c) Electroluminescence intensity plot of monolayer WSe_2 as a function of injection current and emission energy. X^o, X^+, X^- and X^I denote neutral, positively charged, negatively charged, and impurity bounded excitons.

Future Plans

We plan to further illuminate the energy relaxation of hot-carriers in the integer QH regime in graphene, and possibly in the fractional QH regime, which is beyond the single particle picture. We will also investigate the single particle, composite particle, spin, and pseudospin dynamics in 2D TMD heterostructures[5,6], which may lead to new physical phenomena not accessible in current studies of monolayers.

References

1. Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Nat Phys 10, 343 (2014).
2. Gong, Z. et al. Nat Commun 4, Article number: 2053 | DOI: 10.1038/ncomms3053 (2013).
3. Jones, A. M. et al. Nat Phys 10, 130 (2014).
4. Ross, J. S. et al. Nature nanotechnology 9, 268 (2014).
5. Huang, C. et al. Nature Materials doi:10.1038/nmat4064 (2014).
6. Pasqual, R. et al., arxiv.org/abs/1403.4985.

Publications

1. C. Huang, S. Wu, A. M. Sanchez, J. J. P. Peters, R. Beanland, J. S. Ross, P. Rivera, W.Yao, D. H. Cobden, X. Xu, "Lateral heterojunctions within monolayer semiconductors", ***Nature Materials***, doi: 10.1038/NMAT4064 (2014).
2. J. A. Crosse, X. Xu, M. S. Sherwin, R. B. Liu, "Low power ultra-broadband terahertz sideband generation in bilayer graphene", ***Nature Communication*** 5, Article number: 4854 doi:10.1038/ncomms5854;
3. A. Singh, G. Moody, S. Wu, Y. Wu, N. J. Ghimire, J. Yan, D.G. Mandrus, X. Xu, X. Li, "Coherent Electronic Coupling in Atomically Thin MoSe2", ***Phys. Rev. Lett.*** 112, 216804 (2014).
4. X. Xu, W. Yao, D. Xiao, T. F. Heinz, "Spins and Pseudospins in Transition Metal Dichalcogenides", ***Nature Physics*** 10, 343(2014).
5. H. Yu, G. Liu, P. Gong, X. Xu, W. Yao, "Bright excitons in monolayer transition metal dichalcogenides: from Dirac cones to Dirac saddle points", ***Nature Communications*** 5, Article number: 3876 | doi:10.1038/ncomms4876 (2014).
6. S. Wu, S. Buckley, A. M. Jones, J. S. Ross, N. J. Ghimire, J. Yan, D. G. Mandrus, W. Yao, F. Hatami, J. Vučković, A. Majumdar, X. Xu, "Control of Two-Dimensional Excitonic Light Emission via Photonic Crystal", ***2D Materials***, 1 011001 doi:10.1088/2053-1583/1/1/011001 (2014).
8. J. Ross, P. Klement, A. Jones, N. Ghimire, J. Yan, D. Mandrus, T. Taniguchi, K. Watanabe, K. Kitamura, W. Yao, D. Cobden, X. Xu, "Electrically Tunable Excitonic Light Emitting Diodes based on Monolayer WSe2 p-n Junctions", ***Nature Nanotechnology*** 9, 268 (2014).
9. A. M. Jones, H. Yu, J. Ross, P. Klement, N.J. Ghimire, J. Yan, D.G. Mandrus, W. Yao, X. Xu. "Spin-Layer Locking Effects in Optical Orientation of Exciton Spin in Bilayer WSe2." ***Nature Physics*** 10, 130 -134 (2014).
10. R. Chu, X. Li, S. Wu, Q. Niu, W. Yao, X. Xu, and C. Zhang, "Valley-splitting and valley-dependent inter-Landau-level optical transitions in monolayer MoS2 quantum Hall systems", ***Physical Review B*** doi: 10.1103/PhysRevB.90.045427 (2014).
11. J. S. Ross, S. Wu, H. Yu, N.J. Ghimire, A.M. Jones, G. Aivazian, J. Yan, D.G. Mandrus, D. Xiao, W. Yao, X. Xu. "Electrical Control of Neutral and Charged Excitons in a Monolayer Semiconductor." ***Nature Communication*** 4, Article number: 1474 | doi: 10.1038/ncomms2498 (2013).
12. S. Wu, C. Huang, G. Aivazian, J. S Ross, D. H Cobden, X. Xu, "Vapor-Solid Growth of High Quality MoS2 Monolayers With Near-Unity Valley Polarization", ***ACS Nano*** 7, 2768 | doi: 10.1021/nn4002038 (2013)
13. Z. Gong, G. Liu, H. Yu, D. Xiao, X. Cui, X. Xu, W. Yao. "Magnetoelectric Effects and Valley Controlled Spin Quantum Gates in Transition Metal Dichalcogenide Bilayers." ***Nature Communication*** 4, Article number: 2053 | doi: 10.1038/ncomms3053 (2013)
14. H. Yuan, M.S. Bahramy, K. Morimoto, S. Wu, K. Nomura, B. Yang, H. Shimotani, R. Suzuki, M. Toh, C. Kloc, X. Xu, R. Arita, N. Nagaosa, Y. Iwasa. "Zeeman-type Spin Splitting Controlled by an Electric Field." ***Nature Physics*** 9, 563-569 (2013).
15. S. Wu, J.S. Ross, G. Aivazian, A. Jones, Z. Fei, G. Liu, W. Zhu, D. Xiao, W. Yao, D. Cobden, X. Xu. "Electrical Tuning of Valley Magnetic Moment through Symmetry Control in Bilayer MoS2." ***Nature Physics*** 9, 149-153 (2013).

Author Index

Participant List

Participant List

Name	Organization	E-Mail
Abbamonte, Peter	University of Illinois	abbamont@illinois.edu
Averitt, Richard	University of California, San Diego	raveritt@ucsd.edu
Basov, Dmitri	University of California, San Diego	dbasov@ucsd.edu
Bergmann, Uwe	Stanford University	bergmann@slac.stanford.edu
Billinge, Simon	Brookhaven National Laboratory / Columbia Univ.	billinge@bnl.gov
Bozin, Emil	Brookhaven National Laboratory	bozin@bnl.gov
Burns, Clement	Western Michigan University	clement.burns@wmich.edu
Chiang, Tai	University of Illinois at Urbana-Champaign	tcchiang@illinois.edu
Clarke, Roy	University of Michigan	royc@umich.edu
Click, Tammy	ORAU	tammy.click@orau.org
Dean, Mark	Brookhaven National Laboratory	mdean@bnl.gov
Devereaux, Tom	Stanford University	tpd@stanford.edu
Durakiewicz, Tomasz	National Science Foundation	tdurakie@nsf.gov
Dürr, Hermann	Stanford University	hdurr@slac.stanford.edu
Engel-Herbert, Roman	Pennsylvania State University	rue2@psu.edu
Evans, Paul	University of Wisconsin-Madison	evans@engr.wisc.edu
Fogler, Michael	University of California, San Diego	mfogler@ucsd.edu
Fong, Dillon	Argonne National Laboratory	fong@anl.gov
Freeland, John	Argonne National Laboratory	freeland@anl.gov
Fuoss, Paul	Argonne National Laboratory	fuoss@anl.gov
Gedik, Nuh	Massachusetts Institute of Technology	gedik@mit.edu
Gopalan, Venkatraman	Pennsylvania State University	vgopalan@psu.edu
Hasan, M. Zahid	Princeton University	mzhasan@princeton.edu
Headrick, Randall	University of Vermont	rheadrick@uvm.edu
Heinz, Tony	Stanford University	tony.heinz@columbia.edu
Hill, John	Brookhaven National Laboratory	hill@bnl.gov
Hilton, David	The University of Alabama at Birmingham	dhilton@uab.edu
Himpsel, Franz	University of Wisconsin Madison	fhimpsel@wisc.edu

Hruszkewycz, Stephan	Argonne National Laboratory	shrus@anl.gov
Kaindl, Robert	Lawrence Berkeley National Laboratory	RAKaindl@lbl.gov
Kapteyn, Henry	University of Colorado at Boulder	Henry.Kapteyn@colorado.edu
Karaiskaj, Denis	University of South Florida	karaiskaj@usf.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
Kim, Youngduck	Columbia University	yk2629@columbia.edu
Kirchmann, Patrick	Stanford University	kirchman@slac.stanford.edu
Lanzara, Alessandra	University of California, Berkeley	alanzara@lbl.gov
Lee, Wei-Sheng	Stanford University	leews@stanford.edu
Lindenberg, Aaron	Stanford University	aaronl@stanford.edu
Lu, Donghui	Stanford University	dhlu@slac.stanford.edu
Ludwig, Karl	Boston University	ludwig@bu.edu
Mao, Ho-kwang	Carnegie Institution for Science	hmao@carnegiescience.edu
Mao, Wendy	Stanford University	wmao@stanford.edu
Millis, Andrew	Columbia University	millis@phys.columbia.edu
Moore, Robert	Stanford University	rgmoore@slac.stanford.edu
Moritz, Brian	Stanford University	moritzb@slac.stanford.edu
Murnane, Margaret	University of Colorado at Boulder	murnane@jila.colorado.edu
Parise, John	Stony Brook University	john.parise@stonybrook.edu
Pechan, Michael	U.S. Department of Energy	michael.pechan@science.doe.gov
Petkov, Valeri	Carnegie Mellon University	petko1vg@cmich.edu
Reid, Alexander	Stanford University	alexhmr@slac.stanford.edu
Reis, David	Stanford University	dreis@slac.stanford.edu
Rondinelli, James	Northwestern University	jrondinelli@northwestern.edu
Schneider, Michael	National Institute of Standards and Technology	michael.schneider@nist.gov
Schwartz, Andrew	U.S. Department of Energy	andrew.schwartz@science.doe.gov
Shan, Jie	Pennsylvania State University	jus59@psu.edu
Shen, Guoyin	Carnegie Institution of Washington	gshen@ciw.edu

Shen, Zhixun	Stanford University	zxshen@stanford.edu
Shpyrko, Oleg	University of California, San Diego	oshpyrko@ucsd.edu
Skinner, Lawrie	Stony Brook University	lawrie.skinner@stonybrook.edu
Sobota, Jonathan	Stanford University	sobota@stanford.edu
Stephenson, Gregory	Argonne National Laboratory	stephenson@anl.gov
Stöhr, Joachim	Stanford University	stohr@slac.stanford.edu
Struzhkin, Viktor	Carnegie Institution for Science	vstruzhkin@carnegiescience.edu
Trigo, Mariano	Stanford University	mtrigo@slac.stanford.edu
Wen, Haidan	Argonne National Laboratory	wen@aps.anl.gov
Wilson, Lane	U.S. Department of Energy	Lane.Wilson@science.doe.gov
Xiao, Di	Carnegie Mellon University	dixiao@cmu.edu
Xu, Xiaodong	University of Washington	xuxd@uw.edu
You, Hoydoo	Argonne National Laboratory	hyou@anl.gov