X-ray Scattering
Principal Investigators' Meeting

Hilton Washington DC North/Gaithersburg
Gaithersburg, Maryland
November 9–10, 2016

This document was produced under contract number DE-SC0014664 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 abstract book summarizes the scientific content of the 2016 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 9–10, 2016, at the Hilton Washington DC North/Gaithersburg in Gaithersburg, Maryland, is the fifth 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 DMSE X-ray Scattering Principal Investigators' Meeting
Hilton Gaithersburg MD
November 9 & 10, 2016

Wednesday, November 9

7:00 – 8:00 **Breakfast** (Also poster setup, presentation loading on DOE computer. All presentations for Wednesday need to be loaded onto the DOE laptop, and posters for Wednesday should be set up under the corresponding panel label, both prior to the start of the meeting on Wednesday.)

8:00 – 8:10 **BES Welcome and Discussion of the Meeting Format**
Lane Wilson, BES, X-ray Scattering Program Manager

8:10 – 9:15 **Panel A (65-minute ensemble presentation)**

- Venkat Gopalan, Penn State University, **project lead**
  Roman Engel-Herbert (PSU), James Rondinelli (NWU), John Freeland (ANL), Haidan Wen (ANL), Lane Martin (LBNL), Andy Millis (Columbia), Dimitri Basov (Columbia), Rick Averitt (UCSD), Jacques Chakhalian (Arkansas)

9:15 – 10:20 General questions followed by small group discussions at each panelist poster

10:20 – 11:25 **Panel B**

- Zahid Hasan, Princeton **(8 mins)**
- Tai Chiang, University of Illinois UC **(8 mins)**
- Peter Abbamonte, University of Illinois UC **(8 mins)**
- Jason Hancock, University of Connecticut, **project lead (15 mins, ensemble presentation)**, Maxim Dzero, Kent State
- Mark Dean, BNL (Early Career) **(8 mins)**
- Nuh Gedik, MIT **(8 mins)**
- Oleg Shpyrko, University of California – San Diego **(8 mins)**

11:25 – 12:30 General questions and panel discussion followed by small group discussions at each panelist poster

12:30 – 2:00 ****Working lunch with continued Discussions, Introduction by Helen Kerch, Team Lead, Scattering and Instrumentation Sciences, DMSE, BES ****

2:00 – 3:00 **Panel C**

- Thomas Devereaux, SLAC, **project lead (45 mins, ensemble presentation)** ZX Shen, Tony Heinz, Aaron Lindenberg, Wei-Sheng Lee, Hong-Chen Jiang
- Valeri Petkov, Cent. Michigan University, **project lead (15 mins, ensemble presentation)**, Chuan-Jian Zhong, SUNY Binghamton

3:00 – 4:00 General questions and panel discussion followed by small group discussions at each panelist poster

4:00 – 5:05 **Panel D**

- ZX Shen, Stanford/SLAC, **project lead (50 mins, ensemble presentation)** Thomas Devereaux, Robert Moore, Brian Moritz, Patrick Kirchmann, Jonathan Sobota, Makoto Hashimoto, Donghui Lu
- Haidan Wen ANL (Early Career) **(8 mins)**
- Charles Fadley, University of California – Davis **(8 mins)**

5:05 – 6:10 General questions and panel discussion followed by small group discussions at each panelist poster

6:10 – 6:30 **Working Dinner:** End of day remarks, general discussion. Evening: small group meetings, collaborative exchanges

Thursday, November 10

7:00 – 8:00 **Breakfast** (Also poster setup, presentation loading on DOE computer. All presentations for Thursday need to be loaded onto the DOE laptop, and posters for Thursday should be set up under the corresponding panel label, both prior to the start of the meeting on Thursday.)

8:00 – 9:10 **Panel E**

- Xiaodong Xu, University of Washington, **project lead (35 mins, ensemble presentation)**, Haidan Wen (ANL), Nuh Gedik (MIT), Di Xiao (CMU)
- Denis Karaiskaj, University South Florida, **project lead (25 mins, ensemble presentation)**, David Hilton (UAB), Jie Shan (PSU)
- Paul Evans, University of Wisconsin **(8 mins)**

9:10 – 10:15 General questions and panel discussion followed by small group discussions at each panelist poster

10:15 – 11:25 **Panel F**

- Aaron Lindenberg, SLAC, **project lead (30 mins, ensemble presentation)** Will Chueh, David Reis, Mariano Trigo
- Paul Fuoss, ANL, **project lead (40 mins, ensemble presentation)** Brian Stephenson, Hoydoo You, Dillan Fong, Stephan Hruszkewycz, Matthew Highland

11:25 – 12:30 General questions and panel discussion followed by small group discussions at each panelist poster

12:30 – 1:30 **Working Lunch with Discussion**

1:30 – 2:40 **Panel G**

- Dimitri Basov, UC–San Diego/Columbia, **project lead (30 mins, ensemble presentation)**, James Hone (Columbia), Andy Millis (Columbia), Rick Averitt (UCSD), Michael Fogler (UCSD)
- Alessandra Lanzara, LBNL, **project lead (15 mins, ensemble presentation)** Robert Kaindl
- Ian Robinson, BNL, **project lead (25 mins, ensemble presentation)** Simon Billinge, Emil Bozin

2:40 – 3:45 General questions and panel discussion followed by small group discussions at each panelist poster

3:45 – 5:00 **Panel H**

- Wendy Mao, SLAC **(8 mins)**
- Guoyin Shen, Carnegie Institute of Washington, **project lead (25 mins, ensemble presentation)**, David Mao (CIW), Viktor Struzhkin (CIW)
- Margaret Murnane, University of Colorado, **project lead (25 mins, ensemble presentation)**, Henry Kapteyn (Colorado), Tom Silva (NIST)
- Jeffrey Hastings, University of Kentucky **(8 mins)**
- Steven Kevan, LBNL **(8 mins)**, Sujoy Roy (LBNL)

5:00 – 6:10 General questions and panel discussion followed by small group discussions at each panelist poster

6:10 – 6:30 **Working Dinner:** General discussion on new opportunities
End of meeting wrap-up

Table of Contents

Table of Contents

Abstracts

Novel X-Ray Probes of Electronically Heterogeneous Quantum Materials

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

Program Scope

The objective of this project is to define a new approach to studying valence band phenomena in materials in which the electronic structure is intrinsically heterogeneous or disordered. The short-term focus will be on detecting charge order in optimally doped copper-oxides and parameterizing the phenomenology of its intertwining with superconductivity. Our strategy will be to use energy- and momentum-resolved resonant soft x-ray scattering techniques, blurring the lines between what is traditionally called "resonant x-ray diffraction" (RXD) and "resonant inelastic x-ray scattering" (RIXS). For this purpose, we will use a new generation of energy-resolved soft x-ray spectrometers, particularly the new qRIXS instrument at the Advanced Light Source (ALS). This approach may be readily adapted to IR pump-soft x-ray-probe techniques, enabling study of collective bosonic excitations at LCLS.

Recent Progress: *Reexamination of the effective fine structure constant of graphene as measured in graphite*

After four years of effort, we completed a refined and improved study of the influence of screening on the effective fine structure constant of graphene, $\alpha^*(q,\omega)$, as measured in graphite using inelastic x-ray scattering. This follow-up to our previous study [J. P. Reed et al., Science **330**, 805 (2010)] was carried out at the Advanced Photon Source using two times better energy resolution, five times better momentum resolution, and an improved sample chamber with lower background. We compared our results to random-phase approximation (RPA) calculations and evaluated the relative importance of interlayer hopping, excitonic corrections, and screening from high energy excitations involving the σ bands. We found that the static, limiting value of α^* falls in the range 0.25–0.35, which is higher than our previous result of 0.14, but still below the value expected from RPA. We show the reduced value is not a consequence of interlayer hopping effects, which were ignored in our previous analysis, but of a combination of excitonic

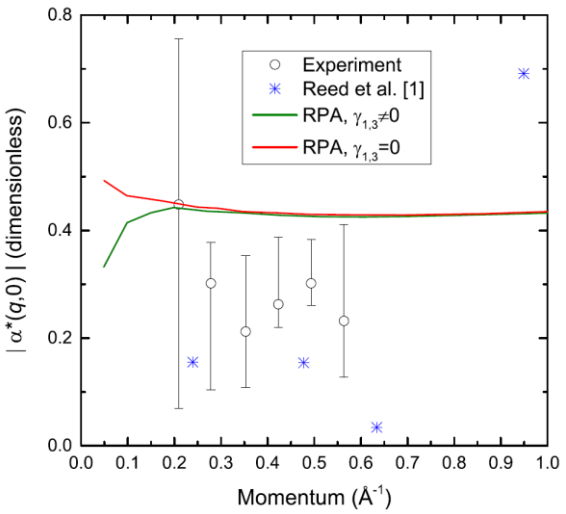


Figure 1 Asymptotic properties of the effective fine structure constant of graphene, as measured in graphite using inelastic x-ray scattering. Our study suggests a limiting value in the range 0.25-0.35, which is significantly lower than the RPA value and explains the absence of an excitonic transition at low temperature.

effects in the $\pi \rightarrow \pi^*$ particle-hole continuum and background screening from the σ-bonded electrons. We found that σ-band screening is extremely strong at distances of less than a few nanometers, and should be highly effective at screening out short-distance, Hubbard-like interactions in graphene as well as other carbon allotropes. The conclusions of this study apply not only to graphene but all Dirac and Weyl-type semimetals [2].

Future Plans: *Resonant x-ray scattering using the qRIXS spectrometer at ALS*

After 30 years of study, the origin of superconductivity in the copper-oxides is still unknown, making these materials an excellent case study for the development of scattering techniques that provide new insight into valence band phenomena. One of the key questions is whether valence band charge order, which is now established to exist in all cuprates [1], is somehow relevant to superconductivity. The challenge is that charge order in optimally doped cuprates, in which superconductivity is most pronounced, is highly disordered. It therefore cannot be studied with conventional soft x-ray scattering techniques, which are plagued by an intense, inelastic fluorescence background, which masks diffuse elastic scattering. To address this problem, we intend to use several new energy-resolved x-ray instruments, notably the qRIXS instrument at ALS, to attempt to detect this order and study how it interacts with superconductivity.

References

1. B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, J. Zaanen, From quantum matter to high-temperature superconductivity in copper oxides, Nature **518**, 179 (2015)

Publications (Oct. 2014 – present | this activity only)

2. Y. Gan, G. A. de la Peña, A. Kogar, B. Uchoa, D. Casa, T. Gog, E. Fradkin, P. Abbamonte, Reexamination of the effective fine structure constant of graphene as measured in graphite, Phys. Rev. B **93**, 195150 (2016)
3. X. M. Chen, A. J. Miller, C. Nugroho, G. A. de la Peña, Y. I. Joe, A. Kogar, J. D. Brock, J. Geck, G. J. MacDougall, S. L. Cooper, E. Fradkin, D. J. Van Harlingen, P. Abbamonte, Influence of Ti doping on the incommensurate charge density wave in 1*T*-TaS_2, Phys. Rev. B **91**, 245113 (2015)
4. T. Ritschel, J. Trinckauf, K. Koepernik, B. Buchner, M. v. Zimmermann, H. Berger, Y. I. Joe, P. Abbamonte, J. Geck, Orbital textures and charge density waves in transition metal dichalcogenides, Nature Phys. **11**, 328 (2015)
5. 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)

See also (Funding info not permitted by journal):

6. P. Abbamonte, 2D Superconductivity: Electric tuning of many-body states, Nature Nano. **11**, 115 (2016)

Transient superconductivity at nano- and meso-scales (DE-SC0012592)

D.N. Basov, James Hone, Andrew Millis (Columbia University)
Richard Averitt, Michael M. Fogler (UCSD)

Executive summary

High-T_c superconductivity is surpassed by few, if any, other unresolved problems in contemporary physics in its richness, complexity, impact on other fields and potential technological importance. Recent discoveries reveal that the highest transition temperatures emerge under extreme experimental conditions such as ~200 GPa pressure, ~MV/cm electric fields or femtosecond optical pulses. This avenue of research is challenging since it requires the development of novel experimental methods and new theoretical tools suitable to tackle the problem of external stimuli at the extremes.

Since August 2014 this team of investigators has been engaged in a program aimed at exploring ultra-fast and nano-scale dynamics of complex materials driven by the goal to investigate and elucidate non-equilibrium properties of superconductors under photo-excitation. Our team has identified three essential pillars of this ambitious program: *i)* development of novel ultra-fast optical techniques for pump-probe studies of materials at the nano-scale in the regime of resonant photo-excitation; *ii)* development of meso-scale antenna structures and hybrid meta-materials needed to obtain strongly enhanced optical fields at the surface of studied superconductors and *iii)* the development of theoretical approaches suitable to explain and predict the response of superconductors under ultra-fast photo-excitation. We have achieved significant progress documented through publications in high impact journals that was only possible because of complimentary expertise of team members covering all aspects of this program. Capitalizing on these recent results, our team is uniquely positioned to make major advances in the area of transient photo-stimulated superconductivity.

On-going and future research is focused on several different classes of exotic superconductors integrated with metamaterials and multi-layered structures including high-T_c cuprates and chalcogenides superconductors. The experimental part is centered at pump-probe experiments where the field of the excitation laser is concentrated in nano- and meso-scale regions using optical antennas and/or using hyperbolic van der Waals (vdW) materials as sub-diffractional focusing “lenses”. We interrogate the photo-induced state using an ample set of spectroscopy and nano-imaging tools operational from THz through infrared (IR) frequencies. This spectral range is particularly informative in the case of superconductors, providing direct access to the electromagnetic signatures of superconductivity including the superfluid density and energy gap. In combination, the material systems investigated by our team will establish a comprehensive physical picture of non-equilibrium superconductivity.

The above experiments and their theoretical analysis will provide insights into non-superconducting metastable states triggered by photo-excitation that compete/coexist with superconductivity. As recently demonstrated by the co-investigators, nano-IR experiments with 10 nm spatial resolution are particularly informative in uncovering novel phases of complex materials that only occur at nano- and/or meso-scale and therefore remain “invisible” for common area-averaging probes. *Basov* and *Averitt* concentrate on pump-probe spectroscopy and nano-imaging experiments. *Averitt* and *Hone* design and fabricate state-of-the-art meta-materials and optical antennas structures. Theoretical and computational studies of ultrafast temporal phenomena are being carried by *Millis* and *Fogler*. Analytical and numerical modeling of time-resolved near-field effects are performed by *Fogler*.

1. Experimental and theoretical highlights.

In this section we will highlight some of the most significant accomplishments by our team since August 2014. This research has resulted in one publication in *Nature Photonics* [1], articles in *Nature Materials* [2] and *Nature Physics* [3], one paper in *Physical Review Letters* [4], articles in *Science* [5] and *Reports on Progress in Physics* [6] along with three other publications in Physical Review B and Journal of Applied Physics. among many other published and recently submitted works. Publications [2], [3], [5] and [6] are co-authored by more than one co-investigator.

1.1 Pump-probe spectroscopy: ultra-high optical fields and ultra-high stability. Developmental work by *Averitt* and *Basov* has resulted in experimental ultrafast optical capabilities using a 1KHz amplifier for mid-infrared pumping (1.2–17 μm → 75 meV–1.0 eV) achieving fluence of ~5 mJ/cm^2 and high-field terahertz pulse generation (0.1–2 THz) with ultra-high peak fields in excess of 400 kV/cm. The dynamics initiated with phonon pumping or electric field driving can be probed at THz, mid-IR, and visible frequencies. This new capability for ultra-high electric fields has been implemented in a stabilized reflection geometry for precision measurements of dynamics on single crystals down to 4 K. Initial phonon pumping studies have been performed on nickelates. Experiments investigating photo-enhanced superconductivity of $La_{2-x}Ba_xCuO_4$ (x =11.5%) are underway to corroborate and extend the measurements of the Hamburg group [7] [8]. Our team is poised to initiate experiments on phonon pumping in A_3C_{60} superconducting samples and apical oxygen modulation studies in underdoped $YBa_2Cu_3O_y$ and related materials. In parallel, *Averitt* has developed a high repetition rate laser beamline (50KHz–1MHz) to obtained intense fields (up to 50 kV/cm) with ultra-high stability needed for high finesse measurements including manipulation of phase coherence in superconductors [9] [10].

1.2 Advanced nano-infrared spectroscopy and imaging. Basov and *Averitt* demonstrated for the first time pump-probe nano-imaging using amplified lasers offering ultra-intense electric fields utilizing a high repetition rate beamline to provide ultra-high stability. These innovations facilitated the discovery of novel hidden phases in correlated oxides including manganites [2] and VO_2. Among many technological leaps that have enabled this work was the implementation of magnetic force microscopy (MFM) simultaneously performed with nano-infrared spectroscopy. MFM experiments are imperative for the nano-scale mapping of the variations of the superfluid density in unconventional superconductors and for identifying magnetically ordered domains. All of these scanning probe experiments are performed in the setting of a unique cryogenic nano-infrared apparatus with ultra-high stability of the suspended scanner developed by *Basov* [3]. *Basov, Hone* and *Fogler* reported for the first time on hyper-spectral pump-probe nano-imaging [1]. This novel experimental technique combines broad-band infrared spectroscopy with 10-nm spatial resolution *imaging.* This novel system is essential for the on-going experiments on local pump-probe studies of transient superconductivity and in the search for competing photo-induced phases.

1.3 Superconductors integrated with meta-materials and van der Waals heterostructures. Simulation, synthesis, and terahertz characterization by *Averitt, Basov,* and *Hone* has enabled sculpting, localization, and enhancement of electromagnetic fields in superconductors using metamaterial resonator devices. These capabilities are crucial for nonlinear far-field and near-field studies providing the means to achieve localized phonon pumping or field-driven effects in superconductors. Our initial work has focused on THz frequencies and we have developed metamaterial “tapes” that can be easily applied (and removed) to single crystals samples, an

example of which is shown in Fig. 1A. For $La_{2-x}Sr_xCuO_4$ (x =15%) single crystals we have investigated coupling between the c-axis Josephson Plasmon Resonance (JPR) and split ring resonators (SRRs). By creating a series of tapes with differing resonator dimensions, we were able to sweep the SRR mode across the JPR to investigate mode coupling, analogous to plasmon-phonon coupling in doped semiconductors [11]. THz spectroscopy data reveal a strong interaction between the superconducting condensate and the SRRs (Fig.1B,C), providing a new approach to interrogate and potentially augment superconductivity.

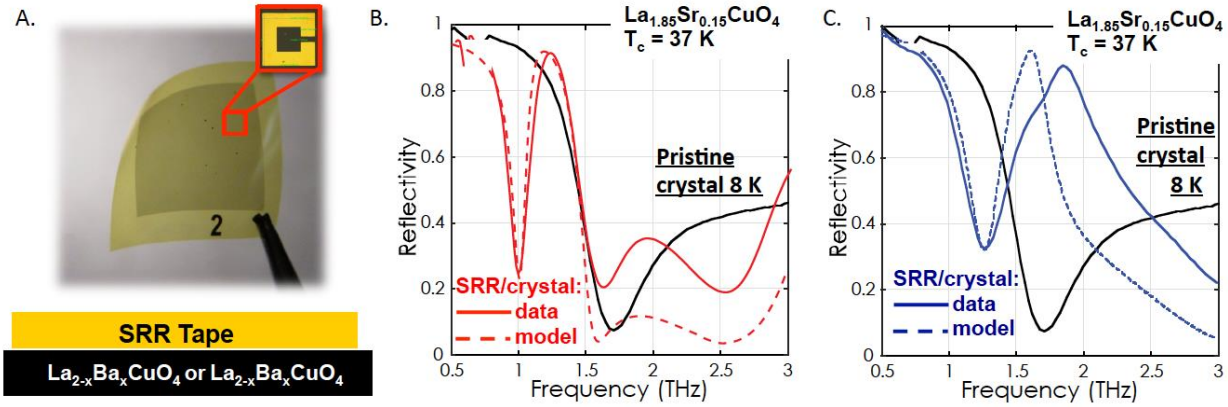


Figure 1: A) Image of metamaterial tape for application to $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Ba_xCuO_4$ crystals. Bottom frame depicts a schematic of the structure with SRR tape attached to the ac-surface of La-based high-T_c materials. B and C): Experimental data along with model simulations. Black solid lines: c-axis reflectance data for pristine $La_{2-x}Sr_xCuO_4$ (x =15%) at T = 8K revealing the characteristic JPR structure. Red and blue solid lines are for structures with SRR tape attached to the same crystal. Red lines (panel B): scale factor 1; blue lines (panel C): scale factor 1.8. The scale factor is proportional to the dimensions of split rings. Simulations grasp the key features of the data attesting to strong interaction between metamaterials resonators and the JPR. More accurate simulations are in progress.

1.4 Non-equilibrium phase diagram of correlated electron materials. Theoretical work of *Millis* demonstrated [12] that the dominant symmetry-allowed coupling between electron density and dipole active phonon modes implies an electron density-dependent squeezing of the phonon state and provides an attractive contribution to the electron-electron interaction. This effect is independent of the sign of the bare electron-phonon coupling whereas the magnitude of this effect is proportional to the degree of laser-induced phonon excitation. Reasonable excitation amplitudes lead to non-negligible attractive interactions that may cause significant transient changes in electronic properties including superconductivity. The mechanism is generically applicable to a wide range of systems, offering a promising route to manipulating and controlling electronic phase behavior in novel materials.

1.5 Plasmon amplification. Theoretical work of *Fogler*, which is motivated experimental results from our team [4], studies dynamical evolution of the collective modes of a photoexcited electron-hole plasma. The key idea is that the gradual change of the instantaneous frequency of the mode is analogous to the adiabatic variation of parameters of a harmonic oscillator. Based on this analogy, *Fogler* showed that depending on the magnitude of the loss, the mode amplitude may increase with time. We discussed several scenarios in which such an amplification of (thermo)plasmons is possible. This amplification does not require any gain media; it occurs during the natural relaxation of the plasma. The principle of adiabatic amplification is general; in [4] we discuss a specific case of thin-film superconductors, which are expected to be low-loss

plasmonic media. We also analyzed the detection of amplified plasmons via pump-probe nano-optical techniques in preparation for experimental studies of these effects.

2. Program objectives, team expertise and ongoing experiments.

Objectives of our proposed program include: *i)* performing systematic studies of ultrafast dynamics of unconventional superconductors and related systems in the previously unexplored regime of nm-scale spatial resolution and ultra-high optical fields; *ii)* developing a theory of a near-field response of this class of materials known for their strong intrinsic and extrinsic inhomogeneities; *iii)* training a new generation of researchers within a program at the intersection of physics, nano-optics, and materials science.

The research tasks that are being addressed by our team are complex and can only be accomplished by a collaborative team with a complementary expertise. *Basov* and *Averitt* will carry out pump-probe experiments using instrumentation developed over the past decade in their groups. Unique structures tailored for ultrafast experiments will be fabricated by *Hone* and *Averitt*. Theoretical and computational studies of transient superconductivity will be carried out by *Millis* and *Fogler*. Analytical and numerical modeling of time-resolved effects in the nano-scale near-field optical phenomena will be accomplished by *Fogler*. Therefore, this team is capable to carry out all elements of the program.

On-going research is focused on light-induced superconductivity. We have prepared, oriented and characterized several crystals of $La_{2-x}Ba_xCuO_4$ with ac-orientation in collaboration with Dr. Genda Gu and Dr. Chris Homes (BNL). We have obtained THz and far-IR spectra as a function of temperature. Pump-probe experiments are being performed with 800 nm excitation, mode-selective excitation in mid-IR frequencies and strong THz fields. In parallel, we investigate pump-probe behavior of hybrid structures (Fig.1) based on $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ crystals. Theory research is focused on the modeling of SRR-JPR coupling and on the understanding of mode-selective ultra-fast excitation of unconventional superconductors.

3. References

[1] G. X. Ni, L. Wang, Goldflam, M. D., M. Wagner, Z. Fei, A. S. McLeod, M. K. Liu, F. Keilmann, B. Özyilmaz, A. H. Castro Neto, J. Hone, M. M. Fogler and D. N. Basov, "Ultrafast optical switching of infrared plasmon polaritons in high-mobility graphene," *Nature,* vol. 10, p. 244, 2016.

[2] J. Zhang, X. Tan, M. Liu, S. Teitelbaum, K. Post, F. Jin, K. A. Nelson, D. N. Basov, W. Wu and R. D. Averitt, "Cooperative photoinduced metastable phase control in strained manganite films," *Nature Mat.,* vol. 15, p. 956, 2016.

[3] A. S. McLeod, E. van Heumen, J. G. Ramirez, S. Wang, T. Saerbeck, S. Guenon, M. Goldflam, L. Anderegg, P. Kelly, A. Mueller, M. Liu, I. K. Schuller and D. N. Basov, "Nanotextured phase coexistence in the correlated insulator V_2O_3," *Nature Phys.* 2016 (in press).

[4] Z. Sun, D. N. Basov and M. M. Fogler, "Adiabatic amplification of plasmons and demons in 2D systems," *Phys. Rev. Lett.,* vol. 117, p. 076805 , 2016.

[5] D. Basov, M. Fogler and J. Garcia de Abajo, "Polaritons in van der Waals Materials," *Science,* vol. 354, p. 195, 2016.

[6] M. Liu, A. J. Sternbach and D. N. Basov, "Nanoscale electrodynamics of strongly

correlated quantum materials," *Rep. Prog. Phys.,* 2016 (in press).

[7] D. Nicoletti, E. Casandruc, Y. Laplace, C. R. Hunt, S. Kaiser, S. S. Dhesi, G. D. Gu, J. P. Hill and A. Cavalleri, "Optically induced superconductivity in striped La2-xBaxCuO4 by polarization-selective excitation in the near infrared," *Phys. Rev. B,* vol. 90, p. 100503(R), 2014.

[8] E. Casandruc, D. Nicoleti, S. Rajasekaran, Y. Laplace, V. Khanna, G. D. Gu, J. P. Hill and A. Cavalleri, "Wavelength-dependent optical enhancement of superconducting interlayer coupling in La1.885Ba0.115CuO4," *Phys. Rev. B,* vol. 91, p. 174502, 2015.

[9] A. Dienst, M. C. Hoffman, D. Fausti, J. C. Petersen, S. Pyon, T. Takayama, H. Takagi and A. Cavalleri, "Bi-directional ultrafast electric-field gating of interlayer charge transport in a cuprate superconductor," *Nature Photon.,* vol. 5, p. 485, 2011.

[10] R. Matsunaga, N. Tsuji, H. Fujita, A. Sugioka, K. Makise, Y. Uzawa, H. Terai, Z. Weng, H. Aoki and R. Shimano, "Light-induced collective pseudospin precession resonating with Higgs mode in a superconductor," *Science,* vol. 345, p. 1145, 2014.

[11] B. B. Varga, "Coupling Plasmons to Polar Phonons in Degenerate Semiconductors," *Phys. Rev.,* vol. 137, p. A1896, 1965.

[12] D. M. Kennes, E. Y. Wilner, D. R. Reichman and A. J. Millis, "Electronic Squeezing of Pumped Phonons: Negative U and Transient Superconductivity," *arXiv:1609:03802,* 2016.

Electronic, Spin, and Lattice Structures and Dynamics of Nanoscale Systems

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

Program Scope: This program focuses on electronic effects in ultrathin films where quantum confinement and dimensional crossover may lead to novel properties and phenomena. We perform a systematic investigation of films with thicknesses ranging from a single layer (2D limit), to multi-layers (quantum-confinement and transition regime), and to the 3D limit (bulk). Of current interest are materials that exhibit charge density waves (CDWs), nontrivial topological states, and superconductivity. Also of interest are composite film systems made of proximity-coupled layers of different classes of materials where coherent quantum mechanical interaction, entanglement, and competition for different types of electronic and lattice ordering may give rise to unusual physical behavior.

Recent Progress: "*Charge Density Wave Transitions in Single-layer, Multi-layer, and Bulk Titanium Diselenide ($TiSe_2$)*"

In the bulk form, $TiSe_2$ exhibits a (2x2x2) commensurate transition at ~205 K. The nature of the transition has been in debate for decades. There is no relevant Fermi surface nesting, and the usual picture of a Peierls distortion does not apply. Two other mechanisms have been proposed, one based on a band-type Jahn-Teller interaction and the other based on an excitonic interaction. We have embarked on a study of single- and multi-layers of $TiSe_2$ grown on bilayer-graphene-terminated SiC. A single layer, with a two-dimensional band structure, is a much simpler case for electronic structure determination. Yet, it is unclear if a single layer would exhibit a CDW transition and, if there is one, what the transition temperature would be, and how it is related to the 3D case. The single layer is potentially a promising platform for developing advanced electronics beyond graphene. Our ARPES measurements show that the single layer exhibits a (2x2) CDW transition at a transition temperature of T_C ~ 232 K, which is substantially higher than the bulk T_C ~ 205 K. An important finding is that band structure effects alone can explain the CDW transition; there is no need to invoke excitonic or other high-order interactions. The measured evolution of the gap as a function of temperature follows closely a BCS-like gap equation as shown in Fig. 1(a). Similar measurements have been made for films of 2, 3, ... 6 layers (see Fig. 1). The measured T_C at 3 layers and beyond is essentially bulk-like, but at 2 layers, the system exhibits a mixture of two T_C's, one bulk-like and the other single-layer-like. The transition temperatures in the bulk and single-layer have been confirmed by x-ray diffraction measurements of the lattice distortion at Sector 33 of the Advanced Photon Source.

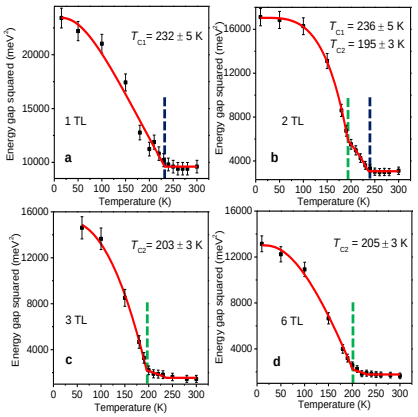


Fig. 1 Measured energy gap squared of $TiSe_2$ as a function of temperature for (a) 1, (b) 2, (c) 3, and (d) 6 trilayers (TL). The red curves are fits using a BCS-type gap equation. Two transition temperatures, T_{C1} for a single layer and T_{C2} for the bulk, are indicated by blue and greens dashed lines, respectively.

Future Plans: We will continue the work on thin films of various materials including charge density wave compounds, topological insulators, topological crystalline insulators, Dirac and Weyl semi-metals, etc. We will also explore the physics of composite film systems made of proximity-coupled layers of different classes of materials

where coherent quantum mechanical interaction, entanglement, and competition for different types of electronic and lattice ordering may give rise to unusual physical behavior.

Publications

1. 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. **201**, 36 (2015).
2. Man-Hong Wong, G. Bian, T. Miller, and T.-C. Chiang, "Topological phase transitions in antimony without gap parity reversal," EuroPhys. Lett. **109**, 17005 (2015).
3. Xiaoxiong Wang, Guang Bian, Peng Wang, and T.-C. Chiang, "Dirac semimetal films as spin conductors on topological substrates," Phys. Rev. B **91**, 125103 (2015).
4. Jie Ren, Li Fu, Guang Bian, Manhong Wong, Tao Wang, Gangqiang Zha, Wanqi Jie, T. Miller, M. Z. Hasan, and T.-C. Chiang, "Spectroscopic studies of CdTe(111) bulk and surface electronic structure," Phys. Rev. B B **91**, 235303 (2015).
5. C.-Z. Xu, Y. Liu, R. Yukawa, L.-X. Zhang, I. Matsuda, T. Miller, and T.-C. Chiang, "Photoemission circular dichroism and spin polarization of the topological surface states in ultrathin Bi_2Te_3 films," Phys. Rev. Lett. **115**, 016801 (2015). Chosen as an Editors' Suggestion.
6. A. Kogar, S. Vig, A. Thaler, M.H. Wong, Y. Xiao, D. Reig-i-Plessis, G.Y. Cho, T. Valla, Z. Pan, J. Schneeloch, R. Zhong, G. Gu, T.L. Hughes, G.J. MacDougall, T.-C. Chiang, and P. Abbamonte, "Surface collective modes in the topological insulators Bi_2Se_3 and $Bi_{0.5}Sb_{1.5}Te_{3-x}Se_x$," Phys. Rev. Lett. **115**, 257402 (2015).
7. A. B. Mei, O. Hellman, C. Schlepütz, A. Rockett, T.-C. Chiang, L. Hultman, I. Petrov, and J. E. Greene, "Reflection thermal diffuse x-ray scattering for quantitative determination of phonon dispersion relations," Phys. Rev. B **92**, 174301 (2015). Chosen as an Editors' Suggestion.
8. P. Chen, Y.-H. Chan, X.-Y. Fang, Y. Zhang, M. Y. Chou, S.-K. Mo, Z. Hussain, A.-V. Fedorov, and T.-C. Chiang, "Charge density wave transition in single-layer $TiSe_2$," Nature Commun. **6**, 8943 (2015).
9. Guang Bian, Caizhi Xu, Tay-Rong Chang, Xiaoxiong Wang, Saavanth Velury, Jie Ren, Hao Zheng, T. Miller, M. Zahid Hasan, and T.-C. Chiang, "Direct transition resonance in atomically uniform topological Sb(111) thin films," Phys. Rev. B **92**, 241401(R) (2015).
10. Guang Bian, Z. F. Wang, Xiaoxiong Wang, Caizhi Xu, Su-Yang Xu, T. Miller, M. Zahid Hasan, Feng Liu, and T.-C. Chiang, "Engineering electronic structure of a 2D topological insulator Bi(111) bilayer on Sb nanofilms by quantum confinement effect," ACS Nano, **10**, 3859 (2016). DOI: 10.1021/acsnano.6b00987
11. Jie Ren, Li Fu, Guang Bian, Jie Su, Hao Zhang, Ryu Yukawa, Longxiang Zhang, Tao Wang, Gangqiang Zha, Wanqi Jie, Rongrong Guo, Tom Miller, M. Z. Hasan, and Tai-Chang Chiang, "An effective approach to improving cadmium telluride (111)A surface by molecular-beam-epitaxy growth of tellurium monolayer," ACS Appl. Mater. Interfaces, **8**, 726 (2016).
12. P. Chen, Y.-H. Chan, X.-Y. Fang, S.-K. Mo, Z. Hussain, A.-V. Fedorov, M.Y. Chou, and T.-C. Chiang, "Hidden order and dimensional crossover of the charge density waves in $TiSe_2$," (submitted).
13. P. Chen, Y.-H. Chan, M.-H. Wong, X.-Y. Fang, M. Y. Chou, S.-K. Mo, Z. Hussain, A.-V. Fedorov, and T.-C. Chiang, "Dimensional effects on the charge density waves in ultrathin films of $TiSe_2$," Nano Lett. (accepted).
14. Xiaoxiong Wang, Peng Wang, Guang Bian, and T.-C. Chiang, "Topological phase transitions in stanene and stanene-like systems by scaling the spin-orbit coupling," EuroPhys. Lett. **115**, 37010 (2016).

Probing excitations in complex oxide heterostructures

M. P. M. Dean, Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, USA, *mdean@bnl.gov

Program scope

This FWP focuses on using advanced x-ray scattering techniques to measure the electronic properties of strongly correlated transition metal oxides and how they relate to the emergent phenomena observed in these materials. The primary tool for this is resonant inelastic x-ray scattering (RIXS) measurements of magnetic and orbital excitations, which encode the electronic structure and magnetic interactions in these states. There is a particular emphasis on extending these studies to measure thin films and heterostructures to gain further understanding of how interfacial effects and laser excitation can be used to further tune the properties of these systems.

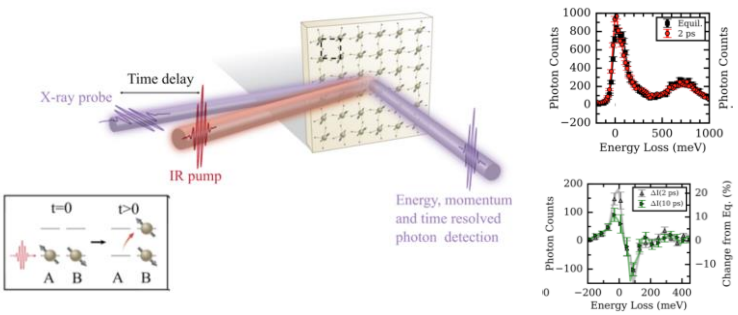


Fig. 1. Left: Conceptual experimental layout. Right top: Excitation spectra of Sr_2IrO_4 in the equilibrium state (black) and 2 ps after photo excitation (red). Right bottom: Difference spectra before and after photo-excitation showing changes in the magnetic excitation around 100 meV. This provides the first glimpse of the presence and nature of 2D short-range magnetic correlations in transient states such as these.

Recent progress

Measuring how the magnetic correlations evolve in doped Mott insulators has greatly improved our understanding of the pseudogap, non-Fermi liquids and high-temperature superconductivity. Recently, photo-excitation has been used to induce similarly exotic states transiently. However, the lack of available probes of magnetic correlations in the time domain hinders our understanding of these photo-induced states and how they could be controlled. We implemented RIXS at a free-electron laser, as illustrated above in Fig.1, to directly determine the magnetic dynamics after photo-doping thin films of the Mott insulator Sr_2IrO_4. We demonstrated that the transient state, 2 ps after the excitation, exhibits strongly suppressed long-range magnetic order, but hosts photo-carriers that induce strong, non-thermal magnetic correlations, which we used to construct a detailed picture of the magnetic recovery mechanism [1].

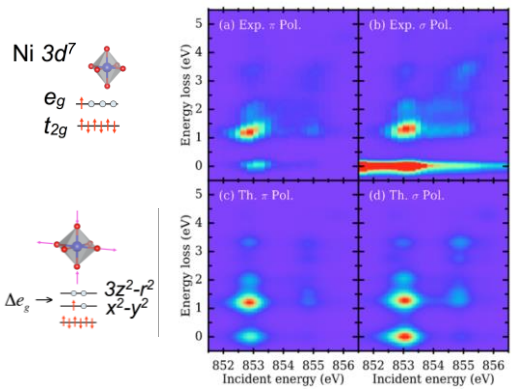
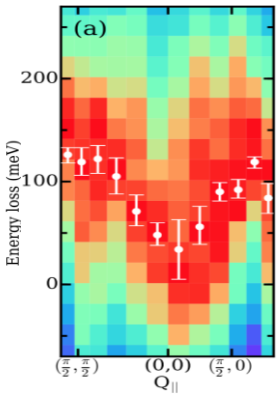


Fig. 2. Far left: Illustration of the putative modification of Ni 3d orbitals in thin films and heterostructures

Left: (a)&(b) plot the measured RIXS intensity in a LTNAO heterostructure. (c)&(d) show multiplet calculations used to extract the real orbital energy levels.

Right: RIXS observation of dispersive magnetic excitations in La_2NiO_4.



Transition metal oxide based heterostructures offer the tantalizing promise of being able to produce new "designer electronic structures" that are unachievable via bulk synthesis. A prototypical example of this is the prediction that it should be possible to drive $LaNiO_3$'s electronic configuration into a state with large orbital polarization in order to mimic the electronic configuration found in the cuprate high temperature superconductors. To date, researchers have interpreted changes in $LaNiO_3$'s electronic configuration in

terms of orbital energy changes, which naturally generates preferential occupation of the lower energy orbital. We applied resonant inelastic x-ray scattering (RIXS) to $LaAlO_3$-$LaNiO_3$-$LaTiO_3$ heterostructures -- a model system with very large orbital polarization. We find that orbital polarization is, in fact, driven by anisotropic hybridization between the Ni and O orbitals and not by changes in orbital energies. This provides an explanation for the limited success of theoretical predictions based on tuning orbital energy levels and implies that future theories should focus on anisotropic hybridization as the most effective means to drive large changes in electronic structure and realize novel emergent phenomena [2].

Future plans

We aim to extend our efforts to probe ultra-fast magnetism in the iridates. More specifically a similar experiment to [1] is planned in which we will directly excite an Ir-O stretching phonon mode with mid-infra-red excitation. In this way, we hope to exhibit direct control of magnetism at the most fundamental level by perturbing and then directly measuring the strength of the magnetic exchange interaction.

Work on nickelate heterostructures is being extended to probe spin degrees of freedom. This includes studies of spin spirals in $LaNiO_3$-$La_{2/3}Sr_{1/3}MnO_3$ superlattices [3]. In particular, we aim to exploit resonant scattering to determine the spin behavior in the $LaNiO_3$ layers and how this contributes to the formation of the magnetic state. Going further, we aim to start studying magnetic excitations at these layers to quantify the strength and directionality of the magnetic interactions. We are currently preparing a publication reporting the first RIXS observation of dispersive magnons in a nickelate starting with layered crystals of La_2NiO_4 (See Fig. 2) [4].

In addition to nickelates, we are panning studies of $LaCoO_3$-based superlattices in which we aim to explain how the Co spin can be switched between different states by the combination of strain and charge transfer. In parallel we are studying artificial Ruddleston-Popper iridates series based on layered combinations of $SrIrO_3$ and $SrTiO_3$.

Publications

1. M. P. M. Dean, Y. Cao, X. Liu, S. Wall, D. Zhu, R. Mankowsky, V. Thampy, X. M. Chen, J. Vale, D. Casa, Jungho Kim, A. H. Said, P. Juhas, R. Alonso-Mori, M. Glownia, A. Robert, J. Robinson, M. Sikorski, S. Song, M. Kozina, H. Lemke, L. Patthey, S. Owada, T. Katayama, M. Yabashi, Yoshikazu Tanaka, T. Togashi, J. Liu, C. Rayan Serrao, B. J. Kim, L. Huber, C.-L. Chang, D. F. McMorrow, M. Först, and J. P. Hill, "Ultrafast energy and momentum resolved dynamics of magnetic correlations in photo-doped Mott insulator Sr_2IrO_4", Nature Materials 15, 601-605 (2016)

2. G. Fabbris, D. Meyers, J. Okamoto, J. Pelliciari, A. S. Disa, Y. Huang, Z.-Y. Chen, W. B. Wu, C. T. Chen, S. Ismail-Beigi, C. H. Ahn, F. J. Walker, D. J. Huang, T. Schmitt, M. P. M. Dean "Orbital Engineering in Nickelate Heterostructures Driven by Anisotropic Oxygen Hybridization rather than Orbital Energy Levels", Phys. Rev. Lett. 117, 147401 (2016)

3. Jason D. Hoffman, Brian J. Kirby, Jihwan Kwon, Gilberto Fabbris, Derek Meyers, John W. Freeland, Ivar Martin, Olle G. Heinonen, Paul Steadman, Hua Zhou, Christian M. Schlepütz, Mark P. M. Dean, Suzanne G. E. te Velthuis, Jian-Min Zuo, and Anand Bhattacharya, "Oscillatory noncollinear magnetism induced by interfacial charge transfer in superlattices composed of metallic oxides", Phys. Rev. X In press (2016)

4. G. Fabbris, D. Meyers, L. Hozoi, L. Xu, V. M. Katukuri, X. Liu, J. Okamoto, T. Schmitt, A. Uldry, B. Delley, G. D. Gu, D. Prabhakaran, A. T. Boothroyd, J. van den Brink, D. J. Huang and M. P. M. Dean, "X-Rays Observation of Collective Spin Excitations in Spin 1 Quantum Antiferromagnet $La_{2-x}Sr_xNiO_4$", (2016) (In prep.)

Time-Resolved Soft X-Ray Materials Science at the LCLS and ALS

Thomas Devereaux, Zhi-Xun Shen, Wei-Sheng Lee, Zahid Hussain, Yi-De Chuang, HongChen Jiang, Aaron Lindenberg, Tony Heinz

Stanford Institute for Materials and Energy Sciences
SLAC National Accelerator Laboratory and Stanford University, Lawrence Berkeley National Laboratory

Program Scope

This FWP has its core activities in studying novel materials dynamics, with the goal of understanding, controlling and formulating non-equilibrium phenomena and the emergent dynamics of coupled charge, spin, lattice, and orbital degrees of freedom at their natural time- and length-scales, utilizing advanced theory and numerical simulations and a unique set of light sources spanning THz to x-rays, with particular emphasis on science that is enabled by the West Coast light sources: the Linac Coherent Light Source (LCLS) & Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory & the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). We continue our vision to address frontier science problems through advanced instrumentation, X-ray beamtime usage and theory development.

Since the last contractor's meeting, we have made major strides in resonant inelastic x-ray scattering studies of high temperature superconductors as well as investigations of transition metal dichalchogenides in the time domain. Our work has been and will continue to be strongly synergetic with ARPES FWP led by Z.-X. Shen and others in SIMES and beyond.

We have been focused on characterizing symmetry-broken states in strongly correlated materials and their dynamics in- and out-of equilibrium using novel x-ray scattering. Some of the recent highlights are:

- Field-induced charge density wave in YBCO: Together with the scientists at SSRL and LCLS, we have performed x-ray scattering with a pulsed magnet to study charge density wave (CDW) in YBCO under high magnetic field up to 32 T. We found an incommensurate and uni-directional CDW emerges at a finite magnetic field and at temperatures below zero-field T_c, in addition to the other CDW already exists at zero magnetic field. This discovery has provided important missing link between low- and high-field measurements in YBCO [1,2]. We also propose a scenario to explain the relation between the filed-induced and zero-field CDW [2].
- Lattice-driven dynamics in a striped nickelate $La_{1.75}Sr_{0.25}NiO_4$. 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. Together with a Ginzburg-Landau theory, we conclude that the lattice is directly coupled to both spin and charge orders. This works is currently under review [3].

- Direct structural characterization of photo-induced coherent phonon oscillations in $BaFe_2As_2$ and FeSe. Ultrafast optical pulse can excite a coherent A_{1g} mode, which corresponds to coherent oscillations of Fe-AS-Fe bond angle. We directly characterize the time evolution of this bond angle via femtosecond time-resolved x-ray diffraction at LCLS. This information is correlated with the electronic behaviors obtained by time-resolved spectroscopy and theory [4]. We have also extended this methodology to the FeSe film and combined with the time-resolved ARPES work to extract orbital dependent electron-phonon coupling strength. This work is currently under review [5].
- Revealing Charge Density Wave Excitations in Bi-2212 via ultrahigh resolution RIXS: Using the newly commissioned ultra-high resolution RIXS spectrometer at ESRF, we reveal the underlying CDW, its excitation, and its influence on the bond stretching phonon. An intensity anomaly due to the intersection of CDW excitations and phonon is also observed [6]. This work provides a new perspective on understanding the origin of the CDW in cuprates.
- DMRG Simulations of Competing Order: We have performed a density-matrix renormalization group (DMRG) study of the *t*-*J*-type model on a 4-leg cylinder with concentration $\delta = 1/8$ of doped holes [7]. Despite the simplicity of the model, we have unveiled a remarkably complex intertwining between at least 9 forms of order, with an astonishingly complex interplay between uniform d-wave superconductivity (SC) and strong spin and charge density wave ordering tendencies (SDW and CDW).
- Using RIXS to Uncover Elementary Charge, Spin and Lattice Excitations: In two PRX papers, we reported the use of state-of-the-art, unbiased numerical calculations to study the low-energy excitations probed by RIXS. The results highlight the importance of scattering geometry, in particular, both the incident and scattered x-ray photon polarization, and they demonstrate that on a qualitative level the RIXS spectral shape in the cross-polarized channel approximates that of the spin dynamical structure factor. We showed how single phonon excitations can be symmetry projected using RIXS [8,9].
- Modular soft X-ray spectrometer for applications in energy sciences and quantum materials: Our FWP has also been supporting the development of modular soft X-ray spectrometers for applications in energy sciences and quantum materials. Since the last contractor's meeting, we have presented a versatile design of spectrometer based on Hettrick-Underwood optical scheme that has modular mechanical components. The spectrometer's optics chamber can be used with gratings operated in both inside and outside orders, and the detector assembly can be reconfigured separately. The spectrometer can be de-signed to have high spectral resolution, exceeding 10,000 resolving power when using small source and detector pixels, or high throughput at moderate resolution [10].

In addition, our FWP is dedicated to the investigation of the ultrafast structural and electronic dynamics properties exhibited in novel 2D transition metal dichalcogenides, with particular emphasis on the ultrafast dynamics of structural and electronic modification induced by ultrafast control pulses. Highlights include:

- LCLS, SSRL, and at the new SLAC Ultrafast Electron Diffraction (UED) experiments: We have carried out a number of experiments probing atomic-scale dynamics in both monolayer and multilayer TMDC materials [11-15]. In the monolayer limit, measurements at UED provide direct information on electron-phonon coupling time-scales as reflected in the transfer of energy from hot carriers to the lattice, and show first evidence for an ultrafast rippling response developing on picosecond time-scales. At LCLS, we have carried out femtosecond diffraction probes of carrier-induced changes in the out-of-plane lattice response. These show an unexpected carrier-driven compressive response which we show arises from an optical modulation of the van der Waals interaction. Measurements of the monolayer response at LCLS have also been carried out and provide complimentary information to the experiments carried out at UED.
- Optical properties of atomically thin ReS_2 layers [16]: We have examined the electronic properties of a new van-der-Waals layered material, ReS_2, in the limit of mono- and few-layer thickness. In contrast to Mo and W compounds, ReS_2 forms in distorted tetragonal phase. This gives rise to strong in-plane anisotropy in the transport and optical properties. The characteristics of the anisotropic excitons were investigated as a function of layer thickness using both reflection contrast measurements (absorption) and photoluminescence spectroscopy.
- Ultrafast control of valley pseudospin [17]: Access and control of the valley degree of freedom of solids has been a subject of great recent interest. Recently the semiconducting monolayer transition metal dichalcogenides in the MX_2 (M=Mo,W; X= S, Se) family were identified as ideal materials to investigate this intriguing issue, since they exhibit strong valley dichroism, i.e., selectivity of the different valleys to the state of excitation with circularly polarized light. In our recent experimental investigation, we have taken the next step towards control of the valley degree of freedom, demonstrating the possibility of optical *manipulation* of valley excitation. Using the optical Stark effect with circularly polarized light, we were able to dynamically tune the relative energies of the two valleys. This led to a rotation in the pseudospin vector of a coherent state with weights in both valleys, as verified by changes in the polarization state of photoluminescence induced by an ultrafast laser pulse.
- Manipulating Electronic Transport with Light [18]: Using a materials-centric strategy for understanding photo-induced out-of-equilibrium steady states directly from first principles materials modelling, we have found a novel mechanism in which light can be used as a switch for chiral conduction channels of topological origin that are localized at the sample edges. The number of protected conduction channels can be selected by tuning the frequency of the pump laser, where these channels are always localized at a single TMDC band valley, with the other valley remaining trivial. This induced band gap, and thermal stability of the edge modes, scales linearly in applied pump field, while red detuning to optical frequencies below the bulk band gap limits absorption and heating, a major stumbling block in previous proposals.

- Photo-induced, metastable state in TaS_2 [19]: We have investigated the recent observance of photoinduced metastable states in tantalum disulfide. Notably, this state can only be induced with a sub-ps laser pulse, which reversibly switches from the insulating equilibrium state to the conductive metastable state. We employed a combination of ARPES, trARPES and low-energy electron diffraction (LEED) to investigate this photo-induced state. ARPES evidences that the metastable state is characterized by an ungapped Fermi surface near the Γ-point. trARPES suggests that the transition is driven by a transient imbalance of electron and hole populations while LEED does not resolve dramatic structural changes. Our findings provide a deeper understanding of non-equilibrium phase changes in complex materials.

We will update the following recent progresses at this meeting: i) updates on using the LCLS to continue investigating the collective properties of quantum materials in high magnetic field and/or in photo-excited none-equilibrium state; ii) investigating low energy elementary excitations in the energy-momentum space using state-of-the-art RIXS instruments worldwide; iii) updates on the structural dynamics exhibited by TMDC materials and their alloys iv) updates on coherent control of the electronic and valley properties of transition metal dichalcogenide monolayers by suitable ultrafast excitation pulses; v) complimentary theoretical efforts; vi) updates on detector development and *q*-RIXS.

1. S. Gerber, H. Jang, H. Nojiri, S. Matsuzawa, Y. Yasumura, D. A. Bonn, R. Liang, H. N. Hardy, Z. Islam, A. Mehta, S. Song, M. Sikorski, D. Stefanescu, Y. Feng, J. Hastings, S. A. Kivelson, T. P. Devereaux, Z.-X. Shen, C.-C. Kao, W.-S. Lee[+], D. Zhu[#], J.-S. Lee[*]. *Charge Density Wave in $YBa_2Cu_3O_{6.67}$ at High Magnetic Fields*, Science **350**, 949 (2015).
2. H. Jang*, W.-S. Lee,*, H. Nojiri, S. Matsuzawa, H. Yasumura, L. Nie, A. V. Maharaj, S. Gerber, Y. Liu, A. Mehta, C. A. Burns, D. A. Bonn, R. Liang, W. N. Hardy, Z. Islam, S. Song, J. Hastings, T. P. Devereaux, Z.-X. Shen, S. A. Kivelson, C.-C. Kao, D. Zhu, J.-S. Lee, Ideal charge density wave order in the high-field state of the YBCO superconductors. Proc. Nat. Acad. Sci. Accepted.
3. W. S. Lee, Y. F. Kung, B. Moritz, G. Coslovich, R. A. Kaindl, Y. D. Chuang, R. G. Moore, D. H. Lu, P. S. Kirchmann, J. S. Robinson, M. P. Minitti, G. Dakovski, W. F. Schlotter, J. J. Turner, S. Gerber, T. Sasagawa, Z. Hussain, Z. X. Shen and T. P. Devereaux, Non-equilibrium Lattice-driven Dynamics of Stripes in Nickelates using Time-Resolved X-ray Scattering. Submitted.
4. S. Gerber, K. W. Kim, Y. Zhang, D. Zhu, N. Plonka, M. Yi, G. L. Dakovski, D. Leuenberger, P. S. Kirchmann, R. G. Moore, M. Chollet, J. M. Glownia, Y. Feng, J.-S. Lee, A. Mehta, A. F. Kemper, T. Wolf, Y.-D. Chuang, Z. Hussain, C.-C. Kao, B. Moritz, Z.-X. Shen, T. P. Devereaux, and W.-S. Lee, *Direct characterization of photo-induced lattice dynamics in $BaFe_2As_2$.* Nature Communication **6**, 7377 (2015).
5. S. Gerber, S.-L. Yang, D. Zhu, H. Soifer, J. A. Sobota, S. Rebec, J. J. Lee, T. Jia, B. Moritz, C. Jia, A. Gauthier, Y. Li, D. Leuenberger, Y. Zhang, L. Chaix, W. Li, H. Jang, J.-S. Lee, M. Yi, G. L. Dakovski4, S. Song, J. M. Glownia, S. Nelson, K. W. Kim, Y.-D. Chuang, Z. Hussain, C.-C. Kao, R. G. Moore, T. P. Devereaux, W.-S. Lee*, P. S. Kirchmann*, Z.-X. Shen*, Femtosecond electron-phonon lock-in via photoemission and x-ray free-electron laser. Submitted.

6. L. Chaix, G. Ghiringhelli, Y. Y. Peng, M. Hashimoto, B. Moritz, K. Kummer, N. Brookes, Y. He, S. Chen, S. Ishida, Y. Yoshida, H. Eisaki, L. Braicovich, Z.-X. Shen, T. P. Devereaux, W.-S. Lee, Signatures of charge density wave excitations in underdoped cuprates $Bi_2Sr_2CaCu_2O_{8+d}$. In Preparation.
7. John F. Dodaro, Hong-Chen Jiang, and Steven A. Kivelson, Intertwined Order in a Frustrated 4-leg *t*−*J* Cylinder, arXiv:1610.04300, submitted to Physical Rev. B.
8. Chunjing Jia, Krzysztof Wohlfeld, Yao Wang, Brian Moritz, and Thomas P. Devereaux, Using RIXS to Uncover Elementary Charge and Spin Excitations, Phys. Rev. X **6**, 021020 (2016).
9. T. P. Devereaux, A. M. Shvaika, K. Wu, K. Wohlfeld, C. J. Jia, Y. Wang, B. Moritz, L. Chaix, W.-S. Lee, Z.-X. Shen, G. Ghiringhelli, and L. Braicovich, Directly Characterizing the Relative Strength and Momentum Dependence of Electron-Phonon Coupling Using Resonant Inelastic X-Ray Scattering, Phys. Rev. X **6**, 041019 (2016).
10. Yi-De Chuang, Yu Cheng Shao, Alejandro Cruz, Kelly Hanzel, Adam Brown, Alex Frano, Ruimin Qiao, Brian Smith, Edward Domning, Shih-Wen Huang, L.Andrew Wray, Wei-Sheng Lee, Zhi-Xun Shen, Thomas Devereaux, Jaw-Wern Chiou, Way-Faung Pong, Valeriy Yashchuk, Eric Gullikson, Ruben Reininger, Wanli Yang, Jinghua Guo, Robert Duarte, and Zahid Hussain, Modular soft X-ray spectrometer for applications in energy sciences and quantum materials, submitted to Rev. Sci. Inst.
11. D Rhodes et al., Engineering the structural and electronic phases of $MoTe_2$ through W substitution", *arXiv*:1610.02480 (2016).
12. E. M. Mannebach, R. Li, K-A. Duerloo, C. Nyby, P. Zalden, T. Vecchione, F. Ernst, A. H. Reid, T. Chase, X. Shen, S. Weathersby, C. Hast, R. Hettel, R. Coffee, Nick Hartmann, A. R. Fry, Y. Yu, L. Cao, T. F. Heinz, E. J. Reed, H. A. Dürr, X. Wang, and A. M. Lindenberg, Dynamic Structural Response and Deformations of Monolayer MoS_2 Visualized by Femtosecond Electron Diffraction, Nano Lett. **15**, 6889-6895 (2015).
13. S. P. Weathersby et al., Mega-electron-volt ultrafast electron diffraction at SLAC National Accelerator Laboratory, Rev. Sci. Instrum., **86**, 073702 (2015).
14. E.M. Mannebach et al., Ultrafast electronic and structural response of monolayer MoS_2 under intense photoexcitation conditions, ACS Nano, **8**, 10734 (2014).
15. E. Mannebach et al., Dynamic optical control of van der Waals / Casimir interactions in layered transition metal dichalcogenides (submitted) (2016).
16. O. B. Aslan, D. A. Chenet, A. M. van der Zande, J. C. Hone, and T. F. Heinz, Linearly Polarized Excitons in Single- and Few-Layer ReS_2 Crystals, ACS Photon. **3,** 96-101 (2016).
17. Z. Ye, D. Sun, and T. F. Heinz, Optical manipulation of valley pseudospin, Nature Phys. doi:10.1038/nphys3891 (2016) (published online).
18. M. Claassen, C.J. Jia, B. Moritz and T. P. Devereaux, All optical materials design of chiral edge modes in transition-metal dichalcogenides, Nature Comm. 7, 13074 (2016).
19. P. S. Kirchmann et al., Electronic Structure and Switching Pathways of the Hidden State in TaS_2 (in preparation).

Structure and Dynamics of Exotic Ferroic Polarization Configurations

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

Program Scope: Ferroelectric materials exhibit exotic polarization configurations that result from a competition of nanoscale structural, electrical, and mechanical effects. A series of rapid developments in the creation of ferroelectric thin films and nanostructures and in the theoretical methods used to describe them has led to the discovery of vortices, intricate three-dimensional structures of domain boundaries, striped domains and the proposal of even more exotic configurations such as ferroelectric skyrmions. Advanced x-ray coherent scattering and time-resolved diffraction techniques provide the opportunity to probe the fundamental properties of these polarization configurations with excellent structural precision and picosecond-scale time resolution. Our future work has three near-term goals: (1) To probe the atomic-scale structure of exotic ferroelectric domain configurations using x-ray coherent scattering, (2) To obtain insight into the dynamics of nanodomain configurations, and (3) To discover and apply novel x-ray methods for coherent scattering from ferroic nanostructures and interfaces.

Recent Progress: Our current directions build on key recent accomplishments are reported in publications,[P1-P12] and in work that is submitted or being prepared for publication.[R1-R6,R8] Important areas in the context of our future plans are summarized here.

a. Patterns and stability of ferroelectric striped nanodomains. A persistent challenge in x-ray scattering studies of ferroelectric nanodomains has been that incoherent x-ray diffraction patterns allow statistical parameters such as the period and coherence length of the domain pattern to be measured, but do not provide insight into the specific nanoscale configuration. In a series of simulations, we have shown that x-ray coherent scattering can distinguish between local configurations of random stripe domain patterns. Following initial demonstrations with at room temperature, we have used XPCS, in collaboration with Qingteng Zhang and Alec Sandy (ANL), to discover that the decorrelation exhibits a temperature dependent time constant, due to thermal creation and annihilation of pattern defects.[R1] Coherent scattering studies of domain patterns in applied electric fields are in progress.[R2]

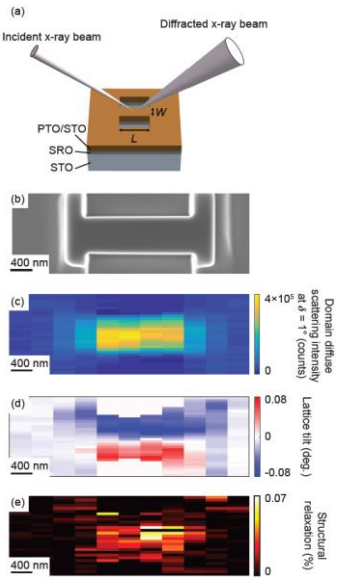


Fig. 1. SEM image and x-ray nanodiffraction maps of the domain diffuse scattering intensity and lattice distortion in PTO/STO nanostructures.

b. Stress and boundary condition effects on ferroelectric stripe domain patterns. The domain pattern (rather than simply its statistics) can be manipulated applied stresses and size effects can be used to control the stripe nanodomain pattern. We have fabricated ridges with hundreds-of-nanometer-scale dimensions using focused ion beam lithography and found that domain walls are aligned along the long axis of the ridge (Fig. 1).[R3] With Stephan Hruskewycz and Paul Fuoss (ANL), we have described strategies in which the domain pattern in ferroelectric nanodomain systems can be imaged using ptychographic techniques.[P1]

c. Ultrafast nanodiffraction studies of complex materials. We have collaborated with scientists at the APS to develop and apply ultrafast methods and to begin to understand the fundamental phenomena associated with the above-bandgap optical excitation of ferroelectrics and other correlated electron systems, resulting in a series of publications beginning in 2013.[R4,P5,P7,P8,P11]

We have found that above-bandgap optical excitation of $BiFeO_3$ yields a structural expansion due to the screening of depolarization fields by excited carriers,[R4,P7,P8,P11] probed the dynamics of the charge density waves in optically excited Cr thin films (with Oleg Shpyrko),[P9] and spatially resolved the nanosecond-scale propagation of the insulator-insulator transition in VO_2,[P5] and found that THz excitation couples to long-duration distortion in $BaTiO_3$ (with Haidan Wen and Aaron Lindenberg).[R5]

d. Nanobeam instrumentation for local optical excitation. The optical excitation of nanostructures presents significant experimental challenges arising from heating and mechanical instability. We have developed low-power optical pumping instrumentation that allows optical excitation with high intensity but very low total power to be combined with x-ray nanobeam techniques, as in Fig. 2.[P8] We have applied this approach to optically excited striped nanodomain systems and found that large optical fluences lead to electronic effects favoring a uniform polarization linked to the depolarization field.[R6]

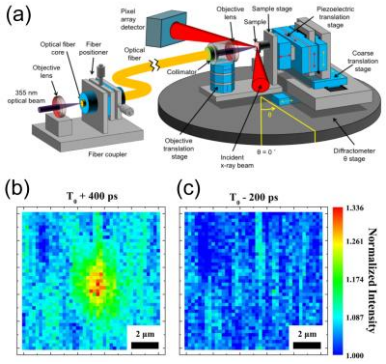


Fig. 2. (a) Optical pump/x-ray nanoprobe instrument. (b) 400 ps after and (c) 200 ps before above bandgap optical excitation in the 2 μm spot at the center of (a).

e. Nanobeam coherent diffraction simulation. We have recently generalized coherent nanobeam diffraction based on wave optical methods developed by Cev Noyan and collaborators (R7) to include more complex thin-film heterostructures.[P2] We have used these methods to (i) characterize the crystalline quality of ultrathin $SrTiO_3$ crystals,[R8] and (ii) to probe the structure of Si/SiGe heterostructures distorted by electrodes.[P3,P12] We have also disseminated these methods via a web-based simulation.[R9]

Future Plans: Our planned work has three components: (i) Structural study of exotic three-dimensional ferroelectric patterns in equilibrium, in applied electric fields, and in applied stresses; (ii) Studies of the ultrafast dynamics of nanodomain patterns in intense optical pulses; and (iii) Extending of coherent diffraction pattern simulation methods from their present use in layered thin film structures to three-dimensions, a crucial step for exotic domain configurations.

References (Indicated with R above.)

R1. Q. Zhang, E. M. Dufresne, P. Chen, J. Park, M. P. Cosgriff, M. Yusuf, Y. Dong, D. D. Fong, H. Zhou, Z. Cai, R. Harder, S. Callori, M. Dawber, P. G. Evans, and A. R. Sandy, "*Thermal Flucutations of Ferroelectric Nanodomains in a Ferroelectric/Dielectric $PbTiO_3/SrTiO_3$ Superlattice*," submitted, (2016).

R2. Q. Zhang, J. Park, J. A. Tilka, Z. Cai, S. Callori, M. Yusuf, M. Dawber, and E. P. G., "*Electric-field driven ferroelectric nanodomain pattern decorrelation*," in preparation, (2016).

R3. J. Park, J. Mangeri, Q. Zhang, S. Callori, M. Yusuf, M. Holt, M. Dawber, S. M. Nakhmanson, and P. G. Evans, "*Polarization nanodomain patterns in ferroelectric/dielectric superlattice nanostructures*," in preparation, (2016).

R4. H. D. 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. L. Li, "*Electronic Origin of Ultrafast Photoinduced Strain in $BiFeO_3$*," Phys. Rev. Lett. **110**, 037601 (2013).

R5. F. C. Chen, Y. Zhu, S. Q. Liu, Y. Li, H. Hwang, N. C. Brandt, J. Lu, F. Quinn, H. Enquist, P. Malden, T. Hu, J. Goodfellow, M. C. Hoffmann, D. Zhu, H. Lemke, J. Glownia, M. Chollet, A. R. Damodaran, J. Park, Z. Cai, I. W. Jung, M. J. Highland, D. A. Walko, J. W. Freeland, P. G. Evans, A. Vailionis, J. Larsson, K. A. Nelson, A. M. Rappe, K. Sokolowski-Tinten, L. W. Martin, H. Wen, and A. M. Lindenberg, "*Ultrafast terahertz-field-driven ionic response in ferroelectric $BaTiO_3$*," submitted, (2016).

R6. Y. Ahn, J. Park, A. Pateras, M. Rich, Q. Zhang, P. Chen, M. H. Yusuf, H. Wen, M. Dawber, and P. G. Evans, "*Photoinduced Domain Pattern Transformation in Ferroelectric/Dielectric Superlattices*," in preparation, (2016).

R7. A. Ying, B. Osting, I. C. Noyan, C. E. Murray, M. Holt, and J. Maser, "*Modeling of kinematic diffraction from a thin silicon film illuminated by a coherent, focused X-ray nanobeam*," J. Appl. Cryst. **43**, 587 (2010).

R8. J. A. Tilka, J. Park, K. C. Sampson, Z. Cai, and P. G. Evans, "*Fabrication and Coherent X-ray Nanobeam Diffraction Characterization of Submicron-Thickness $SrTiO_3$ Crystalline Sheets*," submitted, (2016).

R9. E. Mueller, J. A. Tilka, and P. G. Evans, "*X-ray nanobeam diffraction simulator*," available at: http://xray.engr.wisc.edu/nanobeamsimulation/html/simulation.php (2016).

Publications (2014-2016) (Indicated with P above.)

P1. S. O. Hruskewycz, Q. Zhang, M. V. Holt, M. J. Highland, P. G. Evans, and P. H. Fuoss, "*Structural sensitivity of x-ray Bragg projection ptychography to domain patterns in epitaxial thin films*," Phys. Rev. A **94**, 043802 (2016).

P2. J. Tilka, J. Park, Y. Ahn, A. Pateras, K. C. Sampson, D. E. Savage, J. R. Prance, C. B. Simmons, S. N. Coppersmith, M. A. Eriksson, M. G. Lagally, M. V. Holt, and P. G. Evans, "*Combining experiment and optical simulation in coherent X-ray nanobeam characterization of Si/SiGe semiconductor heterostructures*," J. Appl. Phys. **120**, 015304 (2016).

P3. J. Park, Y. Ahn, K. C. Sampson, D. E. Savage, J. R. Prance, C. B. Simmons, M. G. Lagally, S. N. Coppersmith, M. A. Eriksson, M. V. Holt, and P. G. Evans, "*Electrode-stress-induced nanoscale disorder in Si quantum electronic devices*," APL Mater. **4**, 066102 (2016).

P4. K. M. McElhinny, G. Gopalakrishnan, D. E. Savage, D. A. Czaplewski, M. G. Lagally, M. V. Holt, and P. G. Evans, "*Synchrotron x-ray thermal diffuse scattering probes for phonons in Si/SiGe/Si trilayer nanomembranes*," MRS Advances DOI: 10.1557/adv.2016.352 (2016).

P5. Y. Zhu, Z. Cai, P. Chen, Q. Zhang, M. J. Highland, I. W. Jung, D. A. Walko, E. M. Dufresne, J. Jeong, M. G. Samant, S. S. P. Parkin, J. W. Freeland, P. G. Evans, and H. Wen, "*Mesoscopic structural phase progression in photo-excited VO_2 revealed by time-resolved x-ray diffraction microscopy*," Scientific Rep. **6**, 21999 (2016).

P6. J. Almer, P. Chupas, B. Stephenson, D. Tiede, S. Vogt, L. Young, P. Evans, J. Parise, and R. Suter, "*Emerging Opportunities in High-Energy X-ray Science: The Diffraction-Limited Storage Ring Frontier*," Synchrotron Radiation News **29**, 12 (2016).

P7. Y. Li, C. Adamo, P. Chen, P. G. Evans, S. M. Nakhmanson, W. Parker, C. E. Rowland, R. D. Schaller, D. G. Schlom, D. A. Walko, H. Wen, and Q. Zhang, "*Giant optical enhancement of strain gradient in ferroelectric $BiFeO_3$ thin films and its physical origin*," Scientific Rep. **5**, 16650 (2015).

P8. J. Park, Q. Zhang, P. Chen, M. P. Cosgriff, J. A. Tilka, C. Adamo, D. G. Schlom, H. Wen, Y. Zhu, and P. G. Evans, "*Spatially confined low-power optically pumped ultrafast synchrotron x-ray nanodiffraction*," Rev. Sci. Instrum. **86**, 083904 (2015).

P9. A. Singer, M. J. Marsh, S. H. Dietze, V. Uhlir, Y. Li, D. A. Walko, E. M. Dufresne, G. Srajer, M. P. Cosgriff, P. G. Evans, E. E. Fullerton, and O. G. Shpyrko, "*Condensation of collective charge ordering in chromium*," Phys. Rev. B **91**, 115134 (2015).

P10. 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).

P11. 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).

P12. 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 Rep. **4**, 4218 (2014).

Characterization of magnetic, nanostructured, and energy-relevant materials using advanced photoemission and x-ray techniques

Charles S. Fadley, Dept. of Physics, UC Davis and Materials Sciences Division, LBNL

Program Scope

We will further develop standing-wave soft and hard x-ray photoemission and resonant inelastic scattering and apply these techniques to magnetic, complex oxide, and superconducting systems.

Recent Progress

In past studies, we have shown that standing-wave photoemission (SWPS) is a powerful tool for studying the depth dependence of various properties (atomic concentration, chemical and magnetic state, and valence electronic structure-including SWARPES) [1,2]. Particular emphasis is on measuring interface-specific properties, which can be critical determinants of behavior in many materials systems, including e.g. 2DEG formation [2]. In this prior work, the SW has been generated by Bragg reflection from a multilayer (ML) either as the sample, or on which the sample is grown. In the work to be discussed in this PI meeting, we have extended the technique to make use of Bragg reflection from single-crystal/epitaxial systems (SC) to generate standing waves that scan through the unit cell, thus providing a new dimension of sensitivity. Specific studies carried out under the current DOE grant are:

- Soft- and hard- x-ray ML SWPS and SWARPES is applied to the oxide system $LaCrO_3/SrTiO_3$ (LCO/STO), for which there is interface-induced polarization and ferroelectricity [Chambers, et al. PRL 107, 206802 (2011)]. Very large SW effects are found and these permit determining the concentration profiles through the interfaces and the LCO and STO contributions to the valence-band densities of states [3]. The analysis of soft x-ray SWARPES is currently in progress.
- Following earlier work in which hard x-ray ARPES (HARPES) was first demonstrated [Gray et al. Nature Materials 11, 957 (2012)], hard x-ray Bragg reflection from single-crystal (SC) planes is used to carry out SWPS, including HARPES, from GaAs and the dilute magnetic semiconductor (Ga,Mn)As [4]. By making use of core-level data, we have been able to decompose the HARPES results into their atomic contributions, yielding for the first time element- and k-resolved data. These results are compared with LDA theory in the coherent potential approximation.
- Soft x-ray SC-SWPS, is used to study BSCCO, with preliminary results permitting the decomposition of the valence-level density of states into atomic-layer contributions [5]. The results are compared to LDA theory, including for the first time the superstructure modulations along the crystallographic b axis.
- The ML-SW technique is applied for the first time to RIXS, in particular for the system $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) and $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) [6]. Thin films of LSCO develop weak ferromagnetism associated with charge transfer of spin-polarized electrons from the

ferromagnetic LSMO [De Luca et al., Nature Comm. 5, 5626 (2014)]. SW effects on the different RIXS loss peaks (magnon, bimagnon, d-d excitations, charge-transfer excitations) permit concluding that some do not have the same origin in depth, with more quantitative analysis to determine their depth profiles in progress. The aim here is to give RIXS more direct depth and interface sensitivity for the first time.

Future Plans

We will further analyze the results discussed above, follow these studies onward to obtain additional data and theory, and and prepare publications for them. We will also apply the SC SWPS and SWARPES methods to topological insulator materials, and continue the application of ML SWPS to liquid-solid interfaces, based on pioneering work from prior DOE support [7,8], as well as to semiconductor membrane materials.

References

[1] "Momentum-resolved electronic structure at a buried interface from soft X-ray standing-wave angle-resolved photoemission", A. X. Gray, J. Minár, L. Plucinski, M. Huijben, A. Bostwick, E. Rotenberg, S.-H. Yang, J. Braun, A. Winkelmann, D. Eiteneer, A. Rattanachata, A. Greer, G. Rijnders, D. H. A. Blank, D. Doennig, R. Pentcheva, J.B. Kortright, C. M. Schneider, H. Ebert, and C. S. Fadley, Europhysics Letters 104, 17004 (2013).

[2] "Energetic, spatial, and momentum character of the electronic structure at a buried interface: The two-dimensional electron gas between two metal oxides", S. Nemšák, G. Pálsson , A.X. Gray, D.Eiteneer, A.M. Kaiser, G. Conti, A.Y. Saw, A. Perona, A. Rattanachata, C. Conlon, A. Bostwick, V. Strocov, M. Kobayashi, W.Stolte, A. Gloskovskii, W. Drube , M.-C. Asencio, J. Avila, J. Son, P. Moetakef, C. Jackson, A. Janotti, C. G. Van de Walle , J. Minar, J. Braun, H. Ebert, J.B. Kortright, S. Stemmer, and C. S. Fadley, Phys. Rev. B 93, 245103 (2016).

[3] "Interface composition and electronic structure of $LaCrO_3/SrTiO_3$ from standing wave- and resonant core- and valence- photoemission", S.-C. Lin, R.B. Comes, C.-T. Kuo, S.M. Heald, S.R. Spurgeon, D.M. Kepaptsoglou, Q.M. Ramasse, M. Engelhard, J. Rault, S. Nemšák, P.V. Sushko, S.A. Chambers and C.S. Fadley, to be published.

[4] "Standing-wave hard x-ray angle-resolved photoemission: element- and momentum-resolved band structure for a dilute magnetic semiconductor", S. Nemšák, L.Plucinski, M. Eschbach, S. Döring, C. Schlueter, T.-L. Lee, , S. Borek, J. Minar, J. Braun, H. Ebert, C.M. Schneider, C.S. Fadley, to be published.

[5] "Depth-resolved electronic structure of the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ from standing-wave soft x-ray angle-resolved photoemission", C.-T. Kuo, S.-C. Lin, A.F. Santander-Syro, A. Bostwick, L. Moreschini, J. Rault, A. Taleb-Ibrahim, S.-T. Pi, W.F. Goh, W.E. Pickett, C. S. Fadley, to be published.

[6] "Determining the depth distribution of RIXS excitations at a superconductor/half-metallic ferromagnet interface through standing-wave excitation" , C.-T. Kuo , S.-C. Lin, G. Ghiringhelli, G. De Luca, N. Brookes, D. Di Castro, M. Huijben, Y.Y. Ping, L. Braicovich, C.S. Fadley, to be published.
[7] "Aqueous Solution/Metal Interfaces Investigated in operando by photoelectron spectroscopy", O. Karslıoğlu, S. Nemšák, I. Zegkinoglou, A. Shavorskiy, M. Hartl, F. Salmassi, E.M. Gullikson, M.L. Ng, Ch. Rameshan, B. Rude, D. Bianculli, A.A. Cordones-Hahn, S. Axnanda, E.J. Crumlin, P.N. Ross, C.M. Schneider, Z. Hussain, Z. Liu, C.S. Fadley, H. Bluhm, Faraday Soc. Disc., 2015, 180, 35 (2015).
[8] "Aqueous Solution/Metal Interfaces Investigated in operando by photoelectron spectroscopy", O. Karslıoğlu, S. Nemšák, I. Zegkinoglou, A. Shavorskiy, M. Hartl, F. Salmassi, E.M. Gullikson, M.L. Ng, Ch. Rameshan, B. Rude, D. Bianculli, A.A. Cordones-Hahn, S. Axnanda, E.J. Crumlin, P.N. Ross, C.M. Schneider, Z. Hussain, Z. Liu, C.S. Fadley, H. Bluhm, Faraday Soc. Disc., 2015, 180, 35 (2015)

Publications during the past two years

[1] "Aqueous Solution/Metal Interfaces Investigated in operando by photoelectron spectroscopy", O. Karslıoğlu, S. Nemšák, I. Zegkinoglou, A. Shavorskiy, M. Hartl, F. Salmassi, E.M. Gullikson, M.L. Ng, Ch. Rameshan, B. Rude, D. Bianculli, A.A. Cordones-Hahn, S. Axnanda, E.J. Crumlin, P.N. Ross, C.M. Schneider, Z. Hussain, Z. Liu, C.S. Fadley, H. Bluhm, Faraday Soc. Disc., 2015, 180, 35 (2015), doi: 10.1039/C5FD00003C.
[2] "Depth profiling charge accumulation from a ferroelectric into a doped Mott insulator",M. Marinova, J. E. Rault, A. Gloter, S. Nemšák, G. K. Pálsson, J.-P. Rueff, C. S. Fadley, C. Carrétéro, H. Yamadag, K. March, V. Garcia, S. Fusil, A. Barthélémy, O. Stéphan, C. Colliex, M. Bibes, Nano Letters 15, 2533−2541 (2015).
[3] "Satellite Band Structure in Silicon Caused by Electron-Plasmon Coupling", Johannes Lischner, G. K. Pálsson, Derek Vigil-Fowler, S. Nemsak, J. Avila, M. C. Asensio, C. S. Fadley, and Steven G. Louie, Phys. Rev. B 91, 205113 (2015)
[4] "Observation by resonant angle-resolved x-ray photoemission of a critical thickness for 2-dimensional electron gas formation in $SrTiO_3$ embedded in $GdTiO_3$", S. Nemšák, G. Conti, G.K. Pálsson, C. Conlon, S. Cho, J. Avila, M.-C. Asensio, P. Moetakef, C. Jackson, A. Janotti, C. G. Van de Walle, C. M. Schneider, S. Stemmer, and C. S. Fadley", Appl. Phys. Lett. 107, 231602 (2015).
[5] "Hard X-ray Photoemission: An Overview and Future Perspective", invited introductory chapter in the book Hard X-ray Photoemission, J. C. Woicik, Editor, Springer Springer Series in Surface Sciences, Volume 59, pages 1-34 (2016).
[6] "Energetic, spatial, and momentum character of the electronic structure at a buried interface: The two-dimensional electron gas between two metal oxides", S. Nemšák, G. Pálsson , A.X. Gray, D.Eiteneer, A.M. Kaiser, G. Conti, A.Y. Saw, A. Perona, A. Rattanachata, C. Conlon, A. Bostwick, V. Strocov, M. Kobayashi, W.Stolte, A. Gloskovskii, W. Drube , M.-C. Asencio, J. Avila, J. Son, P. Moetakef, C. Jackson, A. Janotti, C. G. Van de Walle , J. Minar, J. Braun, H. Ebert, J.B. Kortright, S. Stemmer, and C. S. Fadley, Phys. Rev. B 93, 245103 (2016).

[7] “Depth-Resolved Electronic Structure of Buried Layers and Interfaces in a $LaNiO_3/SrTiO_3$ Superlattice from Soft X-ray Standing-Wave Angle-Resolved Photoemission”, D. Eiteneer, G. K. Pálsson, S. Nemšák, A. X. Gray, A. M. Kaiser, J. Son, J. LeBeau, G. Conti, A. Y. Saw, A. Rattanachata, A. Keqi, A. A. Greer, A. Bostwick, E. Rotenberg, E. M. Gullikson, S. Ueda, K. Kobayashi, A. Janotti, C. Van de Welle, A. Blanca-Romero, R. Pentcheva, S. Stemmer C. S. Fadley, J. Electron Spectrosc. 211, 70-81 (2016).

[8] “Interface driven superconductor to insulator transition in ultra-thin manganite-cuprate superlattices” S. Middey, G. Conti, A.X. Gray, C.-T. Kuo, A. M. Kaiser, S. Ueda, K. Kobayashi, D. Meyers, M. Kareev, I. C. Tung, Jian Liu, C. Fadley, J. Chakhalian, and J. W. Freeland. Scientific Reports 6, Article number: 33184 (2016).

Synchrotron Radiation Studies

Paul H. Fuoss, G. Brian Stephenson, Hoydoo You, Dillon D. Fong, Stephan O. Hruszkewycz, Matthew J. Highland, Materials Science Division, Argonne National Laboratory

Program Scope

This program is focused on *in situ* studies of materials synthesis, interfacial chemistry, and the nature and dynamics of the heterogeneities that drive exceptional properties of materials. Through innovative use of the Advanced Photon Source, National Synchrotron Light Source II, the Linac Coherent Light Source and other internationally leading x-ray sources, our research develops and utilizes new x-ray techniques such as Bragg coherent diffraction imaging and x-ray photon correlation spectroscopy to understand fundamental aspects of processing and functioning of materials. Through this work, the program develops x-ray tools that are necessary to characterize complex materials systems; applies those tools to forefront problems in materials science; and helps to provide the basic experimental understanding necessary for the development of breakthrough materials.

Recent Progress

The power of *in situ* and *operando* x-ray techniques will be greatly extended by transitioning from incoherent to coherent x-ray sources. Building on our recent studies of crystal growth, phase transformations, and electrochemical reactions, we are exploring and developing coherent x-ray techniques to resolve the arrangements and evolution of defects that determine behavior of materials. We are developing surface-sensitive Bragg coherent diffraction imaging (BCDI) and x-ray photon correlation spectroscopy (XPCS) techniques to look at dynamic processes on surfaces. We have invented BCDI reconstruction algorithms that greatly reduce the required amount of data and the complexity of data collection. Our goal is to exploit the latest x-ray sources and detectors in experiments to reveal and control dynamic processes in materials.

In Situ Studies of Materials Synthesis and Transformation: Atomic layer deposition (ALD) is a powerful technique for the conformal growth of thin films. However, much remains to be understood regarding ALD growth processes, particularly during the earliest stages that are often key to the resulting film structure and properties. We recently employed a suite of *in situ* synchrotron x-ray techniques to study ZnO deposition by ALD [P15]. Comparing growth on SiO_2 and c-plane Al_2O_3, we found that crystallographic texture development starts with the initial deposits and evolves until reaching island coalescence. The in-plane strain was tensile, most likely due to the formation of grain boundaries. Interestingly, while (001) fiber texture was observed for ZnO/SiO_2, three distinct in-plane textures were observed for ZnO/Al_2O_3 (even at low deposition temperatures), each of which exhibited the three-fold symmetric properties of the

Al (0001) plane. This was mostly due to lowering of the interface energy by the formation of dislocation networks and the Al-O-Zn bonds across the interface. The growth process was studied further by *in situ* x-ray absorption near-edge and extended fine structure spectroscopy [P7], which provided more information on the structure of the islands prior to coalescence. We are now extending our investigations to other materials and metal-organic chemical vapor deposition (MOCVD), with the goal of using coherent x-ray beams to monitor the dynamics of epitaxial growth.

Complex oxide materials exhibit a wide range of functional behaviors, from ferroelectric insulators to superconductors, arising from the natural competition between different underlying ground states. By understanding how phase transitions occur in the complex oxides, novel states of matter may be created by coupling various functionalities and reversibly modulating material properties with an appropriate stimulus. We recently applied *in situ* XPCS toward the study of $SrCoO_x$, a correlated system that demonstrates profound changes in properties with oxygen stoichiometry. It reversibly transforms from a ferromagnetic metal ($SrCoO_3$) to an antiferromagnetic insulator ($SrCoO_{2.5}$) as oxygen is removed from the anion sublattice, providing a model example of how redox chemistry may be used to manipulate electromagnetic properties. Although we discovered that the transformation is fully reversible from a structural standpoint, the XPCS results showed that the dynamics of oxygen vacancy ordering differs greatly for reduction versus oxidation. These results are motivating further studies of dynamics as a function of the $SrCoO_x$ misfit strain, where the substrate lattice parameter is used to tune overall phase transition behavior.

Coherent X-Ray Studies of Surface Dynamics: Surfaces of Au crystals were thought not to interact with gas molecules such as CO and O_2 and were catalytically inactive for CO oxidation reactions.[1] Recently, we found that CO strongly interacts with Au(100) surface, adsorbs, and lifts the hex reconstruction above ~1 Torr. We also studied the interaction of O_2, and found that it also adsorbs and lifts the reconstruction at 1 Torr or higher pressures. However, while CO adsorbs to the hex phase of the surface, O_2 appears to adsorb to the part of the surface where the hex phase is lifted. As a result, O_2 exhibits volcano-type reactivity [P6] where the lifting reaction is highest in an intermediate transition temperature (see Fig. 1). These results motivate our continued development of interface-sensitive ptychography in order to directly image the active areas during simultaneous exposure to CO and O_2.

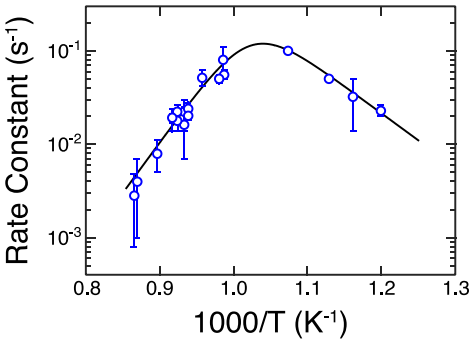


Fig. 1: Rate constants for hex to cubic transition upon oxygen flow.

Bragg Coherent Diffraction Imaging: Increasingly, Bragg coherent x-ray diffraction imaging (BCDI) is being used to measure the evolution of nanoscale strain in crystals under working conditions.[2] A significant accomplishment is our development of theoretical and computational

frameworks for a new Bragg ptychography technique that reconstructs 3D structural images of a single crystal thin film from a set of 2D diffraction patterns measured at a single angle [P4, P17]. To simplify and accelerate strain measurement with complex sample environments, we have invented 3D coherent diffraction methods that require no sample motion and substantially fewer measurements including 1) utilizing polychromatic coherent x-rays to screen populations of nanoparticles [P8], 2) scanning energy rather than sample angle to measure and invert 3D Bragg peaks [P3], and 3) invented a time-resolved BCDI approach that integrates information from earlier time steps to reduce the experimental measurements required for image reconstruction [P10].

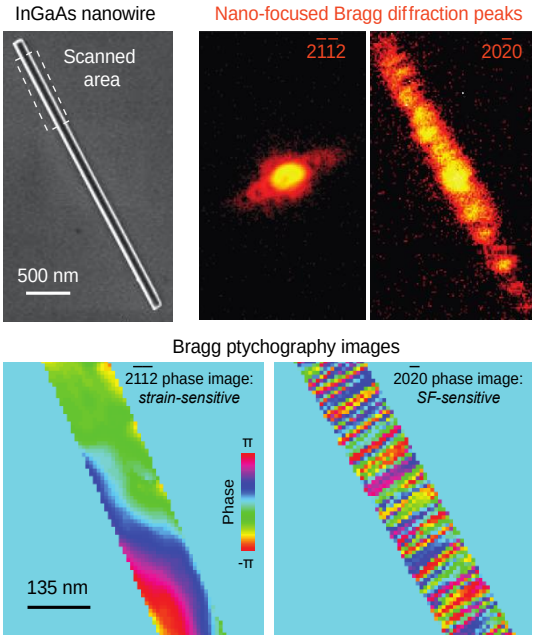


Fig. 2. Bragg ptychography experiments performed at the HXN beamline at NSLS-II reveal strain and stacking fault distributions in an InGaAs nanowire (with Northwestern's Lauhon group). Two contrast mechanisms were used by inverting scans at different Bragg peaks.

Ultrafast Dynamics: Understanding the evolution of atomic-scale dynamics of amorphous materials that occurs at the glass transition has been recognized as outstanding fundamental problems for many decades.[3] While theory and simulation have become increasingly sophisticated, definitive experimental observations remain a challenge because conventional scattering techniques are insensitive to the relevant temporal and spatial correlations. Recently, LCLS developed the capability to create two x-ray pulses at integer multiples of the linac RF frequency (i.e. 350 picosecond separation). We used that capability, along with an x-ray split-and-delay instrument and the latest x-ray detectors developed by LCLS, to measure double-pulse XPCS from supercooled ortho-terphenyl at high wave number (e.g. up to 3 $Å^{-1}$) and probe dynamics of liquids in this important, unexplored spatio-temporal region.

Future Plans

New tools are on the horizon that can revolutionize the science of materials synthesis. Coherent x-ray techniques such as XPCS will enable us to see beyond the average behavior of a fluctuating system and reveal the microscopic arrangements, correlations, and dynamics via complex space/time correlations that go beyond standard instantaneous pair correlations. We will study MOCVD of GaN, to illustrate fundamental materials synthesis issues that are broadly applicable as well as relevant to critical energy applications. We will observe dynamics of three types of processes: a) island formation during layer-by-layer and 3D growth; b) island coarsening after growth; and c) surface step dynamics during step-flow growth and at equilibrium. Results will be compared with kinetic Monte Carlo simulations to provide guidance

and interpretation. This set of experiments will provide the first XPCS measurements of island and step dynamics during MOCVD growth, and will pave the way for future coherent x-ray studies of materials synthesis mechanisms.

Surface reconstructions interact strongly with reactants in gas adsorption reactions or electrochemical reactions as discussed, and influence critically catalytic or electrocatalytic activities of the surfaces. Therefore, visualizing real space images of the reconstructed domains and the domain dynamics are fundamental to understanding catalytic and electrocatalytic behavior of the surfaces. Such real-space visualization becomes possible by applying ptychographic imaging techniques to the surface reconstructions in high-pressure gas or in electrolytes. Reflection ptychography, which we have developed for stepped surfaces, will be further developed to image the domains of hex reconstruction.

Future work in Bragg coherent diffraction imaging (BCDI) will build on recent progress in facilitating in-situ measurement of evolving strain fields in nanoscale crystalline volumes under realistic conditions. By designing single-particle BCDI experiments that utilize simpler data collection methods with improved time resolution, we will probe deeper into scientific questions where in-situ 3D visualization is critical. Specifically, we will use the APS to reveal details of catalytic activity on metal nanoparticle surfaces under different electrochemical conditions. We will also explore strain fields and strain relaxation during annealing of quantum materials (e.g. nanodiamonds) and work to enable simultaneous BCDI and optical characterization of nitrogen-vacancy centers. In addition, we will continue to develop, at NSLS-II and APS, Bragg ptychography methods for 3D imaging of strain in extended crystals with a focus on correlating 3D strain distributions with compositional fluctuations in III-V heterostructures.

Finally, initial experiments utilizing the ultra-fast pump-probe microscopy instrument at sector 7ID of the APS made spatially and temporally resolved x-ray scattering measurements that mapped metal-to-insulator transitions in VO_2 [P12], studied the response if $BaTiO_3$ to enhanced THz radiation, and examined in-plane ballistic thermal transport in complex oxides. We will build on these results to develop materials and techniques for ultra-fast THz pump, x-ray probe studies of nanostructured complex oxides. Particular emphasis will be placed on real-time studies of filament formation in memristor materials and THz field enhancement through the formation of metallic nanostructures.

References

[1] J. Schwank, Gold Bull **18**, 2 (1985).
[2] F. Hofmann, Nat Mater **14**, 756 (2015).
[3] K. Kim and S. Saito, J Chem Phys **138**, 12A506 (2013).

Publications

P1) M. J. Highland, E. Perret, C. M. Folkman, D. D. Fong, C. Thompson, P. H. Fuoss and J. A. Eastman, *The effect of SrO doping on $LaGaO_3$ during synthesis via magnetron sputtering*, Crystal Growth and Design, accepted, (2016).

P2) F. Chen, Y. Zhu, S. Liu, Y. Qi, H.Y. Hwang, N.C. Brandt, J. Lu, F. Quirin, H. Enquist, P. Zalden, T. Hu, J. Goodfellow M.-J. Sher, M.C. Hoffmann, D. Zhu, H. Lemke, J. Glownia, M. Chollet, A.R. Damodaran, J. Park, Z. Cai, I.W. Jung, M.J. Highland, D.A. Walko, J.W. Freeland, P.G. Evans, A. Vailionis, J. Larsson, K.A. Nelson, A.M. Rappe, K. Sokolowski-Tinten, L.W. Martin, H. Wen, and A.M. Lindenberg, *Ultrafast terahertz-field-driven ionic response in ferroelectric $BaTiO_3$*, Physical Review B (Rapid), in press, (2016)

P3) W. Cha, A. Ulvestad, M. Allain, V. Chamard, R. Harder, S. Leake, J. Maser, P. H. Fuoss and S. O. Hruszkewycz, *Three dimensional variable-wavelength x-ray Bragg coherent diffraction imaging*, Physical Review Letters, in press, (2016).

P4) S. O. Hruszkewycz, M. Allain, M. V. Holt, C. E. Murray, J. R. Holt, P. H. Fuoss and V. Chamard, *High resolution three dimensional structural microscopy by single angle Bragg ptychography*, Nature Materials, in press, (2016).

P5) S. O. Hruszkewycz, Q. Zhang, M. V. Holt, M. J. Highland, P. G. Evans, P. H. Fuoss, *Structural sensitivity of x-ray Bragg projection ptychography to domain patterns in epitaxial thin films*, Physical Review A **94**, 043803 (2016).
DOI: 10.1103/PhysRevA.94.043803

P6) A. Loheac, A. Barbour, V. Komanicky, C. Zhu, J. Collini, A. Ruffino, Y. Liu, H. You, and M.S. Pierce, *Interaction of Molecular Oxygen with Hexagonally Reconstructed Au (001) Surface*, Journal of Physical Chemistry C, **120**, 23001 (2016).
DOI: 10.1021/acs.jpcc.6b07020

P7) M. H. Chu, L. Tian, A. Chaker, V. Cantelli, T. Ouled, R. Boichot, A. Crisci, M. I. Richard, O. Thomas, J.-L. Deschanvres, H. Renevier, D. D. Fong, and G. Ciatto, *An atomistic view of the incipient growth of zinc oxide nanolayers*, Crystal Growth and Design **16**, 5339-5348 (2016). DOI: 10.1021/acs.cgd.6b00844

P8) W. Cha, W. Liu, R. Harder, R. Xu, P. H. Fuoss, and S. O. Hruszkewycz, *Utilizing broadband x-rays in a Bragg coherent x-ray diffraction imaging experiment*, Journal of Synchrotron Radiation **23**, 1241 (2016). DOI: 10.1107/S1600577516010523

P9) Steinke, M. Walther, F. Lehmkuehler, P. Wochner, J. Valerio, R. Mager, M. A. Schroer, S. Lee, W. Roseker, A. Jain, M. Sikorski, S. Song, R. Hartmann, M. Huth, L. Strueder, M. Sprung, A. Robert, P. H. Fuoss, G. B. Stephenson, and G. Gruebel, *A liquid jet setup for x-ray scattering experiments on complex liquids at free-electron laser sources*, Review of Scientific Instruments **87**, 063905 (2016). DOI: 10.1063/1.4953921

P10) Ulvestad, A. Tripathi, S. O. Hruszkewycz, W. Cha, S. M. Wild, G. B. Stephenson, and P. H. Fuoss, *Coherent diffractive imaging of time-evolving samples with improved temporal resolution*, Physical Review B **93**, 184105 (2016). DOI: 10.1103/PhysRevB.93.184105

P11) Jun-Hyuk Kim, Gihan Kwon, Hankwon Lim, Chenhui Zhu, Hoydoo You, Yong-Tae Kim, *Effects of transition metal doping in Pt/M-TiO_2 (M = V, Cr, and Nb) on oxygen reduction reaction activity*, J. of Power Sources **320**, 188(2016). DOI: 10.1016/j.jpowsour.2016.04.019

P12) Y. Zhu, Z.H. Cai, P.C. Chen, Q.T. Zhang, M.J. Highland, I.W. Jung, D.A. Walko, E.M. Dufresne, J. Jeong, M.G. Samant, S.S.P. Parkin, J.W. Freeland, P.G. Evans, and H.D. Wen, *Mesoscopic structural phase progression in photo-excited VO_2 revealed by time-resolved x-ray diffraction microscopy*, Scientific Reports **6**, 21999 (2016). DOI: 10.1038/srep21999

P13) Yihua Liu, Andi Barbour, Vladimir Komanicky, and Hoydoo You, *X-ray Crystal Truncation Rod Studies of Surface Oxidation and Reduction on Pt(111)*, Journal of Physical Chemistry C **120**, 16174 (2016). DOI: 10.1021/acs.jpcc.6b00492

P14) A. Barbour, A. Alatas, Y. Liu, C. Zhu, B. M. Leu, X. Zhang, A. Sandy, M. S. Pierce, X. Wang, S.-W. Cheong, and H. You, *Partial glass isosymmetry transition in multiferroic hexagonal $ErMnO_3$***,** Physical Review B **93**, 054113, (2016). DOI: 10.1103/PhysRevB.93.054113

P15) R. Boichot, L. Tian, M.-I. Richard, A. Crisci, A. Chaker, V. Cantelli, S. Coindeau, S. Lay, T. Ouled, C. Guichet, M. H. Chu, N. Aubert, G. Ciatto, E. Blanquet, O. Thomas, J.-L. Deschanvres, D. D. Fong, and H. Renevier, *Evolution of Crystal Structure During the Initial Stages of ZnO Atomic Layer Deposition*, Chemistry of Materials **28**, 592 (2016). DOI: 10.1021/acs.chemmater.5b04223

P16) E.M. Hopper, E. Perrit, B.J. Ingram, H. You, K.C. Chang, P.M. Baldo, P.H. Fuoss, and J.A. Eastman, *Oxygen Exchange in $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ Thin-Film Heterostructures under Applied Electric Potential*, J. of Physical Chemistry C, **119**, 19915 (2015). DOI: 10.1021/acs.jpcc.5b05505

P17) S.O. Hruszkewycz, M. Holt, M. Allain, V. Chamard, S. Polvino, C. Murray, and P.H. Fuoss, *Efficient modeling of Bragg coherent x-ray nanobeam diffraction*, Optics Letters, **40**, 3241 (2015). DOI: 10.1364OL.40.003241

P18) M. J. Highland, D. D. Fong, G. Ju, C. Thompson, P. M. Baldo, P. H. Fuoss, and J. A. Eastman, *In-situ x-ray studies of compositional control during synthesis of $LaGaO_3$ by radio frequency-magnetron sputtering*, Appl. Phys. Lett. **107**, 081606 (2015). DOI: 10.1063/1.492975311/3/14

P19) R.M. Karl, A. Barbour, V. Komanicky, C. Zhu, A. Sandy, M.S. Pierce, and H. You, *Charge-induced equilibrium dynamics and structure at the Ag(001)-electrolyte interface*, Physical Chemistry Chemical Physics, **17**, 16682 (2015). DOI: 10.1039/c5cp02138c

P20) H. Zhou and D. D. Fong, *In situ X-ray Scattering of Epitaxial Oxide Thin Films*, A chapter in Epitaxial Growth of Complex Metal Oxides, Eds. G. Koster, G. Rijnders, and M. Huijben, Woodhead Publishing (Elsevier) (2015). DOI: 10.1016/B978-1-78242-245-7.00010-5

P21) C. Zhu, R. Harder, A. Diaz, V. Komanicky, A. Barbour, R. Xu, X. Huang, Y. Liu, M.S. Pierce, A. Menzel , and H. You, *Ptychographic x-ray imaging of surfaces on crystal truncation rod*, Appl. Phys. Lett., **106**, 101604 (2015). DOI: 10.1063/1.4914927

P22) N. Laanait, Z. Zhang, C.M. Schleputz, J. Vila-Comamala, M.J. Highland and P. Fenter, *Full-field X-ray reflection microscopy of epitaxial thin-films*, Journal of Synchrotron Radiation, **21**, 1252 (2014). DOI: 10.1107/S1600577514016555

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

Selective visualization of Floquet-Bloch and Volkov states in a topological insulator

Periodically driven systems are emerging as promising platforms to realize novel quantum states of matter. Temporal modulation of a quantum system can be used to generate new phases via Floquet theory. One way to achieve this in solid-state systems is to use the oscillating electric field of intense laser light in a Time and Angle Resolved Photoemission Spectroscopy (Tr-ARPES) experiment[1, 2]. In this case, photons coherently interact with Bloch electrons in the solid to generate hybrid dressed states known as Floquet-Bloch states. Characteristic signatures of Floquet-Bloch states in the Tr-ARPES spectra include replicas of the original band structure that are separated by the driving photon energy

The challenge is understanding how these states dynamically interact with other equilibrium and photo-induced states. In particular, another type of photon-electron dressed state arises when light coherently couples to free electrons near the surface of the solid. These states are known as Volkov states and they are used to study non-linear optics in atoms and semi-conductors. They can be generated when light interacts with free electron-like final states in a Tr-ARPES experiment. A central question is how Floquet-Bloch states interact with these Volkov states.

We used Tr-ARPES on the topological insulator Bi_2Se_3 to selectively study the transition between these two states[2]. Figure 1a and 1b show the Tr-ARPES spectra along the k_x and the k_y directions respectively, taken with linear P-polarized pump i.e. one that has both an in-plane electric field component along k_x and an out-of-plane electric field along k_z. The spectra are composed of a manifold of Dirac cones separated by the driving pump energy. Here we note that the Dirac cones are not exact replicas of each other. Rather, the replication of the Dirac cone is asymmetric between the $+k_x$ and $-k_x$ directions.

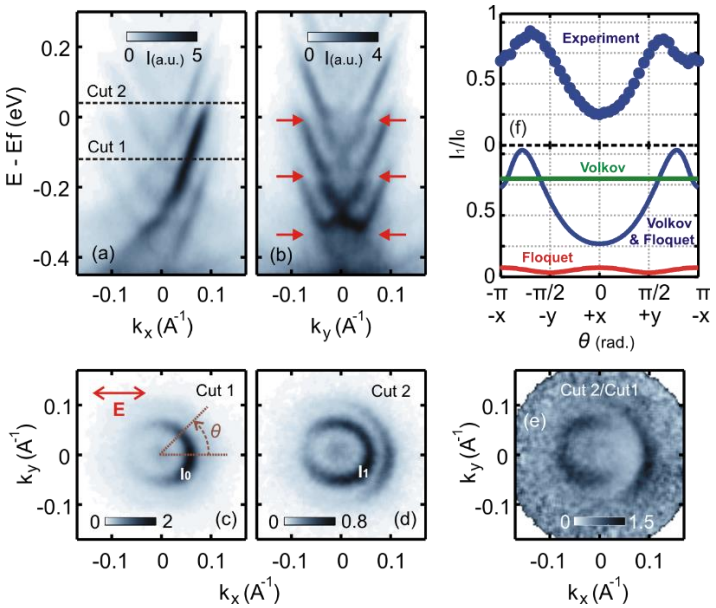


Fig. 1: Tr-ARPES spectra of Bi_2Se_3 for mid-IR linear P-polarized pump with an electric field along k_x and k_z **(a)** Spectra along the k_x direction and **(b)** along the k_y direction. **(c)** Constant energy cut along dashed line 'Cut 1' and **(d)** 'Cut 2' in (a). I0 and I1 indicate the surface state contours for the original Dirac cone and first order side band respectively **(e)** The constant energy cut in (d) is divided by the cut in (c) **(f)** upper: distribution of I1/I0 as a function of angle (□) measured from the $+k_x$ direction. Lower: calculated angular distribution of I_1/I_0. Blue trace corresponds to interference between Floquet-Bloch and Volkov states. (From ref [2])

This asymmetry is more evident in constant energy cuts separated by the driving photon energy, taken along the original (n_0) and first order (n_1) sideband (Fig. 1c, 1d). In order to minimize the effects of spin-texture as well as detector non-linearities, we divide these constant energy cuts (I_1/I_0) and plot the result in Fig.1e. If the n_1 sideband were an exact replica of the n_0 sideband, then I_1/I_0 would be constant as a function of the electron momentum. However, as can be seen in Fig.1e and in Fig.1f, I_1/I_0 is stronger along the $-k_x$ direction than along the $+k_x$ direction indicating that the dressed bands strongly depend on the direction of the electron momentum.

This observed asymmetry is directly related to electrons scattering from Floquet-Bloch to Volkov states[3] which we confirm by performing numerical calculations of the Tr-ARPES intensity using the non-equilibrium two time correlation function of the driven electrons[4] combined with our experimental parameters. Fig. 1f shows the results of this calculation for three different cases: (i) Floquet states only (ii) Volkov states only and (iii) Mixing between Floquet and Volkoc states. As can be seen, case (iii) closely matches the observed angular dependence in the intensity of the first order sideband. The calculation also captures the strong asymmetry in I_1/I_0 between $+k_x$ and $-k_x$, which would not be present for pure Floquet-Bloch (case i) or pure Volkov states (case ii). These results not only imply the presence of both Floquet-Bloch and Volkov states but also point to selective transitions between the two.These selective transitions are a direct consequence of Volkov states being generated primarily due to the out-of-plane E-field for P-polarized pump while Floquet-Bloch states are generated by an in-plane electric field. We recently published these results in ref [2].

Future Plans

We are currently studying formation and decay dynamics of Floquet-Bloch states. We would like to understand whether the intensity of these states directly track the time evolution of the laser pulse or there is an inherent timescale that sets their response. We are also working on establishing these states in materials beyond topological insulators. We are using high harmonic generation based light source with a custom monochromater to reach high (~30 eV) energies to probe higher wavevectors.

References

1. "*Observation of Floquet-Bloch States in a Topological Insulator*" Y.H. Wang, Hadar Steinberg, P. Jarillo-Herrero, and N. Gedik ***Science 342,*** 453 (2013)
2. "*Selective scattering between Floquet-Bloch and Volkov states in a topological insulator*" Fahad Mahmood, Ching-Kit Chan, Dillon Gardner, Young Lee, Patrick A. Lee, Nuh Gedik ***Nature Physics 12,*** 306–310 (2016)
3. "*Interference in Floquet-Volkov transitions*"S. T. Park *Physical Review A* 90, 013420 (2014)
4. "*Theoretical Description of Time-Resolved Photoemission Spectroscopy: Application to Pump-Probe Experiments*" J. K. Freericks, H. R. Krishnamurthy, and Th. Pruschke*Physical Review Letters* 102, 136401 (2009)

Publications

1. "*Selective scattering between Floquet-Bloch and Volkov states in a topological insulator"* Fahad Mahmood, Ching-Kit Chan, Dillon Gardner, Young Lee, Patrick A. Lee, Nuh Gedik ***Nature Physics 12,*** 306–310 (2016)
2. "*Intervalley biexcitons and many-body effects in monolayer MoS_2*" Edbert J. Sie, Alex J. Frenzel, Yi-Hsien Lee, Jing Kong, and Nuh Gedik ***Phys. Rev. B 92,*** 125417 (2015)
3. "*Valley-selective optical Stark effect in monolayer WS_2"* Edbert J. Sie, James W. McIver, Yi-Hsien Lee, Liang Fu, Jing Kong, Nuh Gedik, ***Nature Materials 14,*** 290–294 (2015)
4. "*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, ***Phys. Rev. Lett. 113***, 166801 (2014)
5. "*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)

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures (Grant No. DE-SC0012375).

V. Gopalan & R. Engel-Herbert (Penn State), J. Chakhalian (Rutgers), L. Martin (Berkeley), D. N. Basov & A. Millis (Columbia), R. D. Averitt (UCSD), J. W. Freeland & H. Wen (Argonne), J. M. Rondinelli (Northwestern).

PROGRAM SCOPE

Transition metal oxides, also referred to as complex oxides, present a myriad of fascinating ground states ranging from Mott-Hubbard insulator to correlated metal, ferroelectricity, magnetism and superconductivity. A crucial finding is that these novel equilibrium phases, although often robust, are typically proximal to other, equally fascinating states of matter that are *transient* or *metastable*. Under these conditions only modest changes are necessary to switch systems between drastically different ground-states, resulting in exquisite sensitivity to external influences that include temperature, pressure or uniaxial strain, electric and magnetic fields.

In this review, we will present a few examples of discovery and teamwork, where transient or metastable states have been observed in complex oxides. In a superlattice ferroelectric system, we demonstrated the evolution of a metastable "supercrystal" phase with 15-20nm periodicity using ultrafast laser excitation; this phase is not achievable by thermodynamic processes. Terahertz tuning of novel vortex ferroelectric phases is demonstrated. In a manganite system, we demonstrate the creation of photoinduced ferromagnetic metal phase not found in the equilibrium phase diagram of this material, as well as the creation of a new phase that is as yet unidentified. In a strained nickelate film system, a combination of LCLS and optical pump-probe studies reveal a novel decoupling of magnetism and charge ordering on a 100 fs time scale. We present theoretical advances in effectively coupling electromagnetic radiation to lattice modes in complex oxides, in the switching of the metal-insulator transition in correlated oxides, and in understanding the origin of negative correlation by lattice pumping.

The team has 26 publications, including the discovery of a polar metal (*Nature* **533**, 68 (2016)), correlated metals as transparent conductors (*Nature Materials* **15**, 204 (2016)), polar vortices (*Nature* **530**, 198-201 (2016)), as well as theory development works by Millis (Phys. Rev. Lett. **115**, 266802 (2015), Phys. Rev. **B 93**, 115126 (2016)) and Rondinelli (Sci. Rep. **6**, 25121 (2016)). Overall 17 graduate students/postdocs have received training. Students and postdocs have had an interdisciplinary, inter-institutional experience, including joint advising, working visits to Argonne National Lab and LCLS. Biweekly teleconferences have created a strong team spirit. Theorists and experimentalists are closely interacting with each other on a regular basis. In-person team meetings have taken place at UCSD in February, and the American Physical Society in March, 2016.

RECENT PROGRESS

This ultrafast team has really gelled together well. Progress is being made in completing the theory-synthesis-characterization loop in the team. The key highlights of the past year are:

(1) Synthesis of a range of oxides is in full bloom in the team, between our three synthesis members. These include manganites, nickelates, titanates, vanadates, zirconates, and heterostructures,

(2) A number of discoveries have been made with Ultrafast characterization using visible, infrared, THz, and Xrays. These studies are described in more detail in the future plans section; they will mature and be published in the coming year.

(3) Theory has played an integrated role with experiments in a number of publications, e.g. discovery of polar metal (*Nature* **533**, 68 (2016)), correlated metals as transparent conductors (*Nature Materials* **15**, 204 (2016)), polar vortices (*Nature* **530**, 198-201 (2016)), as well as theory development works by Millis (Phys. Rev. Lett. **115**, 266802 (2015), Phys. Rev. **B 93**, 115126 (2016)) and Rondinelli (Sci. Rep. **6**, 25121 (2016)).

(4) Our **LCLS proposal** on nickelates was successful. A recent run has exciting results that are briefly mentioned below; the theory groups are at present working actively with experimental team to formulate a model for the ultrafast magnetic order collapse.

Select Highlights from Published Articles:

Polar Metals by Geometric Design: (*Nature* (2016); *Acknowledgment for Theory and SHG work*):

It is exceedingly unusual to find a polar metal that exhibits long-range ordered dipoles owing to cooperative atomic displacements aligned from dipolar interactions as in insulating phases. Here we describe the quantum mechanical design and experimental realization of room-temperature polar metals in thin-film ANiO$_3$ perovskite nickelates using a strategy based on atomic scale control of inversion-preserving (centric) displacements. We achieve both a conducting polar monoclinic oxide that is inaccessible in compositionally identical films grown on (001) substrates, and observe a hidden, previously unreported, non-equilibrium structure in thin-film geometries. We expect that the geometric stabilization approach will provide novel avenues for realizing new multifunctional materials with unusual coexisting properties.

Correlated Metals as Transparent Conductors (*Nature Materials* **15**, 204 (2016); *Acknowledgment for Synthesis of CaVO$_3$*):

The fundamental challenge for designing transparent conductors used in photovoltaics, displays and solid-state lighting is the ideal combination of high optical transparency and high electrical conductivity. A new paradigm for identifying high-conductivity, high-transparency metals is proposed, which relies on strong electron–electron interactions resulting in an enhancement in the carrier effective mass. This approach is experimentally verified using the correlated metals SrVO$_3$ and CaVO$_3$, which demonstrate excellent performance when benchmarked against ITO.

Engineered Mott ground state in LaTiO$_{3+\delta}$/LaNiO$_3$ heterostructure (*Nature Communications* **7**, 10418 (2016); *Acknowledgment for synchrotron work and material synthesis. Confirms earlier theory prediction by Millis*)

In pursuit of creating cuprate-like electronic and orbital structures, artificial heterostructures based on LaNiO$_3$ have inspired a wealth of exciting experimental and theoretical results. However, to date there is a very limited experimental understanding of the electronic and orbital states emerging from interfacial charge transfer and their connections to the modified band structure at the interface. Towards this goal, we have synthesized a prototypical superlattice

composed of a correlated metal $LaNiO_3$ and a doped Mott insulator $LaTiO_{3+\square}$, and investigated its electronic structure by resonant X-ray absorption spectroscopy combined with X-ray photoemission spectroscopy, electrical transport and theory calculations. The heterostructure exhibits interfacial charge transfer from Ti to Ni sites, giving rise to an insulating ground state with orbital polarization and e_g orbital band splitting. Our findings demonstrate how the control over charge at the interface can be effectively used to create exotic electronic, orbital and spin states.

Exotic Polar phenomena in oxide superlattices and compositionally graded films (*Acknowledgment for chemical studies while growing films*).

Nature Mater. (2016): Whereas electric-field control has been demonstrated for ferroelectric 180 deg domain walls, similar control of ferroelastic domains has not been achieved. Here, using controlled composition and strain gradients, we demonstrate deterministic control of ferroelastic domains that are rendered highly mobile in a controlled and reversible manner in compositionally graded $PbZr_{1-x}Ti_xO_3$ heterostructures

Nature **530**, 198-201 (2016): In recent years, complex spin topologies have emerged as a consequence of the electronic band structure and the interplay between spin and spin–orbit coupling in materials. Here we produce complex topologies of electrical polarization—namely, nanometre-scale vortex–antivortex (that is, clockwise–anticlockwise) arrays that are reminiscent of rotational spin topologies—by making use of the competition between charge, orbital and lattice degrees of freedom in superlattices of alternating lead titanate and strontium titanate layers.

Magnetic Interactions at the Nanoscale in Trilayer Titanates (*Phys. Rev. Lett*. **116**, 076802 (2016) & *Appl. Phys. Lett.* **107**, 191602 (2015); *Acknowledgment for synchrotron work*)**:**

We report on the phase diagram of competing magnetic interactions at the nanoscale in engineered ultrathin trilayer heterostructures of $LaTiO_3$-$SrTiO_3$-$YTiO_3$, in which the interfacial inversion symmetry is explicitly broken and leads to the formation of a spatially separated two-dimensional electron liquid and high density two-dimensional localized magnetic moments at the $LaTiO_3$-$SrTiO_3$ and $SrTiO_3$-$YTiO_3$ interfaces, respectively. Our results provide a route with prospects for exploring new magnetic interfaces, designing a tunable two-dimensional *d*-electron Kondo lattice, and potential spin Hall applications.

Ultrafast Terahertz Gating of a Multiferroic and Giant Nonlinear Optical Response: (*Adv. Mater.* **27**, 6371-6375 (2015); *Acknowledgment for synthesis and synchrotron work*)

We report measurements showing large amplitude modulations in the nonlinear optical response and ferroelectric polarization in multiferroic $BiFeO_3$ thin films, driven by sub-picosecond THz electric fields. Measurements with probe energies below the band gap where the linear absorption is low show similar nonlinear responses, a key aspect with respect to device applications. Measurements of the polarization dynamics at the morphotropic phase boundary show possibilities for significantly enhancing the response of materials to ultra-fast bias fields.

Charge Order and Antiferromagnetism in epitaxial ultrathin films: (*Phys. Rev. B* **92**, 235126 (2015); *Acknowledgment for synchrotron work.*)

We present a study of reduced dimensionality on charge and antiferromagnetic orderings in ultrathin $EuNiO_3$ films on $NdGaO_3$ substrates using hard and soft resonant x-ray scattering to investigate the presence of electronic and magnetic orderings. Despite the ultrathin nature of the films, they exhibit the bulk-like order parameters up to room temperature, suggesting that the spontaneously coherent Mott ground state in the highly distorted rare-earth nickelates can be successfully sustained even when constrained towards two-dimensionality.

Taming the Dynamical Sign Problem in Quantum Many-Body Problems: (Phys. Rev. Lett. **115**, 266802 (2015); *Acknowledgment for theory development*).

Current nonequilibrium Monte Carlo methods suffer from a dynamical sign problem that makes simulating real-time dynamics for long times exponentially hard. We propose a new "inchworm algorithm," based on iteratively reusing information obtained in previous steps to extend the propagation to longer times. The algorithm largely overcomes the dynamical sign problem, changing the scaling from exponential to quadratic. We use the method to solve the Anderson impurity model in the Kondo and mixed valence regimes, obtaining results both for quenches and for spin dynamics in the presence of an oscillatory magnetic field.

Ultrafast Correlated Electron Phenomena in Vanadates (*Scientific Report*, **6**, 21999 (2016); *Acknowledgment for diffraction work at Argonne*).

The ability to simultaneously track the spatial and temporal evolution of such systems is essential to understanding mesoscopic processes during a phase transition. Using state-of-the-art time-resolved hard x-ray diffraction microscopy, we directly visualize the structural phase progression in a VO_2 film upon photoexcitation. The time-dependent x-ray diffraction spatial maps show that the in-plane phase progression in laser superheated VO_2 is via a displacive lattice transformation as a result of relaxation from an excited monoclinic phase into a rutile phase. The speed of the phase front progression is quantitatively measured, and is faster than the process driven by in-plane thermal diffusion but slower than the sound speed in VO_2.

FUTURE PLANS

Discovery of a New Ferroelastic Insulating Phase in Manganite

(Averitt, Basov, Chakhalian, Freeland, Rondinelli, Millis, Wen)

We are investigating photo-induced transformations of the electronic and magnetic response in complex oxides including strained $La_{0.67}Ca_{0.33}MnO_3$ (LCMO). Our most interesting result is the discovery of a metastable ferromagnetic *ferroelastic* phase that is obtained at higher excitation fluence (~10 mJ/cm^2) or with pressure from an AFM tip. We are currently investigating this new photoinduced phase in detail and are working with theorists to determine what structural changes are required to stabilize this novel state.

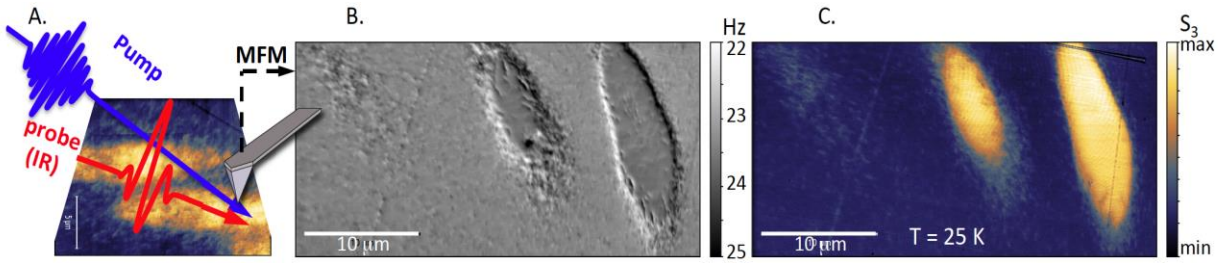


Fig.1: A combination of nano-IR and MFM data developed at UCSD enables complete characterization of the electronic transport and magnetism in photo-induced domains of $La_{0.67}Ca_{0.33}MnO_3$. Panel A: experiment schematics. We utilized Ti:Sapphire Regenerative Amplifier for switching and quantum cascade laser operating at □=11 μm to probe nano-IR contrast. Panels B and C show (MFM) and nano-IR contrast.

Decoupling of Electronic and Magnetic Properties at Ultrafast Timescales in Nickelates

(Ultrafast LCLS and Mid-IR pumping experiments; Freeland, Averitt, Wen, Millis, Rondinelli, Chakhalian)

Nickelates are an intriguing class of materials where strongly coupled degrees of freedom coordinate to create a transition from a metallic to insulating state. One of the key question is which of the degrees of freedom (charge vs magnetism) is the important driver of the phase transition. Using epitaxial growth to apply strain Chakhalian and Freeland have shown it is possible to remove the charge degree of freedom from the problem. To push this understand further, we have been pushing the measurements into the ultrafast realm using X-rays with Wen and Freeland and Optical Probes with Averitt.

Optical pumping*:* The key experiment shown here was our LCLS beamtime at the end of April 2016. During this experiment we were using a combined probe to explore both the magnetism following optical excitation as well as the electronic structure using time-resolved X-ray absorption. We simultaneously recorded the magnetic scattering and absorption resonances. By sitting at the energy marked with a vertical line, we tracked the time delay between and optical (800 nm) pump and the 100 fsec X-ray probe in both channels. We found that the magnetism collapses in 250 fsec while the electronic structure evolves more slowly over 450 sec. *This shows that the magnetism is the first to collapse but that the electronic structure needs more time to reconfigure*. Optical pump – Thz probe data suggests that it might even take 2-3 psec before the carriers free into a metallic phase. *To our knowledge these are the first data to ever show a disconnect on this time-scale and we are working with our theory team* (Rondinelli and Millis) to understand these very recent results.

Mid-IR Pumping: We were also able to collapse the magnetic state with direct phonon excitation in the mid-IR region (15 um). As shown in Fig. 2(c), the timescale of phonon excitation is much slower since the lattice degree of freedom needs psec timescales to evolve. We believe this data might be too fast for substrate phonons launched into the film and might be a direct excitation of the $NdNiO_3$ film.

We also have preliminary results using Mid-IR pumping and THz probing. *Importantly, we now have sufficient mid-infrared pulse fluence (~1mJ/cm^2) to enable phononpumping studies with THz probe*. We note that this experiment also operates for phonon-pump, optical-probe which will enable even higher excitation fluence for optical excitation, the pump and probe beams can be focused more tightly in comparison to probing with far-infrared THz pulses. During the next performance period, this experiment will be used to investigate phonon pumping in strained LCMO films (which exhibit metastable ferromagnetic metallic and insulating state with optical excitation) to determine if other excitation pathways enable metastable phase transitions in this intriguing material system. This experiment will also be utilized to investigate other materials including the nickelate and calcium vanadates.

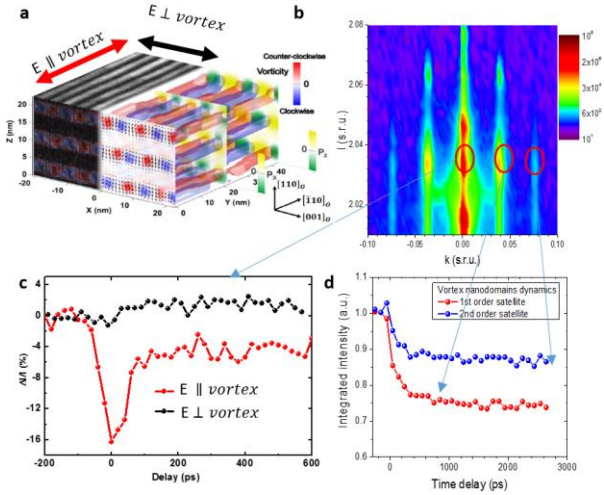


Figure 2. a) Transmission electron microscopy and phase field simulation of confined vortex states in $PbTiO_3$ layer from a $(PbTiO_3)_{10}/(SrTiO_3)_{10}$ superlattice; b) Reciprocal space mapping of the collinear and vortex domains; c) Vortex diffraction intensity change after a THz field excitation with an peak field of 1 MV / cm; The polarization of the THz field is either parallel or perpendicular to the vortex chains as shown in a). d) Vortex satellites intensity changes as a function of time upon 400 nm optical excitation.

Ultrafast Terahertz-field control of Novel Vortex states in $PbTiO_3/SrTiO_3$ super lattice (Wen, Freeland, Martin, Basov, and Gopalan).

Recently, a new state of matter, uni-dimensional arrays of ferroelectric vortices with alternating chirality was created by leveraging the competition between charge, orbital and lattice degrees of freedom in $PbTiO_3/SrTiO_3$ superlattices (**Figure 2,a,b**). available before in collinear ferroelectrics.

We demonstrate, for the first time, an ultrafast electric field control of vortex states using THz field excitation and hard x-ray diffraction measurements. In sharp contrast to the optical control, the ultrafast THz field pulses can directly influence electric polarization reversibly depending on the relative polarization of the electric field and the vortex chains.

Design and Control of Mott Transitions in Vanadates (Engel-Herbert, Averitt, Wen, Rondinelli)**:**

We have fully optimized the growth of $La_{1-x}Sr_xVO_3$ using Hybrid molecular beam epitaxy for any value of *x*, which provides a fully tunable platform to study the effects of the emergence of the Mott insulating gap ($LaVO_3$) from the strongly correlated metal phase ($SrVO_3$). *In so doing we have serendipitously found that at the phase boundary between the Mott insulator phase and the metallic phase, there is a very interesting relation between the metal and insulator phases with the application of disorder near the quantum critical point*. Upon increasing disorder a universal insulating phase emerges at low temperature, while disorder destabilizes the high temperature-metallic non-Fermi liquid phase, and a Fermi liquid reemerges.

We now also have a well-proven and highly optimized algorithm for experiments to extract the dynamics of octahedral rotations. This is the first step for *phonon pumping*

experiments that directly pump octahedral modes. Rondinelli is exploring the effect of strain-induced changes in the structure of $LaVO_3$ on magnetic ordering temperatures using DFT.

Theory of Ultrafast Phenomena (Rondinelli, Millis)**:**

Bandgap Engineering with Stimulated Raman Scattering . We have proposed a dynamical way to control the electronic bandgap of a material by excitation of a first-order Jahn-Teller (FOJT) Raman mode, utilizing impulsive stimulated Raman scattering. We find that when the phonon modulation vector coincides with the antiferromagnetic vector, spin splitting occurs at the **Γ**-point. The total process can be described as a light-induced Zeeman-like effect, and allows a light-induced transformation from an indirect to a direct transition.

Raman-Infrared Mode Coupling in d^n Titanates. We are pursuing a systematic study to address how the electronic state in orthorhombic titanates, ranging from d^0 to d^1, tunes the interaction strengths between IR and Raman modes. This understanding is sought to establish 'design guidelines' for creating artificial superlattice structures. The guidelines will are to be used by thin film growth team members to enable phononic excitations and designed electronic metal-insulator transition. This work is in review at Phys. Rev. B.

Ultrafast control of magnetism by nonlinear coupling in d^1 systems. $LaTiO_3$ (LTO) and $YTiO_3$ (YTO) are isostructural titanates, however the amplitude of the octahedral rotations are significantly different. Investigating the difference between these systems allows us to understand the role of magnetic order on the electron-phonon interaction and to validate our dynamical design rules.

Manipulation of the polar mode in the noncentrosymmetric metal $Ca_3Ru_2O_7$. $Ca_3Ru_2O_7$ is a noncentrosymmetric metal with rich structural, electronic and magnetic phase diagrams. We have investigated this system to explore the role of the polar mode to the metallicity and the magnetism properties. Experimental collaboration in ongoing in Gopalan group.

***Optical pumped non-equilibrium orbital states in Complex Manganites*.** Recent pump-probe experiment carried out by Averitt's group has shown that sufficient laser intensity can be used to pump the $La_{1-x}Ca_xMnO3$ (LCMO) to an abnormal ferromagnetic insulating state (FM-I), which does not exist at that specific doping level in the phase diagram. By applying DFT-PBE+*U* calculations we have spent portions of this period searching for possible atomic structures and orbital states that stabilized this electronic phase.

Optical antiferroelectric-to-ferroelectric phase transition in Lead Zirconate.
PI Martin has grown lead zirconate ($PbZrO_3$) and our objective is to induce a phase transition from the antiferroelectric ground state to a ferroelectric state via nonlinear phonon coupling using laser light.

New methods for solving the nonequilibrium many-body problem: Monte Carlo methods (which play a key role in equilibrium calculations) suffer from a severe dynamical sign problem, motivating us to investigate other methods, in particular based on exact diagonalization methods based on matrix product state methods for dramatically reducing the size of the needed Hilbert space.

PUBLICATIONS

1. "Polar Metals by Geometric Design," T. H. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. J. Ryan, Y. Choi, J.-W. Kim, J. R. Patzner, S. Rzchowski, X. Q.Pan, **V. Gopalan, J. M. Rondinelli**, C-B. Eom, doi:10.1038/nature17628, *Nature* (2016). The work at Pennsylvania State University was supported by the DOE–BES, under award number DE-SC0012375 (Y.Y., V.G.) who performed the optical measurements. D. P. who performed the theory work at Northwestern University,was supported by the DOE–BES DE-SC0012375.

2. *Correlated metals as transparent conductors*, Lei Zhang, Yuanjun Zhou, Lu Guo, Weiwei Zhao, Anna Barnes, Hai-Tian Zhang, Craig Eaton, Yuanxia Zheng, Matthew Brahlek, Hamna F Haneef, Nikolas J Podraza, Moses HW Chan, **Venkatraman Gopalan**, Karin M Rabe, **Roman Engel-Herbert**, *Nature Materials* **15**, 204 (2016). The Department of Energy through Grant DE-SC0012375 (M.B., R.E.-H.), M.B. synthesized $CaVO_3$ thin films. L.Z. and R.E.-H. conceived and designed the experiments.

3. A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. Clarkson, C. Schlepuetz, A. R. Damodaran, P. Shafer, E. Arenholz, L. R. Dedon, A. Vishwanath, A. M. Minor, L. Q. Chen, J. F. Scott, **L. W. Martin**, R. Ramesh, Observation of polar vortices in oxide superlattices. *Nature* **530**, 198-201 (2016). L.R.Deon acknowledges support from the US Department of Energy, Office of Basic Energy Sciences (DE-SC0012375) for the chemical analysis of the superlattice structures.

4. Y. Cao, X. Liu, M. Kareev, D. Choudhury, S. Middey, D. Meyers, J.-W. Kim, P.J. Ryan, **J.W. Freeland** and **J. Chakhalian**, Engineered Mott ground state in $LaTiO_{3+\delta}/LaNiO_3$ heterostructure, *Nature Communications* **7**, 10418 (2016). J.C. and X.L. were supported by the Department of Energy grant DE-SC0012375 for synchrotron work at the Advanced Photon Source and material synthesis.

5. J. C. Agar, A. R. Damodaran, M. B. Okatan, J. Kacher, C. Gammer, R. K. Vasudevan, S. Pandya, L. R. Deon, R. V. K. Mangalam, G. A. Velarde, S. Jesse, N. Balke, A. M. Minor, S. V. Kalinin, **L. W. Martin**, Highly-mobile ferroelastic domain walls in compositionally-graded ferroelectric thin films. *Nature Mater.* (2016). DOI: doi:10.1038/nmat4567 (will be a News and Views in Nature Mater.) L.R.D. acknowledges support from the Department of Energy, Basic Energy Sciences under grant No. DE-SC0012375 for chemical studies of the materials.

6. Y. Cao, Z. Yang, M. Kareev, X. Liu, D. Meyers, S. Middey, D. Choudhury, P. Shafer, J. Guo, **J. W. Freeland**, E. Arenholz, L. Gu, and **J. Chakhalian**, Magnetic Interactions at the Nanoscale in Trilayer Titanates *Phys. Rev. Lett*. **116**, 076802 (2016). X. L. was supported by the Department of Energy Grant No. DE- SC0012375 for his synchrotron work.

7. G. X. Ni, L. Wang, M. D. Goldflam, M. Wagner, Z. Fei, A. S. McLeod, M. K. Liu, F.Keilmann, B. Özyilmaz, A. H. Castro Neto, J. Hone, M. M. Fogler and **D. N. Basov** "*Ultrafast optical switching of infrared plasmon polaritons in high-mobility graphene*" *Nature Photonics* **10**, 244 (2016). (supported by this project, but the grant number as published has a typo).

8. Taming the dynamical sign problem in real-time evolution of quantum many-body problems, Guy Cohen, Emanuel Gull, David. R. Reichman, Andrew J. Millis, Phys. Rev. Lett. **115**, 266802 (2015). A. J. M. and G. C. acknowledge support from the Department of Energy under Grant No. DE-SC0012375.

9. F. Chen, J. Goodfellow, S. Liu, I. Grinberg, M. C. Hoffmann, A. R. Damodaran, Y. Zhu, X. Zhang, I. Takeuchi, A. Rappe, **L. W. Martin**, **H. Wen**, A. M. Lindenberg, Ultra-fast terahertz gating of polarization and giant nonlinear optical response in $BiFeO_3$ thin films. *Adv. Mater.* **27**, 6371-6375 (2015). L.W.M. and H.W. acknowledge support from the Department of Energy under Grant No. DE-SC0012375.

10. D. Meyers, S. Middey, M. Kareev, J. W. Kim, P. Shaffer, P. Ryan, and **J. Chakhalian**, Charge ordering and magnetism in ultra-thin $EuNiO_3$ thin films, *Phys. Rev. B* **92**, 235126 (2015). J.C. was supported by the Department of Energy Grant No. DE-SC0012375 for synchrotron work.

11. Photoinduced phase transitions in narrow-gap Mott insulators: the case of VO_2, Zhuoran He, Andrew J. Millis, Phys. Rev. **B 93**, 115126 (2016). This research is supported by the Department of Energy under Grant No. DE-SC0012375.

12. X. Liu, D. Choudhury, Y. Cao, M. Kareev, S. Middey, and **J. Chakhalian**, Metallic interface in non-$SrTiO_3$ based titanate superlattice, *Appl. Phys. Lett.* **107**, 191602 (2015). Y.C. and X.L. acknowledge the support by the Department of Energy Grant No. DESC0012375.

13. Y. Cao, P. Shafer, X. Liu, D. Meyers, M. Kareev, S. Middey, J. W. Freeland, E. Arenholz, and **J. Chakhalian**, Magnetism and electronic structure of $YTiO_3$ thin film, *Appl. Phys. Lett.* **107**, 112401 (2015). X.L. acknowledges the support by the Department of Energy grant DESC0012375.

14. H.-T. Zhang, L. R. Dedon, **L. W. Martin**, **R. Engel-Herbert**, Self-regulated growth of $LaVO_3$ thin films by hybrid molecular beam epitaxy. *Appl. Phys. Lett.* **106**, 233102 (2015). L.R.D. and L.W.M. acknowledge support from the Department of Energy under Grant No. DE-SC0012375 for RBS measurements and analysis.

15. *Accessing a growth window for $SrVO_3$ thin films*, M. Brahlek, L. Zhang, C. Eaton, H.-T. Zhang, and R. Engel-Herbert, Applied Physics Letters **107**, 143108 (2015). M.B. and R.E.H. acknowledge the Department of Energy (Grant No. DE-SC0012375) for the growth, XRD, transport measurements, and preparation of the manuscript

16. Yi Zhu, Zhonghou Cai, Pice Chen, Qingteng Zhang, Matthew J. Highland, Il Woong Jung, Donald A. Walko, Eric M. Dufresne, Jaewoo Jeong, Mahesh G. Samant, Stuart S. P. Parkin, John W. Freeland, Paul G. Evans & Haidan Wen, Mesoscopic structural phase progression in photo-excited VO2 revealed by time-resolved x-ray diffraction microscopy, *Scientific Reports*, **6**, 21999 (2016). H. W. and J. F. acknowledge the support for the data analysis from the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-SC0012375.

17. M. Gu and **J,M. Rondinelli**, Ultrafast Band Engineering and Thermal Spin Currents in Antiferromagnetic Oxides, Scientific Reports (2016). doi:10.1038/srep25121

18. R. Gao, Y. Dong, H. Xu, H. Zhou, Y. Yuan, **V. Gopalan**, C. Gao, D. D. Fong, Z. H. Chen, Z. Luo, **L. W. Martin**, Interfacial octahedral rotation mismatch control of the symmetry and properties of $SrRuO_3$. *ACS Appl. Mater. Inter.* Mar. 2016. **DOI:** 10.1021/acsami.6b02864

19. F. Chen, Y. Zhu, S. Liu, Y. Qi, H. Hwang, N. C. Brandt, J. Lu, F. Quirin, H. Enquist, P. Zalden, T. Hu, J. Goodfellow, M. C. Hoffman, D. Zhu, H. Lemke, J. Glowina, M. Chollet, A. R. Damodaran, J. Park, Z. Cai, I. W. Jung, M. J. Highland, D. A. Walko, **J. W. Freeland**, P. G. Evans, A. Vailionis, J. Larsson, K. Nelson, A. M. Rappe, K. Sokolowski-Tinten, **L. W. Martin**, **H. Wen**, A. M. Lindenberg, Terahertz electric-field-driven ionic response in ferroelectrics. accepted *Phys. Rev. B* 2016. Accepted. (https://journals.aps.org/prb/accepted/fb072K4dA4919309b1d68e251b5ffe43a226cffb3).

20. A. R. Damodaran, J. C. Agar, Z. Chen, S. Pandya, R. Xu, L. Dedon, S. Sareminaeini, **L. W. Martin**, New Modalities of Strain-control of ferroelectric thin films (invited review). *J. Phys. Condens. Matter*, http://dx.doi.org/10.1088/0953-8984/28/26/263001

21. **D. Meyers**, Jian Liu, J. W. Freeland, **S. Middey**, M. Kareev, Jihwan Kwon, J. M. Zuo, Yi-De Chuang, J.-W. Kim, P. J. Ryan, and J. Chakhalian, "*Pure electronic metal-insulator transition at the interface of complex oxides" , Scientific Reports* doi:10.1038/srep27934). In bold are the people for synchrotron work and growth efforts.

22. H.-T. Zhang, L. Dedon, L. W. Martin, R. Engel-Herbert, Self-regulated growth of $LaVO_3$ thin films by hybrid molecular beam epitaxy. under review *Appl. Phys. Lett.* 2015 http://dx.doi.org/10.1063/1.4922213.

23. F. Chen, J. Goodfellow, S. Liu, I. Grinberg, M. C. Hoffmann, A. R. Damodaran, Y. Zhu, P. Zalden, X. Zhang, I. Takeuchi, A. Rappe, L. W. Martin, H. Wen, A.M. Lindenberg, Ultrafast terahertz gating of the polarization and giant nonlinear optical response in $BiFeO_3$ thin films. *Advanced Materials*, **27**, 6371 (2015). DOI: 10.1002/adma.201502975.

24. E. Breckenfeld, Z. Chen, A. R. Damodaran, L. W. Martin, Effects of nonequilibrium growth, nonstoichiometry, and film orientation on the metal-to-insulator transition in $NdNiO_3$ thin films. *ACS Appl. Mater. Inter.* **6**, 22436-22444 (2014).

25. H. Wen, M. Sassi, Z. Luo, C. Adamo, D. G. Schlom, K. M. Rosso, X. Zhang "Capturing ultrafast photoinduced local structural distortion of $BiFeO_3$", doi:10.1038/srep15098 (2015).

26. N. Wagner and **J.M. Rondinelli**, Theory-guided Machine Learning in Materials Science, *Front. Mater.* **3**, 28 (2016). N.W. was supported by DOE grant number DE-SC0012375 for the machine learning analysis.

RIXS investigations of correlated and topological phases in *f*-electron materials

Jason N. Hancock, Department of Physics and Institute for Materials Science, University of Connecticut, Storrs, CT 06269, USA

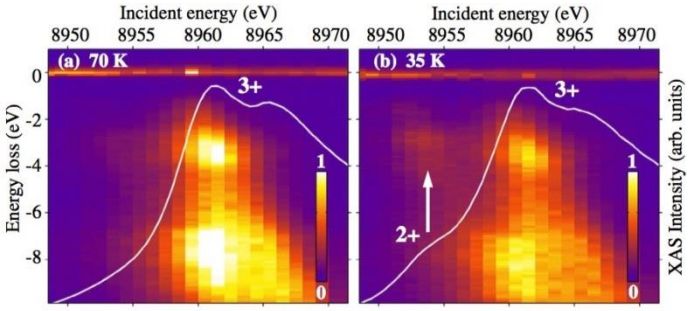
Maxim Dzero, Department of Physics, Kent State University, Kent, OH 44242, USA

Program Scope

Due to strong scientific interest in high-temperature superconductivity (where it is known to exist) and the large exchange energy scales in 3*d* materials classes, a natural historical progression of the resonant inelastic X-ray scattering (RIXS) technique has left many stones unturned further down the periodic table. Nowadays, energy resolution achievements motivated by light metal science has positioned us to turn this developing technique on a broader range of materials. *f*-electron materials host interesting phase competition and have exploded as an arena for materials which may hold nontrivial electronic topology. Using current-generation synchrotron techniques and facilities in the US and abroad, our collaboration has shown that useful signal can be reaped in the context of Yb- and Sm-based materials in the soft and hard X-ray regimes.

Recent Progress

We present recent and new results on an exemplary material $YbInCu_4$, which shows a first-order phase valence transition where the order parameter may be characterized as the *f*-count. This temperature-driven instability has been discussed in connection to the Kondo valence collapse scenario, but the relative insensitivity of volume to valence change has left an open hole in this explanation. A density-of-states effect has long been hypothesized, and only recently have we used RIXS to present strong evidence of a quasi-gap in the itinerant state density, as probed through the Yb 5d-derived bands using L_3-edge (3*p* to 5*d*) RIXS. This quasigap was not observed using optical spectroscopy and cannot be observed using photoemission, due to the known surface-related phenomena in this class of materials. We will also present a first look using related approaches to Sm-based materials.



Color plot of the Yb-L_3 RIXS plane of $YbInCu_4$ with the absorption spectrum (solid white line) measured at (a) 70 and (b) 35 K. The arrow shows and enhancement of RIXS scattering induced by the valence transition which appears only through the +2 intermediate state.

Separately, we also present $M_{4,5}$-edge (3*d* to 4*f*) RIXS spectra on the same material and show that a completely disjoint set of information can be determined by exciting primarily 4*f* states in the "direct" RIXS process. Here, we see spin-orbit excitations as well as signature of the hybridization gap detected in optical experiments, but now with valence and orbital selectivity and momentum control.

Future Plans

This is a new program, but we have already investigated some rare-earth hexaborides using *L*-edge RIXS. With collaborator Jian-xin Zhu (LANL), we show the relation between calculation and experiment and plan to extend this theory-experimental cooperation to cluster modeling. We are developing high-energy-resolution *L*-edge RIXS at rare earth edges in cooperation with the APS IXS team and intend to investigate rare earth materials using the new generation of soft RIXS instrumentation.

References

[1] I. Jarrige, A. Kotani, H. Yamaoka, N. Tsujii, K. Ishii, M. Upton, D. Casa, J. Kim, T. Gog, and J. N. Hancock, Kondo interactions from band reconstruction in YbInCu4, Physical Review Letters, 114, 126401 (2015)

[2] J. N. Hancock and I. Jarrige, The promise of resonant inelastic X-ray scattering for f-electron materials, Journal of Magnetism and Magnetic Materials, 400, 41 (2016).

[3] J. N. Hancock, T. McKnew, Z. Schlesinger, J. L. Sarrao, and Z. Fisk, Kondo Scaling in the Optical Response of YbIn1−xAgxCu4 Physical Review Letters 92, 186405 (2004)

[4] S. R. Garner, J. N. Hancock, Y. W. Rodriguez, Z. Schlesinger, B. Bucher, Z. Fisk, J. L. Sarrao, Optical Study of the Electronic Phase Transition of Strongly Correlated YbInCu4, Physical Review B 62, R4778 (2000)

Publications

This is a new program (August 2016).

DOE/BES Grant No. DOE/BES DE-FG-02-05ER46200/Hasan

DOE/BES/X-ray PI Meeting, November, 2016

Discovery of New Topological Phases of Matter: Platform for emergent Dirac, Majorana and Weyl fermions

M. Zahid Hasan

Dept. of Physics, Princeton University

Email: mzhasan@princeton.edu

Topological materials can host Dirac, Majorana and Weyl fermions as emergent excitations and possess unusual ultrafast (X-ray or optical) response. In topological insulators and related superconductors, the topological fermions are robust in the presence of a gap ***(Hasan & Kane, Rev. of Mod. Phys. 82, 3045 (2010)***). A Weyl semimetal is the rare exception in this scheme which is a topologically robust conductor whose emergent bulk excitations are Weyl fermions. The chiralities associated with the Weyl nodes can be understood as topological charges, leading to split monopoles and anti-monopoles of Berry curvature field in momentum space. Due to this topology it is expected to exhibit Fermi arc states on its surface (Wan et.al., 2011). These arcs are discontinuous or disjoint segments of a two dimensional Fermi contour with non-trivial spin textures, which are terminated onto the projections of the Weyl nodes on the surface observed recently in experiments. Our theoretical predictions (***Huang, Xu et.al., Nature Commun. 2015, Science Adv. 2016***) and experimental demonstrations (***Xu, Belopolski et.al., Science (2015), Nature Physics 2015, Science Adv. 2015, Science Adv. 2016***) reveal that these arc quasiparticles can only live on the boundary of a 3D crystal which collectively represents the realization of a new state of quantum matter unlike Dirac Fermi arcs (***Xu, Liu et.al., Science (2015); Jia, Xu & Hasan (mini-review in); Nature Materials 2016***). Strong spin-orbit interaction and crystalline symmetries can also lead to a strong tilt of the Weyl cone which manifestly break Lorentz invariance. We present evidence that the LaAlGe materials family host such a state of matter which can be used to test ideas on quantum gravity and space-time geometry in early universe. We obtained new results on a topological nodal-line semimetal state in (Pb/Tl)TaSe2 (***Bian et.al., Nature Commun. 2016***) which also superconducts at low temperatures possibly suggesting a new platform to investigate the interplay of superconductivity and topology leading to a new Majorana platform. I report recent results on the ultrafast response of topological materials including the discovery of gigantic surface life-time of an intrinsic topological insulator revealed via time-resolved (pump-probe) ARPES.

Our future work will involve search and discovery of novel topological materials and study of their electronic ultrafast response phenomena.

Magnetization Dynamics and Soft X-Ray Vortex Beam Formation in Nanoscale Magnetic Metamaterials

PI: J. Todd Hastings, Electrical and Computer Engineering, University of Kentucky
Collaborators: Lance E. De Long, Physics, University of Kentucky; Sujoy Roy, Advanced Light Source, LBNL; Wai-Kwong Kwok, Materials Science Division, ANL

Program Scope

The current program seeks to understand the dynamics of magnetic artificial spin ices (ASI) and to use this understanding to control the angular momentum of scattered x-ray beams. The ASI of interest are periodic arrays of sub-micron-scale, elongated segments of ferromagnetic (FM) thin films as shown in Figure 1. The frustrated topology and mesoscopic segment size causes them to resist thermal equilibration into long-range order. The equilibration time for such ASI can be varied over many decades, and, as a result, ASI can serve as models for understanding systems far from equilibrium. Moreover, control of these processes and engineering of their time scales may allow ASI to be programmed into states with useful functions such as magnetic logic or phase control of an x-ray beam. ASI designed and fabricated at the University of Kentucky will be characterized using X-ray photon coherent scattering (XPCS) at LBNL's Advanced Light Source. Complimentary magnetic force microscopy and magnetic manipulation experiments will be carried out at Argonne National Laboratory.

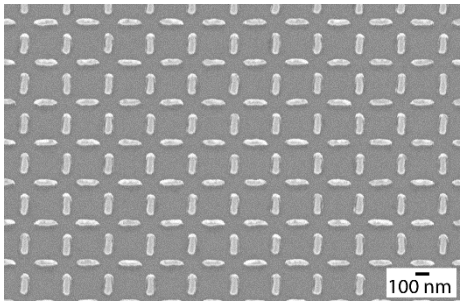


Figure 1. SEM image of a square ASI patterned in a permalloy ($Ni_{0.8}Fe_{0.2}$) thin film of 25-nm thickness, with segment width w = 50 nm, length L = 150 nm, and lattice spacing d = 300 nm. After [1].

Recent Progress

This program started in September 2016; however, preliminary data obtained under other support indicates that relaxation time for permalloy square ASI depends on film thickness as expected from prior work with Kagome[2,3] and square ASI.[4,5] As shown in Figure 2, a 25-nm thick ASI shows weak and slow relaxation while a 3-nm thick sample (passivated with 2-nm thick Al/AlO_x) shows greater relaxation over a similar time scale. Figure 3 shows magnetic scattering from these structures can exhibit a minimum near the centers of Bragg peaks which is sensitive to applied magnetic field. This is attributed to the formation of magnetically charged superdomain walls.[1] However, structure factor calculations indicate that a texture consisting of four superdomains of a certain type, shown in Figure 4, could give rise to similar structure in the Bragg peak. In this case, the minimum arises from optical phase singularities, and introduces the possibility of imparting controllable orbital angular momentum to the x-ray beam.

Future Plans

XPCS will be used to characterize magnetic textures, topological defects, magnetic relaxation, spin ice behavior and possible phase transitions in artificial frustrated lattices. We plan to tune the magnetic dynamics by controlling (1) relaxation of the lattice symmetries, (2) thickness of the FM film, and (3) composition of the FM material. In addition, we will seek geometries and field cycling protocols that can produce central minima, and possibly OAM, in the diffracted beams. Comparison of experimental and simulated magnetic scattering signatures will provide insight into the origin of this phenomenon and means of controlling it. This work will be complemented by MFM measurement, and possibly manipulation,[6] of ASI structures with static or slowly varying magnetic textures that yield phase singularities.

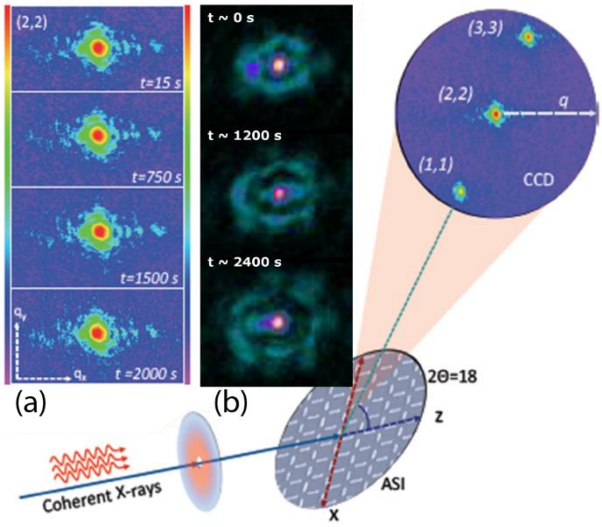


Figure 2. Experimental geometry for XPCS with **(a)** time series of the speckle intensity near the (2,2) Bragg peak from a 25-nm thick square ASI, and **(b)** time series from a 3-nm thick sample showing greater evolution of the diffuse scattering.

References

[1] J. T. Lee et al., preprint arXiv:1609.07828 (2016).
[2] O. Sendetskyi et al., Physical Review B 93, 224413 (2016).
[3] L. Anghinolfi et al., Nature Communications 6, 8278 (2015).
[4] S. Morley et al. preprint arXiv:1603.09375 (2016).
[5] J. Perron et al. Physical Review B 88, 214424 (2013).
[6] Y.-L. Wang et al. Science 352, 962 (2016).

Publications There have been no BES supported publications to date.

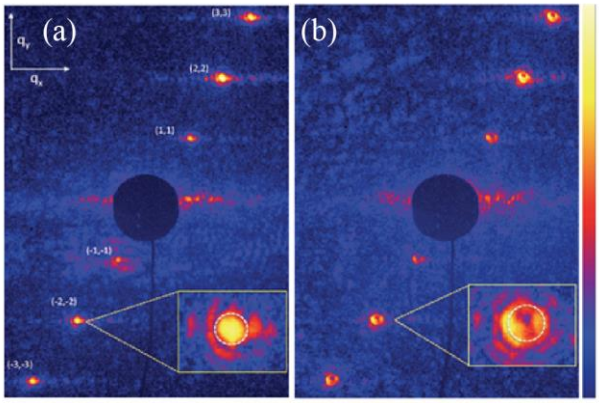


Figure 3. **(a)** Bragg peaks from resonant x-ray scattering for a square ASI at zero applied field. **(b)** The peaks exhibit central minima when H≈10^2 Oe is applied along the beam propagation direction.

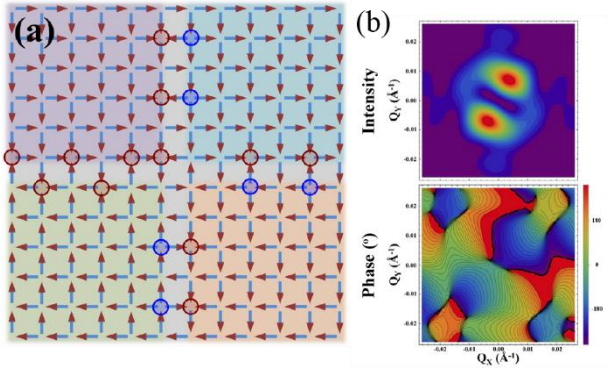


Figure 4. **(a)** A candidate magnetic texture that yields phase singularities in a scattered x-ray beam. **(b)** Simulated magnetic resonant scattering at a Bragg peak from the structure in (a). A central minimum in the Bragg peak intensity corresponds to two phase singularities in this case.

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

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. **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. **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. **Charge and spin phenomena in charge density wave TMDs:** Understand charge and spin phenomena in charge density wave TMDs.

Recent Progress

Our experiment has demonstrated the unique Landau level (LL) structure in monolayer TMDs. The robust valley and spin splitting of the zero-energy LL in TMDs, resulted from inversion symmetry breaking and spin-orbit interactions, respectively,

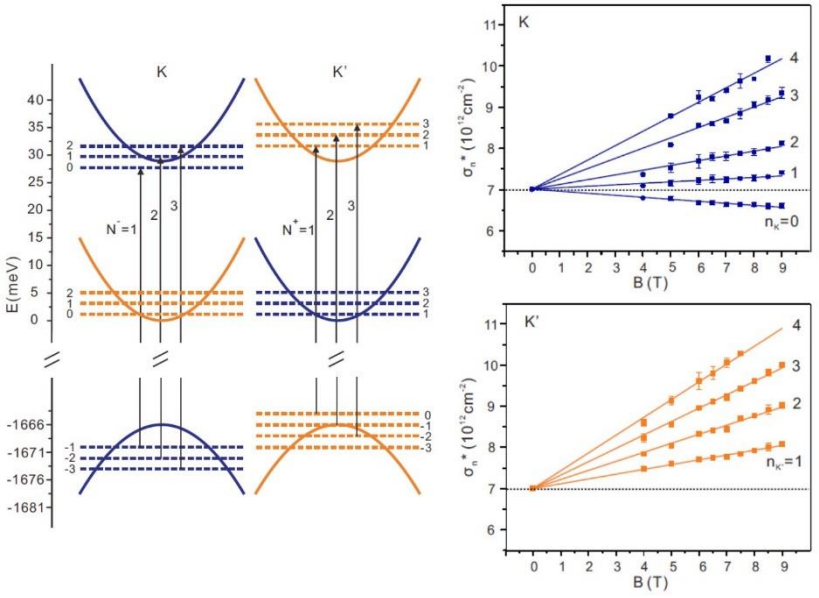


Figure 1: (Left) The LL structure of monolayer WSe_2 at 9 T for doping at 5.9×10^{12} cm^{-2}. (Right) The doping densities σ_{n^*} required to fill LL $n_K = 0 - 4$ (at the K valley) and $n_{K'} = 1 - 4$ (at the K' valley) are shown as a function of magnetic field B. Solid lines are linear fits to the experimental data (symbols) [1].

opens up new possibilities for studies of unconventional LL physics and quantum Hall effect in a 2D semiconductor [1].

We have provided a detailed description of the electron-phonon interactions and their possible role on the dephasing mechanism of direct excitons in atomic monolayer TMDs. The temperature dependence and excitation density dependence of the dephasing in atomic monolayers indicate that the electron phonon interactions play an important role in the rapid dephasing, and as a result, the large residual homogeneous linewidths in this material system. Calculations of the phonon energies and phonon DOS determined these phonon energies as the E' and E" phonon modes, which could facilitate the rapid dephasing observed in TMDs. The large residual homogeneous linewidth at low excitation densities and low temperature observed experimentally is well in agreement with the efficient exciton relaxation through phonon emission at all temperatures, reported in the theoretical studies [2].

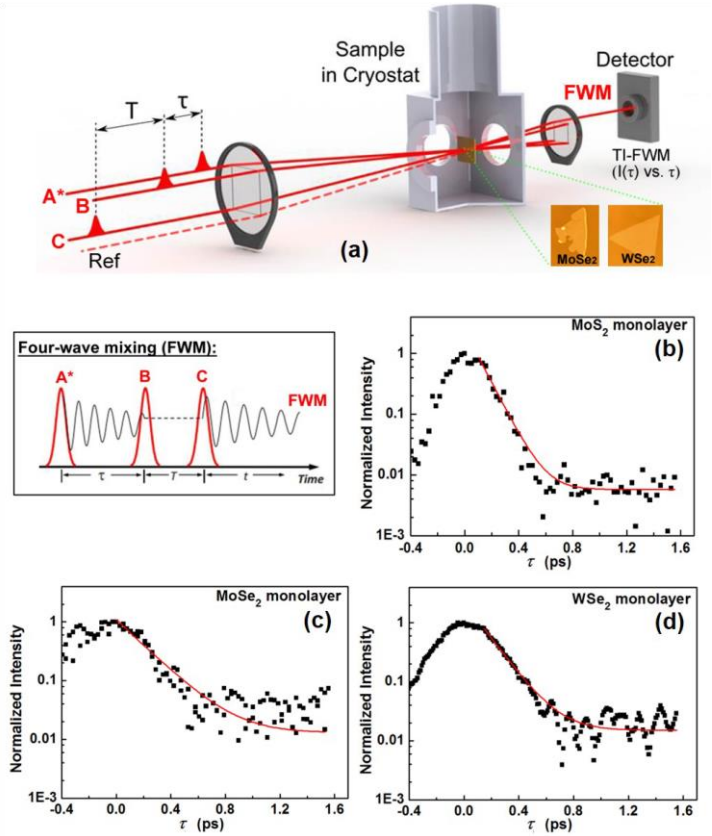


Figure 2: (a) The four phase-stabilized linearly polarized beams obtained from the multi-dimensional optical nonlinear spectrometer (MONSTR) instrument are focused on the sample, which is held in the cryostat at 5 K. (b-d) Time-integrated FWM of atomic monolayers (a) MoS2 (b) MoSe2 and (c) WSe2. The black symbols are the experimental data whereas the red line is the single exponential fit [2].

We have performed two-dimensional Fourier transform spectroscopy on undoped and modulation doped quantum wells in external magnetic fields as high as 10 Tesla. In the undoped sample we observe the formation of a novel state of matter that is generated by the Coulomb induced nonlinear scattering of quasiparticles. This state emerges under external magnetic fields due to nonlinear interactions between Landau levels, which is described by a short-range broken translation symmetry leading to memory effects. This is revealed by time-dependent density functional theory calculations performed to simulate our experiments. As a result, the discrete and degenerate Landau levels are coupled to a continuum state. The characteristic signature of this peculiar continuum state is the emergence of elongated spectral line shapes at the Landau level energies shown in Fig 3 (C, left), which are exposed by the multidimensional nature of our spectroscopic technique. This behavior is expected to be further enhanced in the modulation doped sample by the increased probability of

scattering events, due the higher concentration of free carriers. Surprisingly, the elongation of the lines in the two-dimensional frequency plot is completely absent in the lowest Landau level spectra in Fig 3 (C, right), obtained from the modulation doped quantum well between 8 and 10 Tesla. Time-dependent density functional theory calculations elucidate the physical mechanism behind the absence of the continuum formation in the doped quantum well, as a combination of Coulomb screening and orbital localization effects [3].

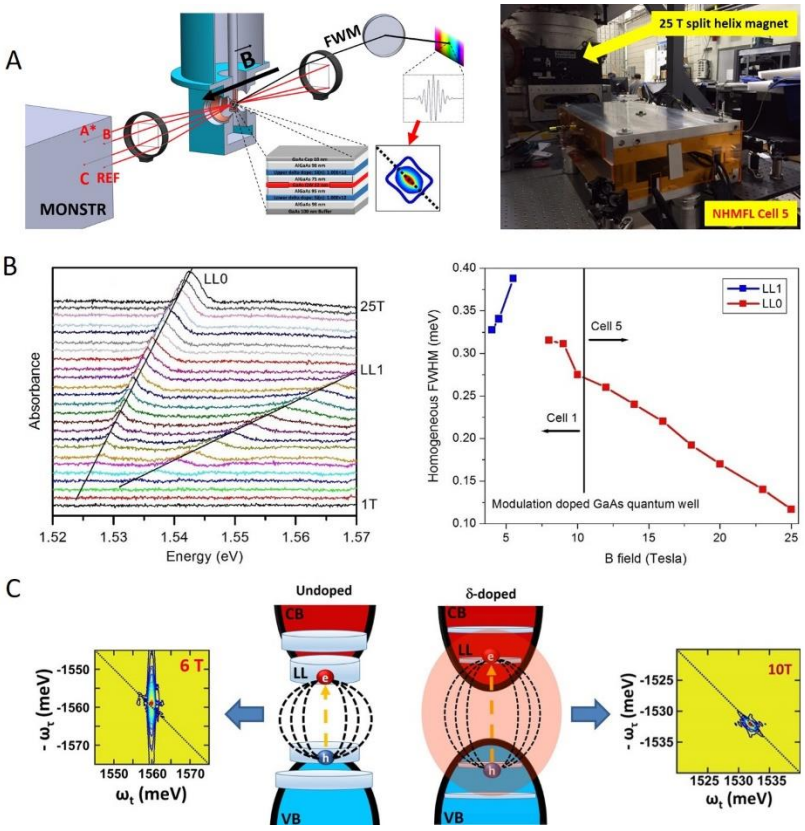


Figure 3: (A) Schematic of the experimental setup: The four phase stabilized laser beams are provided by the MONSTR instrument. The recently implemented experimental setup in Cell 5 at the National High Magnetic Field Lab (NHMFL) in Tallahassee. (B) (Left) Absorption spectra of the lowest Landau levels. (Right) Homogeneous linewidth versus magnetic fields up to 25 Tesla for LL1 and LL0. (C) Simplified schematic of the Landau levels and band structure in the undoped (left) and modulation doped (right), leading the the 2DFT lineshapes observed experimentally [3].

We observe a peculiar behavior of the quantum coherence originating from the lowest Landau level LL0 and next Landau level LL1. With increasing magnetic field, the quantum coherence of LL1 decreases, and as a result the homogeneous linewidth increases. Whereas for lowest Landau level LL0 the opposite effect occurs, the quantum coherence increases with increasing magnetic fields. We have investigated this effect in cell 5 all the way to 25 Tesla and this observation seems to hold. The absorption data together with the retrieved homogeneous linewidths are shown in Fig 3 (B).

Charge density waves (CDWs) are periodic modulations of conduction electron densities and the associated lattice distortions in solids. Dimensionality has profound effects on CDW instabilities, as in many other phase transition phenomena. On the one hand, reduced dimensionality strengthens Peierls instabilities (due to Fermi surface nesting) and electron–phonon interactions (due to reduced dielectric screening), favoring stronger CDWs. On the other hand, stronger fluctuation effects from both finite temperatures and disorders tend to destroy long-range CDW coherence in low-dimensional systems. Although long-range CDW coherence is well known

in quasi-one-dimensional and quasi-two-dimensional systems, the interplay of these effects in the exact two-dimensional limit remains unknown. Van der Waals materials that can be separated into stable layers of atomic thickness provide an ideal platform for investigations of CDWs and their relation with superconductivity in the two-dimensional limit. In this study, combining optical and electrical transport method, we observe both the charge density wave and the superconducting phase in TMD NbSe2 down to the monolayer limit (Fig. 4, top). The superconducting transition temperature decreases on lowering the layer thickness, but the newly observed charge-density-wave transition temperature increases from 33 K in the bulk to 145 K in the monolayer. Such highly unusual enhancement of charge density waves in atomically thin samples can be understood to be a result of significantly enhanced electron–phonon interactions in two-dimensional $NbSe_2$ and is supported by the large blue shift of the collective amplitude vibration observed in our experiment (Fig. 4, bottom). Our results open up a new window for search and control of collective phases of two-dimensional matter, as well as expanding the functionalities of these materials for electronic applications [4].

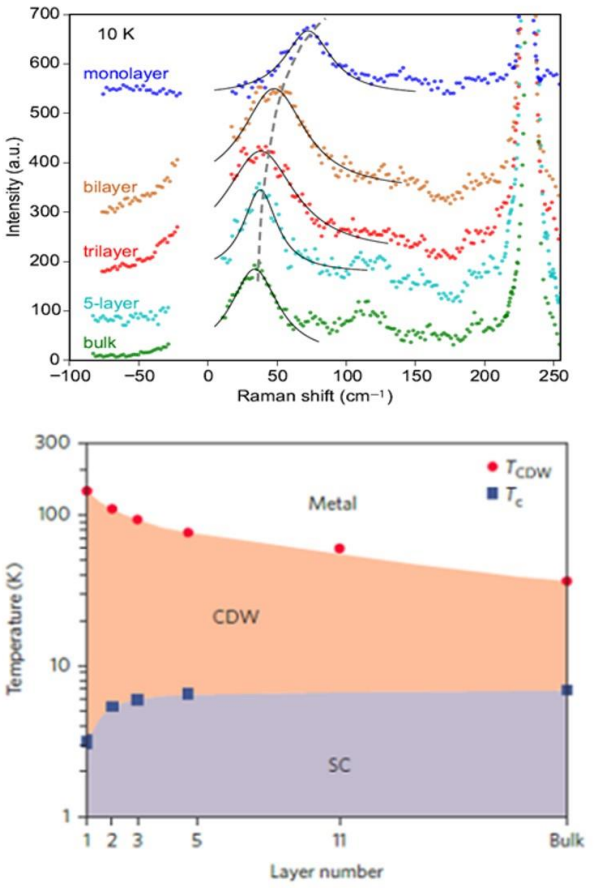


Figure 4: Top: A-channel Raman spectra of $NbSe_2$ of varying thickness at 10 K (symbols). The dashed line illustrates the blue shift of the amplitude mode frequency with decreasing layer thickness. Bottom: Thickness–temperature phase diagram for $NbSe_2$. [4].

The properties of 2D TMDs arising from strong spin–orbit interactions and valley-dependent Berry curvature effects have recently attracted considerable interest. Although single-particle and excitonic phenomena related to spin–valley coupling have been extensively studied, the effects of spin–valley coupling on collective quantum phenomena remain less well understood. Here we report the observation of superconducting monolayer $NbSe_2$ with an in-plane upper critical field of more than six times the Pauli paramagnetic limit, by means of magneto transport measurements. The effect can be interpreted in terms of the competing Zeeman effect and large intrinsic spin–orbit interactions in non-centrosymmetric $NbSe_2$ monolayers, where the electron spin is locked to the out-of-plane direction. Our results provide strong evidence of unconventional Ising pairing protected by spin–momentum locking, and suggest further studies of non-centrosymmetric superconductivity with unique spin and valley degrees of freedom in the two-

dimensional limit. These results have been published in Nature Physics [5] (See Ref. 5 and figures therein).

Future Plans

We will further investigate the increase of the quantum coherence with increasing magnetic fields on monoatomic layer TMDs. Examining this effect at cell 5 under much higher magnetic fields will help elucidate the underlying physics. We also have started a theoretical effort to better understand this effect. Furthermore, improvement in material quality, in the CVD growth of monoatomic layer TMDs will help the experiment. In addition to high quality CVD grown samples, we have received very large exfoliated samples that can be optically located inside the magnet. These samples exhibit superb material quality.

We will continue to study high mobility TMD semiconductor under high magnetic fields. Systematic studies on the effect of doping, magnetic field, and electric field will be studied on natural bilayer and artificial bilayers. Furthermore, we will investigate the terahertz (THz) transport properties of monolayer MoS_2. This will be done on wafer scale MoS_2 monolayer samples grown by chemical vapor deposition. We will first study the effect of electrostatic doping on the complex conductivity spectrum of MoS_2 up to a few THz's and extract the transport parameters such as the carrier density and scattering rate. We also plan to measure the non-equilibrium transport properties, i.e. following ultrafast optical excitation by a visible optical pulse.

Investigate the interlayer excitons in semiconducting TMD heterostructures (such as $MoSe_2/WSe_2$). We will use 2D optical spectroscopy to investigate the interlayer excitons in this double quantum well system. Here we would like to emphasize a new capability we have developed. We are now capable of using the MONSTR setup with a microscope objective and reach a spatial resolution in the excitation spot size of 3-5 μm, while taking advantage of the phase stability that the MONSTR setup offers.

References

[1] Z. Wang, J. Shan, and K. F. Mak, "Valley- and spin-polarized Landau levels in monolayer WSe2" Nature Nanotechnology (2016). DOI: 10.1038/nnano.2016.213

[2] P. Dey, J. Paul, Z. Wang, C. E. Stevens, C. Liu, A. H. Romero, J. Shan, D. J. Hilton, and D. Karaiskaj, "Optical Coherence in Atomic-Monolayer Transition-Metal Dichalcogenides Limited by Electron-Phonon Interactions" Phys. Rev. Lett. 116, 127402 (2016).

[3] J. Paul, C. E. Stevens, H. Zhang, P. Dey, D. McGinty, S. A. McGill, R. P. Smith, J. L. Reno, V. Turkowski, I. Perakis, D. J. Hilton, and D. Karaiskaj, "Coulomb induced coupling of Landau levels in intrinsic and modulation-doped quantum wells" Nature Nanotechnology (submitted).

[4] X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, “Strongly enhanced charge-density-wave order in monolayer $NbSe_2$.” Nature Nanotechnology **10**, 765 (2015).

[5] X. Xi, Z. Wang, W. Zhao, J. Park, K. T. Law, H. Berger, L. Forro, J. Shan, and K. F. Mak, “Ising pairing in superconducting $NbSe_2$ atomic layers.” Nature Physics **12**, 139-143 (2016)

Publications

(1) P. Dey, J. Paul, G. Moody, C. E. Stevens, N. Glikin, Z. D. Kovalyuk, Z. R. Kudrynskyi, A. H. Romero, A. Cantarero, D. J. Hilton, and D. Karaiskaj, “Biexciton formation and exciton coherent coupling in layered GaSe”, The Journal of Chemical Physics, **142**, 212422 (2015). http://dx.doi.org/10.1063/1.4917169

(2) X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, “Strongly enhanced charge-density-wave order in monolayer $NbSe_2$.” Nature Nanotechnology **10**, 765 (2015). Highlighted by Nature Nanotechnology News & Views 10, 737–738 (2015).

(3) X. Xi, Z. Wang, W. Zhao, J. Park, K. T. Law, H. Berger, L. Forro, J. Shan, and K. F. Mak, “Ising pairing in superconducting $NbSe_2$ atomic layers.” Nature Physics **12**, 139-143 (2016). Highlighted by Nature Physics News & Views 12, 112– 113 (2016).

(4) P. Dey, J. Paul, Z. Wang, C. E. Stevens, C. Liu, A. H. Romero, J. Shan, D. J. Hilton, and D. Karaiskaj, “Optical Coherence in Atomic-Monolayer Transition-Metal Dichalcogenides Limited by Electron-Phonon Interactions” Phys. Rev. Lett. **116**, 127402 (2016).

(5) X. Xi, H. Berger, L. Forro, J. Shan, and K. F. Mak, "Gate tuning of electronic phase transitions in two-dimensional NbSe2," Phys. Rev. Lett. **117**, 106801 (2016).

(6) Z. Wang, J. Shan, and K. F. Mak, “Valley-spin polarized Landau levels in monolayer WSe_2” Nature Nanotechnology (2016) DOI: 10.1038/nnano.2016.213.

(7) Z. Wang, L. Zhao, K.F. Mak, and J. Shan, “Probing the spin-polarized electronic band structure in monolayer transition metal dichalcogenides by optical spectroscopy,” Nano Lett. (Submitted).

(8) K. F. Mak and J. Shan “Photonics and optoelectronics of two-dimensional semiconductor transition metal dichalcogenides,” Nature Photonics, **10,** 216-226 (2016).

(9) J. Paul, C. E. Stevens, H. Zhang, P. Dey, D. McGinty, S. A. McGill, R. P. Smith, J. L. Reno, V. Turkowski, I. Perakis, D. J. Hilton, and D. Karaiskaj, “Coulomb induced coupling of Landau levels in intrinsic and modulation-doped quantum wells” Nature Nanotechnology (submitted).

(10) C. E. Stevens, A. V. Stier, J. Paul, H. Zhang, P. Dey, T. Stroucken, S. W. Koch, S. A. Crooker, and D. Karaiskaj, "Naturally Occurring Dicke Superradiance" Nature Photonics (submitted).

(11) C. E. Stevens, P. Dey, J. Paul, Z. Wang, H. Zhang, A. H. Romero, J. Shan, D. J. Hilton, D. Karaiskaj, "The role of electron-phonon interactions on the coherence lifetime of monolayer transition metal dichalcogenides" Journal of Physics: Conference proceedings (2016) In press.

Nanoscale Dynamical Heterogeneity in Complex Magnetic Materials

Steve Kevan, Principal Investigator
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720
and
Physics Department, University of Oregon, Eugene, OR 97403

Primary collaborators

NEMM Group (F. Hellman, P. Fischer, J. Bokor, S. Salahuddin, Lin-Wang Wan)
Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720

Sujoy Roy
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720

Eric Fullerton
Center for Memory and Recording Research, USCD, La Jolla, CA 92093

Thermally Driven Spin Phases

Thermal fluctuations over broad spatial and temporal scales determine a system's entropy and therefore play a key role in phase stability, transport, and other target properties. For example, the role of fluctuations is a defining feature in soft and biological systems, where many modes exist at energy comparable to kT and therefore carry enough entropy to dominate the free energy. Similar thinking is applicable to hard material systems in a limited context, when there are low energy manifolds of strongly coupled modes - a defining feature of many complex oxide materials and structures that exhibit unusual emergent properties. It is also true of magnetic and spin systems, e.g., artificial spin ices, thin films near spin reorientation transitions, and in skyrmion systems stabilized by thermal fluctuations.

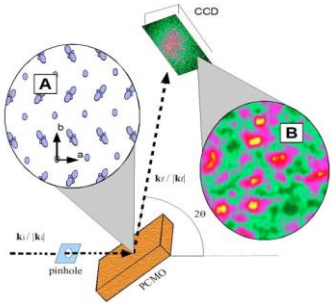


Fig. 1: Scattering a spatially coherent x-ray beam off a heterogeneous material produces speckle-diffraction patterns that encode spatial and temporal correlations that are measured in x-ray photon correlation spectroscopy (XPCS). Coherent diffraction imaging uses the same experimental arrangement, but applies emerging phase retrieval techniques to provide real-space images. Operating near x-ray core level resonances provides useful chemical and magnetic scattering contrast.

In this project, we to apply resonant coherent soft x-ray scattering techniques (Fig. 1) to probe nanoscale spatiotemporal correlations in magnetic films. 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. Our progress in the past year involved three complementary efforts:

1) Applying phase retrieval algorithms to image magnetic imhomogeneities with <10 nm spatial resolution. We have resolved the domain walls in a model amorphous $SbCo_5$ film using an emerging technique called ptychography and correlated their position to inclusions, probably of nanoscrystalline inclusions of a Co-Sb phase of similar composition.
2) Measuring the phase behaviors and magnetic fluctuations in amorphous FeGd films. We have observed Bloch skyrmions, and bound pairs of these, at room temperature. We have determined the (T,H) phase diagram of these structure using magnetic scattering and have probed their internal structures with Lorentz TEM and x-ray microscopy. In collaborative studies, we have probed these films with magnetization and FMR techniques, and modeled their existence with micromagnetic simulations. We have also observed and characterized evidence for Barkhausen-like cascades in the stripe and skyrmion phases using magnetic x-ray scattering.
3) We have probed and modeled the phase behaviors, ordering, and motion of square artificial spin ice lattices. Using magnetic x-ray scattering, we have demonstrated the existence of superdomains with magnetically charged domain walls at non-zero applied field.

Plans for the next year

Our plans for the future include

1) We will continue our studies of skyrmions, particularly of bound skyrmion pairs, in amorphous FeGd films as a function of applied field and current density. We will study the magnetoresistance of these films as a function of phase and skyrmion lattice orientation. We will also try to control the in-plane orientation of the skyrmion pairs and measure associated magnetoresistance.
2) We will continue to measure the real-space structure to magnetic textures of the skyrmion phases using ptychography, full-field x-ray microscopy, and Lorentz TEM. We are particularly interested in finding protocols that stabilize other exotic skyrmion structures – triplets, quartets, anti-skyrmions, etc. The FeGd system is an unusually tunable system, and even the stripe phase near has an unusual degree of spin canting that helps determine the skyrmion structures as the field and temperature are varied.
3) We will study other 3d/rare earth alloy magnetic films, e.g., TbCo, GdFeCo, to look for unusual spin structures.
4) We will continue our studies of artificial spin ices, particularly those with smaller and thinner magnetic islands, which will exhibit superparamagnetic fluctuations that can be studied with correlation spectroscopy.

Ultrafast Materials Science Program

Alessandra Lanzara, Robert A. Kaindl

Materials Sciences Division, E. O. Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720

Program Scope: The quest to study materials on extremely short intervals of time arises from the fundamental scales of their quantum excitations and collective interactions. Ultrashort light pulses can therefore act as a tool to unravel the intrinsic forces that drive correlated ground states, as well as to generate novel phases that have no equivalent in thermal equilibrium. The Ultrafast Materials Science program exploits advanced ways in which light can be used to interrogate and manipulate novel quantum materials via short and intense light pulses. Scientific areas of current interest include the creation, interrogation and control of quasiparticle distributions and topologies in materials with ultrashort and intense light fields, as well as the use of tailored vibrational and electronic excitations to explore novel light-induced phases. Materials of present interest include two-dimensional materials with non-trivial band topologies and strongly correlated materials such as unconventional superconductors.

Our program includes a closely coordinated effort between experiment and theory and state of the art advanced ultrafast tools, such as time, spin, and angle resolved photoemission spectroscopy, with spin detection of unprecedented sensitivity and with a unique extreme-ultraviolet source yielding access to electronic dynamics across the full Brillouin zone. Ultrafast optical and broadband THz setups enable excitation and time-resolved studies of fundamental excitations and low-energy collective modes. Experiments are guided by advanced theory of non-equilibrium dynamics.

Recent Progress:

* **Development of an XUV HHG tr-ARPES system**: We have completed the commissioning of a unique setup for extreme-UV (XUV) trARPES at high repetition rates, and have applied it to first experiments. The setup combines a unique 50-kHz source of narrowband XUV pulses with sophisticated ARPES instrumentation [1]. High-harmonic generation with a cascaded UV-driven scheme results in a bright XUV flux with up to 3×10^{13} photons/s at the source (10^{10}-10^{11} photons/s at the sample), based on a 100-fold boost of the conversion efficiency. The 22.3 eV harmonic is narrowband and directly isolated with metal foils, without the need for a complex XUV monochromator. This enables a new class of trARPES studies with high sensitivity, energy resolution and momentum access throughout the Brillouin zone. In first experiments, the high fidelity was demonstrated in studies of the photo-induced phase transition of the CDW material $TiSe_2$ as well as via rapid Fermi surface mapping in Bi 2212.

* **Mapping k-dependent recombination dynamics in TMD:** Using XUV trARPES we studied the electron dynamics across the full Brillouin zone of $MoSe_2$. Fine band structure details such as the spin-orbit (SO) splitting at the K-point were resolved in equilibrium, with quality approaching synchrotron ARPES data. Photo-excitation around 1.5 eV revealed a rapid occupation of the K-point conduction-band states, followed by momentum-space transfer to the Σ-point in 80 fs – representing the direct observation of intervalley scattering. Moreover, an intriguing time-dependent energy shift is observed, along with an energy difference when comparing the dispersion of photo-excited unbound electrons excited above the conduction band threshold with the signature of resonantly-generated excitonic states. This points to the first direct observation of bandgap excitons in ARPES, i.e. the extraction of the electron out of the Coulomb-bound *e-h* pair via the photoemission process.

* **Revealing entangled spin and orbital texture of unoccupied states in TI**: Using UV time and spin resolved ARPES (STARPES) we have studied the effect of band inversion driven by spin orbit interaction on the formation of a topological surface state, by measuring the spin polarization of the transiently occupied states above EF in a prototypical topological insulator Bi2Se3. The studies have been made possible by using a high efficiency and high-resolution spin-resolved photoelectron spectrometer. By measuring the dependence of the orientation of the photoelectron spin polarization on the photon polarization we observed a spin-polarized unoccupied surface resonance within the bulk conducting band, with an helical spin texture opposite to that of the TSS but entangled spin and orbital textures similar to that of the TSS. We propose that the spin textures of the unoccupied surface resonance and topological surface state are intimately related and coevolve from a pair of Rashba-like states through the Spin orbit interaction band inversion [2].

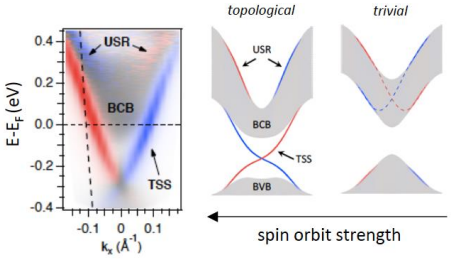


Figure 1. (left) Spin resolved electronic structure of occupied and unoccupied states of Bi2Se3.

(right) Tight binding calculations showing that the TSS and unoccupied spin resonance evolve into a trivial Rashba-pair through the process of band inversion.

* **Stimulated emission of Cooper pairs in a Superconductor**: Recombination dynamics of non-equilibrium quasiparticles is usually understood within the phenomenological Rothwarf-Taylor (RT) model, whose basic ingredient is simple bimolecular recombination. In a superconductor, short time scale dynamics on the other hand, also play an important role, as it is directly related with the superconducting gap formation. To better understand the mechanism behind gap melting and recovery we have performed a VUV tr-ARPES experiments. We found that the non equilibrium quasiparticles population in the superconducting state have a slower buildup than in the normal state, when the pump pulse is too weak to deplete the entire superconducting condensate [3]. For pump pulse strong enough instead, the buildup time is the same. These results, together with the peculiar momentum dependence can be explained with a model of stimulated recombination of broken Cooper pairs into the superconducting condensate.

* **Symmetry breaking and pseudogap in Nickelates**: Complex oxides can exhibit an intriguing self-organization of atomic-scale charge, spin and vibrational patterns, which can fluctuate in time and space. Such broken-symmetry phases have recently attracted renewed interest due to the observation of charge-density waves within the enigmatic pseudogap phase of high-temperature superconductors. However, the dynamic coupling between the electronic and vibrational constituents during melting and symmetry-breaking formation of stripes has remained elusive so far. We have carried out transient terahertz studies to directly track the crystal lattice symmetry upon melting of the atomic-scale electronic stripes in the model stripe system $La_{2-x}Sr_xNiO_4$, to clarify the dynamic 'glue' that holds together the stripe constituents [4]**.** For this, the Ni-O bending vibration was employed as a "fingerprint" of the lattice symmetry: in the long-range

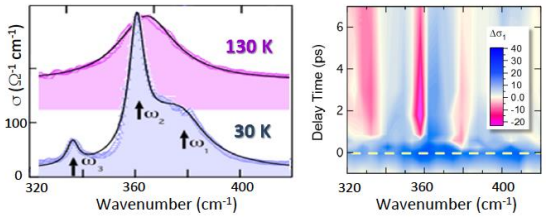


Figure 1. Dynamics of vibrational symmetry breaking. Top: Ni-O bending mode with stripe-induced side peaks. Bottom: Transient THz response showing complex melting dynamics.

ordered stripe phase at low temperatures, phonon side peaks are optically activated due to momentum back-folding of the phonon dispersion at the charge-ordering wave vector. We find a complex, multi-component dynamics following the ultrafast optical quench of stripe order. Almost immediately, a broadband conductivity increase occurs due to electronic charge dynamics. Instead, the sharp zone-folded Ni-O side peaks disappear only with a significant time delay, revealing the reaction time of the crystal symmetry, which remains initially "frozen". The experiments thus expose a hidden complexity in the dynamics of atomic-scale charge stripes.

Future Plans: We plan to pursue two main thrusts, distinguished by the materials physics and nature of the excitation induced by the light pulses on the material. In the first, we aim to clarify the creation of new quasiparticle distributions and topologies in materials with ultrashort light pulses. Here, ultrashort pulses of varying intensities will be employed – starting from perturbative excitation and control up to field strengths that are comparable to the lattice potential and enable modification of the electronic structure itself. Materials of interest include low-dimensional layered systems and spin-orbit coupled materials such as transition-metal dichalcogenides. In the second thrust, we plan to investigate the response of unconventional superconductors to ultrashort light pulses. This includes studies that perturbatively excite non-equilibrium dynamics of incoherent quasiparticles, and unveil different cooperative orders in the correlated ground state (and their relationship to superconductivity). At higher intensities, tailored mid-IR excitation can access entirely new regimes and emergent non-equilibrium phases.

References

[1] H. Wang, Y. Xu, S. Ulonska, J.S. Robinson, P. Ranitovic, and R.A. Kaindl. "Bright High-repetition-rate Source of Narrowband Extreme-ultraviolet Harmonics beyond 22 eV,"
Nature Communications **6**, 7459 (2015).

[2] C. Jozwiak, J. A. Sobota, K. Gotlieb, A. F. Kemper, C. R. Rotundu, R. J. Birgeneau, Z. Hussain, D. H. Lee, Z. X. Shen, and A. Lanzara, Spin polarized surface resonances accompanying topological surface state formation. In press *Nature Comm.* (2016). DOI: 10.1038

[3] W. T. Zhang, T. Miller, C. L. Smallwood, Y. Yoshida, H. Eisaki, R. A. Kaindl, D. H. lee, A. Lanzara. "Stimulated emission of Cooper pairs in a high temperature cuprate-superconductor", Scientific Report 6, 29100 (2016)

[4] G. Coslovich, A. F. Kemper, S. Behl, B. Huber, H. A. Bechtel, T. Sasagawa, M. C. Martin, A. Lanzara, and R. A. Kaindl, "Ultrafast Dynamics of Vibrational Symmetry Breaking in a Charge-ordered Nickelate," *Science Advances* (in review), arXiv:1603.07819 (2016).

Publications (2015–2016)

1. H. Wang, Y. Xu, S. Ulonska, J.S. Robinson, P. Ranitovic, and R.A. Kaindl. "Bright High-repetition-rate Source of Narrowband Extreme-ultraviolet Harmonics beyond 22 eV," *Nature Communications* **6**, 7459 (2015).

2. C. L. Smallwood, W. Zhang, T. Miller, G. Affeldt, K. Kurashima, C. Jozwiak, T. Noji, Y. Koike, H. Eisaki, D. H. Lee, R. Kaindl, A. Lanzara, "Influence of optically quenched superconductivity on quasiparticle relaxation rates in $Bi_2Sr_2CaCu_2O_{8+\delta}$" *Physical Review B* **92**, 161102 (2015).

3. J.H. Buss, R.P. Smith, G. Coslovich, and R.A. Kaindl. "Broadband Transient THz Conductivity of the Transition-Metal Dichalcogenide MoS2," *Proc. SPIE* **9361**, 93611J-1 (2015).

4. T. Miller, C. L. Smallwood, W. Zhang, H. Eisaki, J. Orenstein, A. Lanzara, "Photoinduced changes of the chemical potential in superconducting Bi2Sr2CaCu2O8+δ," *Physical Review B* **92**, 144506 (2015).

5. G. Coslovich, S. Behl, B. Huber, H.A. Bechtel, T. Sasagawa, M.C. Martin, and R.A. Kaindl, "Nanoscale Charge-order Dynamics in Stripe-phase Nickelates Probed via Ultrafast THz Spectroscopy," *Proc. SPIE* **9361**, 93611F-1 (2015).

6. J. Orenstein, and J. S. Dodge, "Terahertz time-domain spectroscopy of transient metallic and superconducting states," *Physical Review B* 92, 134507 (2015).

7. M. C. Langner, S. Zhou, G. Coslovich, Y.-D. Chuang, Y. Zhu, J. S. Robinson, W. F. Schlotter, J. J. Turner, M. P. Minitti, R. G. Moore, W. S. Lee, D. H. Lu, D. Doering, P. Denes, Y. Tomioka, Y. Tokura, R. A. Kaindl, and R. W. Schoenlein, "Ultrafast x-ray and optical signatures of phase competition and separation underlying the photoinduced metallic phase in Pr1-xCaxMnO3," *Physical Review B* **92**, 155148 (2015).

8. 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, and R. W. Schoenlein, "Scattering bottleneck for spin dynamics in metallic helical antiferromagnetic dysprosium," *Physical Review B* **92**, 184423 (2015).

9. C. Jozwiak, C. H. Park, K. Gotlieb, S. G. Louie, Z. Hussain and A. Lanzara, "Method for creating controllable spin-polarized electron source of electron tube e.g. photomultiplier tube involves providing incident light having photon energy and inducing photon emission of surface electron state", US Patent US2015235799-A1; US9142634-B2

10. G. Autès, A. Isaeva, L. Moreschini, J. Johannsen, A. Pisoni, R.Mori, W. Zhang, T. G. Filatova, A. N. Kuznetsov, L. Forr, W. Van den Broek, Y. Kim, K. S. Kim, A. Lanzara, J. D. Denlinger, E. Rotenberg, A. Bostwick, M. Grioni and O. V. Yazyev. "A novel quasi-one-dimensional topological insulator in bismuth iodide β-Bi_4I_4" *Nature Materials* **15**, 154 (2016).

11. J. P. Hinton, E. Thewalt, Z. Alpichshev, F. Mahmood, J. D. Koralek, M. K. Chan, M. J. Veit, C. J. Dorow, N. Barisic, A. F. Kemper, D. A. Bonn, W. N. Hardy, R. Liang, N. Gedik, M. Greven, A.

Lanzara, and J. Orenstein, “The rate of quasiparticle recombination probes the onset of coherence in cuprate superconductors,” *Scientific Reports* **6**, 23610 (2016).

12. C. L. Smallwood, R. A. Kaindl, A. Lanzara, “Ultrafast Angle-Resolved Photoemission Spectroscopy of Quantum Materials”, *Europhysics Letters* **115**, 27001 (2016).

13. C. L. Smallwood, T. L Miller, W. T. Zhang, R. A. Kaindl, A. Lanzara, “Nonequilibrium electron dynamics in a solid with a changing nodal excitation gap”, *Physical Review B* **93**, 235107 (2016).

14. W. T. Zhang, T. Miller, C. Smallwood, T. Yoshida, H. Eisaki, R. A. Kaindl, D. H. Lee, A. Lanzara, “Stimulated emission of Cooper pairs in a high-temperature cuprate superconductor” *Scientific Reports* **6**, 29100 (2016).

Submitted:

15. C. Jozwiak, J. A. Sobota, K. Gotlieb, A. F. Kemper, C. R. Rotundu, R. J. Birgeneau, Z. Hussain, D. H. Lee, Z. X. Shen, and A. Lanzara, Spin polarized surface resonances accompanying topological surface state formation. In press *Nature Comm.* (2016). DOI: 10.1038

16. G. Coslovich, A. F. Kemper, S. Behl, B. Huber, H. A. Bechtel, T. Sasagawa, M. C. Martin, A. Lanzara, and R. A. Kaindl, "Ultrafast Dynamics of Vibrational Symmetry Breaking in a Charge-ordered Nickelate," *Science Advances* (in review), arXiv:1603.07819 (2016).

17. T. L. Miller, W. Zhang, H. Eisaki, and A. Lanzara, "Measuring particle-hole asymmetry in the pseudogap state with time-resolved photoemission," *Phys. Rev. Lett*, submitted (2016).

Structural dynamics in functional materials

Aaron Lindenberg, William Chueh, David Reis, and Mariano Trigo

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

Program Scope

This is a new FWP focused on the goal of understanding and visualizing the role structure and dynamics play in the functionality of materials. *In-situ* and *in-operando* approaches are carried out to probe these processes as they occur, across a broad range of time-scales and length-scales extending down to atomic-scale motions and femtosecond time-scales and up to mesoscale length-scales / dynamics. A central focus is on tuning the emergent properties of functional materials and resolving the intermediate and metastable phases that occur near phase boundaries. Processes are triggered by light, by intercalation/ion doping, by fields, and by pressure (and by combinations of these), making central use of the unique atomic-scale, real-time characterization techniques enabled by facilities at SLAC and other DOE laboratories.

Recent Progress

(A) Switching processes in phase-change materials: We have carried out studies probing the mechanisms underlying electric-field-driven switching processes in phase-change materials. Picosecond THz-frequency electric pulses are used to excite amorphous $Ag_4In_3Sb_{67}Te_{26}$. Field-dependent reversible changes in conductivity (scaling nonlinearly with the applied field) and THz-driven crystallization are observed. The results show that threshold switching can take place within the electric pulse on sub-picosecond time scales, three orders of magnitude faster than previously thought to be possible. This supports purely electronic models of threshold switching and reveals potential applications as an ultrafast electronic switch. [1] Recent LCLS experiments have enabled further measurements identifying intermediate states during the crystalline to amorphous transition when triggered by optical pulses.

(B) Terahertz-field-driven ionic response in ferroelectrics. The dynamical processes associated with electric field manipulation of the polarization in a ferroelectric remain largely unknown but fundamentally determine the speed and functionality of ferroelectric materials and devices. In recent studies we applied single-cycle terahertz pulses as an ultrafast electric field bias to prototypical $BaTiO_3$ ferroelectric thin films with the atomic-scale response probed by femtosecond x-ray scattering techniques at the Linac Coherent Light Source and at the Advanced Photon Source. We show that electric fields applied perpendicular to the ferroelectric polarization drive large amplitude displacements of the titanium atoms along the ferroelectric polarization axis, comparable to that of the built-in displacements associated with the intrinsic polarization and incoherent across unit cells. This effect is associated with a dynamic rotation of the ferroelectric polarization switching on and then off on picosecond timescales. [2] We have

also investigated similar processes in multiferroic $BiFeO_3$ probing the atomic-scale response via nonlinear optical techniques. [3]

(C) Photon-driven rotational disordering in the hybrid perovskites. Femtosecond resolution electron scattering techniques are applied to resolve the first atomic- scale steps following absorption of a photon in the prototypical hybrid perovskite methylammonium lead iodide. Measurements of the time-dependent pair distribution function show an unexpected broadening of the iodine-iodine correlation function while preserving the Pb-I distance. This indicates the formation of a rotationally-disordered halide octahedral structure developing on picosecond time-scales. This work shows the important role of light-induced structural deformations within the inorganic sublattice in elucidating the unique optoelectronic functionality exhibited by hybrid perovskites and provides new understanding of hot carrier–lattice interactions which fundamentally determine solar cell efficiencies. [4]

(D) Ultrafast Measurements Reveal Peierls-like Instability in PbTe:

We combine nonequilibrium lattice dynamics measurements and first principles constrained density functional theory calculations to resolve the mechanism responsible for the incipient ferroelectric behavior in the prototypical bulk thermoelectric PbTe. There has been renewed interest in the materials community regarding the connection between ferroelectricity and thermoelectricity in group IV-VI and related compounds. We find that ultrafast infrared excitation across the direct band-gap transiently stabilizes the paralectric phase, coupling the transverse optical and acoustic phonons propagating along the bonding direction. These near band-gap electrons preferentially interact with the soft-phonons to induce ferroelectric instability. Our results further reconcile the band and bond pictures of ferroelectricity, which has broad implications for broken-symmetry states in materials with strong electron-phonon interactions. [5]

(E) Mechanism of high-wavevector phonon generation by ultrafast light pulses:

We have recently demonstrated that long-wavelength (low-wavevector) optical pulses can generate two-phonon coherences between pairs of phonons at high wavevector. These coherences are the basis for our Fourier-transform inelastic x-ray (FT-IXS) studies of non-equilibrium lattice dynamics. Here we used two-pulse coherent control to distinguish first-order (coherent) phonon from second-order (squeezed) phonon generation. We find that for nearly perfect semi-conductor crystals that the mechanism is dominated by second-order coupling resulting in the generation of squeezed phonon states. We also describe the conditions for high-wave vector coherent phonon generation. The results have implications for studies of electron-phonon interactions and non-equilibrium lattice dynamics initiated by optical excitation. [6]

(F) Microfluidic cells for electrochemical liquid X-ray microscopy: We have developed electrochemical liquid X-ray microscopy that probes ion-insertion nanomaterials in the soft X-ray regime. The platform combines scanning transmission X-ray microscopy (STXM) with

microfluidic electrochemical cells. The first demonstration was carried out on Li_XFePO_4 microplatelet single crystals. The spatio-dynamics of lithium insertion was tracked by monitoring the Fe oxidation state. By carefully optimizing liquid flow, X-ray dose, and sample preparation, we minimized beam-induced interaction and achieved repeated imaging of the same particle at a spatial resolution of ~ 50 nm. This achievement represents the first successful operando soft X-ray imaging of lithiation/de-lithiation at the sub-particle length scale, and reveals the origin and hysteresis of lithium insertion spatio-dynamics. [7]

(G) Soft-X-ray ptychography in liquids: In addition to electrochemical liquid STXM, we have also demonstrated non-Bragg ptychography using the same microscope and microfluidic cell setup, achieving a resolution < 10 nm. Mesoscale microstructural defects not visible in STXM give rise to noticeable contrast, and are providing a rich dataset that correlates mesoscale microstructure defects with redox reactions.

(H) New insights on ion-insertion-induced phase transformation: Simultaneously quantifying nanoscale reaction kinetics and the underlying material composition at the solid-liquid interface is a grand challenge in materials science. By tracking the same particles under multiple lithiation/de-lithiation cycles, we show that nanoscale spatial variations in rate and in composition control the lithiation pathway at the sub-particle length scale, beyond the well-documented phase separation and solid solution pathways at the crystallographic level. Our real-time measurements of the local ion-insertion current density reveal several electrochemical domains within individual primary particles, each of which exhibits a different insertion rate. Upon increased rates of lithiation, we directly observe a suppression of phase separation and elimination of heterogeneity.

(I) Crucial role of surface diffusion in phase transformation of insertion solids: In nanomaterials, surface transport at the interface of a solid and a fluid is significant in determining the overall transport rate. Despite their crucial important to nanomaterials, the effect of surface transport on solid-state phase transformations pathways is not well understood. We use Li_XFePO_4 as a model anisotropic ionic conductor for understanding solid-state phase transformations induced by ion movement. Using STXM, we experimentally measure the time required for solid-solution $Li_{0.5}FePO_4$ to separate into Li-rich and Li-poor phases. We observe that moisture and organic solvents increase the rate of surface transport and thus the rate of phase separation by at least two orders of magnitude compared to an inert environment. Our results show that surface diffusion is a necessary prerequisite for phase separation in $LiFePO_4$, and the relative rates of lithium insertion and surface diffusion ultimately determine whether or not a particle phase-separates.

Future Plans

The above experiments are all connected by a focus on elucidating the atomic-scale structural dynamics which underlie materials functionality. In addition to continuation of these efforts we are currently working on new directions associated with probing the microsecond-picosecond

dynamics associated with ion intercalation processes. Initial measurements underway involve time-resolved optical (pump-probe reflectivity/transmission) and x-ray (Bragg / diffuse scattering) studies of the strain fields and structural phase transitions that occur in 2D transition metal dichalcogenides, carried out *in-situ* within a transparent battery structure to enable reversible tuning of the ion concentration. These efforts connect standard ion impedance spectroscopy to direct measurements of the local structural changes that occur during ion insertion. In addition to intercalation, novel ionic conductors can be impulsively created through optical excitation, through temperature jumps (which can occur on time-scales faster than an ionic hop), or through carrier-driven processes which directly modify the energy barriers which control ionic transport. This opens up possibilities for applying time-domain diffuse scattering approaches (FT-IXS) to probe the interatomic forces that initiate the phase transition and modulate ion transport.

2015-16 Publications

[1] Peter Zalden, Michael J. Shu, Frank Chen, Xiaoxi Wu, Yi Zhu, Haidan Wen, Scott Johnston, Zhi-Xun Shen, Patrick Landreman, Mark Brongersma, Scott W. Fong, H.-S.Philip Wong, Meng-Ju Sher, Peter Jost, Matthias Kaes, Martin Salinga, Alexander von Hoegen, Matthias Wuttig, and Aaron Lindenberg. Picosecond electric-field-induced threshold switching in phase-change materials. *Phys. Rev. Lett.*, **117**, 067601 (2016)

[2] F. Chen, Y. Zhu, S. Liu, Y. Qi, H.Y. Hwang, N.C. Brandt, J. Lu, F. Quirin, H. Enquist, P. Zalden, T. Hu, J. Goodfellow, M.-J. Sher, M.C. Hoffmann, D. Zhu, H. Lemke, J. Glownia, M. Chollet, A. R. Damodaran, J. Park, Z. Cai, I.W. Jung, M.J. Highland, D.A. Walko, J. W. Freeland, P.G. Evans, A. Vailionis, J. Larsson, K.A. Nelson, A.M. Rappe, K. Sokolowski-Tinten, L. W. Martin, H. Wen, and A.M. Lindenberg. Ultrafast terahertz-field-driven ionic response in ferroelectric $BaTiO_3$, *Phys. Rev. B (Rapid Commun.)* (in press) (2016)

[3] F. Chen, J. Goodfellow, S. Liu, I. Grinberg, M. C. Hoffmann, A.R. Damodaran, Y. Zhu, X. Zhang, I. Takeuchi, A. Rappe, L.W. Martin, H. Wen, A.M. Lindenberg. Ultrafast terahertz gating of the polarization and giant nonlinear optical response in $BiFeO_3$ thin films. *Advanced Materials*, **27**, 6371 (2015).

[4] X. Wu, L. Tan, X. Shen, T Hu, K. Miyata, M. Tuan Trinh, R. Li, R. Coffee, S. Liu,2 D.A. Egger, I. Makasyuk, Q. Zheng, A. Fry, J.S. Robinson, X. Wang, X.-Y. Zhu, L. Kronik, A.M. Rappe, A.M. Lindenberg. Light-induced picosecond rotational disordering of the inorganic sublattice in hybrid perovskites. (submitted) (2016).

[5] M. P. Jiang, M. Trigo, I. Savic, S. Fahy, E. D. Murray, C. Bray, J. Clark, T. Henighan, M. Kozina, M. Chollet, J. M. Glownia, M. C. Hoffmann, D. Zhu, O. Delaire, A. F. May, B. C. Sales, A. M. Lindenberg, P. Zalden, T. Sato, R. Merlin, and D. A. Reis. The origin of incipient ferroelectricity in lead telluride. Nat Commun, 7:12291, 07 (2016).

[6] T. Henighan, M. Trigo, M. Chollet, J. N. Clark, S. Fahy, J. M. Glownia, M. P. Jiang, M. Kozina, H. Liu, S. Song, D. Zhu, and D. A. Reis. Control of two-phonon correlations and the mechanism of high-wavevector phonon generation by ultrafast light pulses. Phys. Rev. B, 94:020302, (2016).

[7] J. Lim, Y. Li, D. H. Alsem, H. So, S. C. Lee, P. Bai, D. A. Cogswell, X. Liu, N. Jin, Y.-S. Yu, N. Salmon, D. Shapiro, M. Z. Bazant, T. Tyliszczak, W. C. Chueh. Origin and hysteresis of Li compositional spatiodynamics within battery primary particles. *Science* **353**, 566-570 (2016).

[8] C. Gopal, F. El Gabaly, A. H. McDaniel, W. C. Chueh. Origin and Tunability of Unusually Large Surface Capacitance in Doped Cerium Oxide Studied by Ambient Pressure X-ray Photoelectron Spectroscopy. *Adv. Mater*. **28**, 4692-4697 (2016).

[9] Y. Shi, S. Lee, M. Monti, C. Wang, Z. A. Feng, W. D. Nix, M. F. Toney, R. Sinclair, W. C. Chueh. Growth of Highly Strained CeO_2 Ultrathin Films. *ACS Nano* (2016). *Accepted*

[10] Y. Shi, K. H. Stone, Z. Guan, M. Monti, C. Cao, F. El Gabaly, W. C. Chueh, M. F. Toney. Surface structure of coherently strained ceria ultrathin films. *Phys. Rev. B.* (2016). *Accepted.* .

[11] C. B. Gopal, S. C. Lee, M. Garcia-Melchor, Y. Shi, M. Monti, Z. Guan, R. Sinclair, H. Bluhm, A. Vojvodic, W. C. Chueh. Equilibrium Oxygen Redox Capacity of Ultrathin $CeO_{2-\delta}$ Depends Non-Monotically on Large Biaxial Strain. *Nature Materials* (2016). *Under Review*.

[12] D Rhodes, DA Chenet, BE Janicek, C Nyby, Y Lin, W Jin, D Edelberg, E Mannebach, N Finney, A Antony, T Schiros, T Klarr, A Mazzoni, M Chin, Y Chiu, W Zheng, QR Zhang, F Ernst, JI Dadap, X Tong, J Ma, R Lou, S Wang, T Qian, H Ding, RM Osgood Jr, DW Paley, AM Lindenberg, PY Huang, AN Pasupathy, M Dubey, J Hone, L Balicas. Engineering the structural and electronic phases of $MoTe_2$ through W substitution, *arXiv*:1610.02480 (2016)

[13] T. Hu, M.D. Smith, E. Dohner, M.J. Sher, X. Wu, M. Trinh, A. Fisher, J. Corbett, X.-Y. Zhu, H. Karunadasa, A.M. Lindenberg. Mechanism for broadband light emission from two-dimensional (110) hybrid perovskites. *J. Phys. Chem. Lett.*, **7**, 2258 (2016).

[14] Peter Zalden, Alexander von Hoegen, Patrick Landreman, Matthias Wuttig, and Aaron M. Lindenberg. How supercooled liquid phase-change materials crystallize: Snapshots after femtosecond optical excitation. *Chemistry of Materials* **27**, 5641 (2015).

[15] Jerry L. LaRue, Tetsuo Katayama, Aaron Lindenberg, Alan S. Fisher, Henrik Öström, Anders Nilsson, and Hirohito Ogasawara. THz induced selective catalytic CO oxidation on Ru. *Phys. Rev. Lett.* **115**, 036103 (2015).

[16] E. Szilagyi, J.S. Wittenberg, T.A. Miller, K. Lutker, F. Quirin, H. Lemke, D. Zhu, M. Chollet, J. Robinson, H. Wen, K. Sokolowski-Tinten, and A.M. Lindenberg. Visualization of nanocrystal breathing modes at extreme strains. *Nat. Commun.*, **6**, 6577 (2015)

[17] F.F. Schlich, P. Zalden, A.M. Lindenberg, R. Spolenak. Color switching with enhanced optical contrast in ultrathin phase-change materials and semiconductors induced by femtosecond laser pulses. *ACS Photonics*, **2** 178 (2015)

[18] Simon Wall and Mariano Trigo. "Recent Developments in Ultrafast X-ray Techniques for Materials Science Applications." Synchrotron Radiation News29.5 (2016): 13-18.

[19] S. Fahy, E. D. Murray, and D. A. Reis. Resonant squeezing and the anharmonic decay of coherent phonons. Phys. Rev. B, 93:134308, (2016).

[20] T. Henighan, M. Trigo, S. Bonetti, P. Granitzka, D. Higley, Z. Chen, M. P. Jiang, R. Kukreja, A. Gray, A. H. Reid, E. Jal, M. C. Hoffmann, M. Kozina, S. Song, M. Chollet, D. Zhu, P. F. Xu, J. Jeong, K. Carva, P. Maldonado, P. M. Oppeneer, M. G. Samant, S. S. P. Parkin, D. A. Reis, and H. A. Dürr. Generation mechanism of terahertz coherent acoustic phonons in Fe. Phys. Rev. B, 93:220301, (2016).

[21] T. Chase, M. Trigo, A. H. Reid, R. Li, T. Vecchione, X. Shen, S. Weathersby, R. Coffee, N. Hartmann, D. A. Reis, X. J. Wang, and H. A. Dürr. Ultrafast electron diffraction from non-equilibrium phonons in femtosecond laser heated Au films. Applied Physics Letters, 108(4), (2016).

[22] R. G. Moore, W. S. Lee, P. S. Kirchman, 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. Hays, P. Hering, T. Benson, J.-H. Chu, T. P. Devereaux, I. R. Fisher, Z. Hussain, and Z.-X. Shen. Ultrafast resonant soft x-ray diffraction dynamics of the charge density wave in $TbTe_3$. Phys. Rev. B, 93:024304, (2016).

[23] J. N. Clark, L. Beitra, G. Xiong, D. M. Fritz, H. T. Lemke, D. Zhu, M. Chollet, G. J. Williams, M. M. Messerschmidt, B. Abbey, R. J. Harder, A. M. Korsunsky, J. S. Wark, D. A. Reis, and I. K. Robinson. Imaging transient melting of a nanocrystal using an x-ray laser. Proceedings of the National Academy of Sciences, 112(24):7444–7448, (2015).

[24] D. Zhu, A. Robert, T. Henighan, H. T. Lemke, M. Chollet, J. M. Glownia, D. A. Reis, and M. Trigo. Phonon spectroscopy with sub-mev resolution by femtosecond x-ray diffuse scattering. Phys. Rev. B, 92:054303, (2015).

[25] M. Fuchs, M. Trigo, J. Chen, S. Ghimire, S. Shwartz, M. Kozina, M. Jiang, T. Henighan, C. Bray, G. Ndabashimiye, P. H. Bucksbaum, Y. Feng, S. Herrmann, G. A. Carini, J. Pines, P. Hart, C. Kenney, S. Guillet, S. Boutet, G. J. Williams, M. Messerschmidt, M. M. Seibert, S. Moeller, J. B. Hastings, and D. A. Reis. Anomalous nonlinear x-ray compton scattering. Nat Phys, 11(11):964–970, 11 (2015).

X-ray studies of functional materials under extreme environments

Wendy L. Mao, SLAC National Accelerator Laboratory & Stanford University
Yu Lin, SLAC National Accelerator Laboratory

Program Scope

The overarching goal of our proposed research program is to develop general principles which enable the design of new materials with enhanced performance by elucidating the relationship between lattice and electronic structure and desirable materials properties. The key to being able to address this scientific topic depends on our ability to characterize materials by static and dynamic diagnostics *in-situ* and *in-operando* under extreme conditions over varying length- and time-scales. A suite of X-ray probes will be coupled to static and dynamic compression methods to investigate complex hybrid systems and beyond equilibrium states. More specifically, we are studying hybrid halide perovskites and intercalated transition metal chalcogenide complexes where extreme conditions can tune hierarchical structures with multifunctionality. We are also investigating carbon-based nanomaterials and disordered systems, e.g., metallic glasses, where extreme environments allow us access to expanded pressure-temperature-temporal space and explore phase metastability with potentially enhanced materials functionality. This proposed research could lead to improved understanding of transition mechanisms and the discovery of new transformation pathways for the synthesis of novel phases that are not accessible otherwise. A critical component to these studies is our efforts in X-ray technique development which includes high pressure and variable temperature capabilities using nanoscale X-ray imaging at synchrotron facilities and ultrafast X-ray characterization at LCLS.

Recent Progress

We have been working on a number of static and dynamic compression experiments to elucidate the relationship between structure and material properties. Recent static compression work in a diamond anvil cell on a 3D lead-free halide double perovskite of $Cs_2AgBiBr_6$ shows a significant pressure-induced photoluminescence (PL) enhancement. The PL intensity increases by an order of magnitude as the pressure increases from 0 to 1.9 GPa. Detailed structural investigation is ongoing for understanding the relationship between structural and optical/electronic property changes. We have also conducted the first comparative study of the pressure effect on a series of diamondoids with systematically varying molecular geometries and dimensionalities, ranging from 0D adamantane to 3D [1(2,3)4]pentamantane. We find that the bulk moduli of these diamondoids strongly depend on the materials' molecular geometry. Recent dynamic compression work using an optical laser pump and ultrafast X-ray probe at the Matter in Extreme Conditions (MEC) instrument at LCLS has explored disordered systems which show rapid nucleation and growth of high pressure phases – nearly an order of magnitude faster than previously thought. Shock freezing of liquid water to ice VII is seen in less than ten nanoseconds. Crystallization of fused silica into stishovite is found to begin in only a few nanoseconds suggesting a non-diffusion mediated process.

Future Plans

We plan to focus on a more holistic approach to material properties investigations using both static and dynamic methods. Detailed comparative studies on lead-based and lead-free halide perovskites with either organic or inorganic cations will be investigated to elucidate the role of individual components in contributing to their promising yet still mysterious optoelectronic

properties. Structural studies from both static and dynamic aspects on transition metal chalcogenide intercalated complexes such as $TaS_2(NH_3)$ compared with their pristine counterparts will be carried out for understanding how the functionality of intercalated hybrid materials can be tuned and enhanced to help design new hybrid systems. We are submitting a number of proposals for beamtime at LCLS including investigation of the crystallization of metallic glasses and amorphization of metallic compounds and the development of ultrafast X-ray emission spectroscopy to study pressure-induced spin transitions under shock compression. We will also continue to analyze and model our SiO_2 results from MEC to study its non-equilibrium behavior under dynamic compression. We will work on implementing bright-field imaging with negative absorption contrast and spectroscopic nanoscale transmission X-ray microscopy in extreme environments in SSRL. Additionally, we will work with staff members at both the LCLS and SSRL to refine phase contrast imaging algorithms to use in both the static and dynamic compression work.

Publications

Z. Zhao, H. Wei, and W. L. Mao, Pressure tuning the lattice and optical response of silver sulfide, *Appl. Phys. Lett.* 108, 261902, 2016.

A Jaffe, Y. Lin, C. M. Beavers, J. Voss, W. L. Mao, and H. I. Karunadasa, High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybride Perovskites and Pressure Effects on the Electronic and Optical Properties, *ACS Central Sci.* doi: 10.1021/acscentsci.6b00055.

Z. Zeng, N. Liu, Q. S. Zeng, S. W. Lee, W. L. Mao, and Y. Cui, In situ measurements of lithiation-induced stress in silicon nanoparticles using micro-Raman spectroscopy, *Nano Energy* 22, 105-110.

A.E. Gleason, C. Bolme, H.J. Lee, B. Nagler, E. Galtier, D. Milathianaki, J. Eggert, J. Hawreliak, D. Fratanduono, R. Kraus, G. Collins, W. Yang, and W.L. Mao, Ultrafast crystallization and grain growth in shock compressed SiO_2, *Nature Comm.* doi: 10.1038/ncomms9191, 2015.

Z. Zhao, H. Zhang, H. Yuan, S. Wang, Y. Lin, Q. S. Zeng, Z. Liu, K. D. Patel, G. K. Solanki, Y. Cui, H. Y. Hwang, and W. L. Mao, Pressure induced metallization with absence of structural transition in layered $MoSe_2$, *Nature Comm.*, doi: 10.1038/ncomms8312, 2015.

Z. Zhao, Q. S. Zeng, H. Zhang, S. Wang, S. Hirai, Z. Zeng, and W. L. Mao, Structural transition and amorphization in compressed a-Sb_2O_3, *Phys. Rev. B* 91, 184112.

Z. Zeng, N. Liu, Q. F. Zeng, Q. Zhu, A. R. Oganov, Q. S. Zeng, Y. Cui, and W. L. Mao, A novel phase of $Li_{15}Si_4$ synthesized under pressure, *Adv. Energy Mat.* doi: 10.1002/aenm.201500214, 2015.

M. Wisser, M. Chea, Y. Lin, D. Wu, W. L. Mao, A. Salleo, and J. Dionne, Strain-induced modification of optical selection rules in lanthanide-based upconverting nanoparticles, *Nano Lett.*, doi: 10.1021/nl504738k, 2015.

A. Jaffe, Y. Lin, W. L. Mao, and H. Karunadasa, Pressure-Induced Conductivity and Yellow-to-Black Piezochromism in a Layered Cu–Cl Hybrid Perovskite, *J. Am. Chem. Soc.*, 137, 1673-1678, 2015.

F. Yang, Y. Lin, J. E. P. Dahl, R. M. K. Carlson, and W. L. Mao, Deviatoric Stress-Induced Phase Transitions in Diamantane, *J. Chem. Phys.*doi:10.1063/1.4897252, 2014.

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

Margaret Murnane and Henry Kapteyn, JILA, University of Colorado at Boulder
Tom Silva, NIST Boulder Laboratories

(i) Program Scope

Magnetism has been the subject of scientific inquiry for more than 2000 years; however, it is still an incompletely understood phenomenon. The fundamental length and time scales for magnetic phenomena are nanometers (nm) and femtoseconds (fs). Furthermore, a detailed understanding of nanoscale magnetism has become much more critical in the 21st century with dramatic recent advances in magnetic data storage applications, as bits on a hard disk are already packed at scales of about 20nm. Moreover, a comprehensive microscopic model of how spins, electrons, photons and phonons interact does not yet exist. This understanding is fundamentally constrained in large part by a limited ability to directly observe magnetism on all relevant time and length scales. Fortunately, by combining high harmonic sources with new and existing spectroscopic techniques and theory, we implemented the following for the first time [1-11] –

- Compared advanced experiment and theory to identify the multiple microscopic mechanisms that lead to magnetic quenching on ultrafast time scales.
- Extracted the dynamically-evolving magneto-optic tensor as a ferromagnetic material demagnetizes for the first time.
- Extracted surprising spin-dependent changes in the full conduction band as a material demagnetizes.
- Generated the first circularly-polarized soft X-ray high harmonics.
- Implemented the first tabletop XMCD.
- Implemented the first measurement of the evolution of layer-specific mechanical properties in sub-10nm bilayer films.
- Helped other groups in academe and national labs to duplicate our new high harmonic probe capabilities to uncover new understanding of magnetic materials.

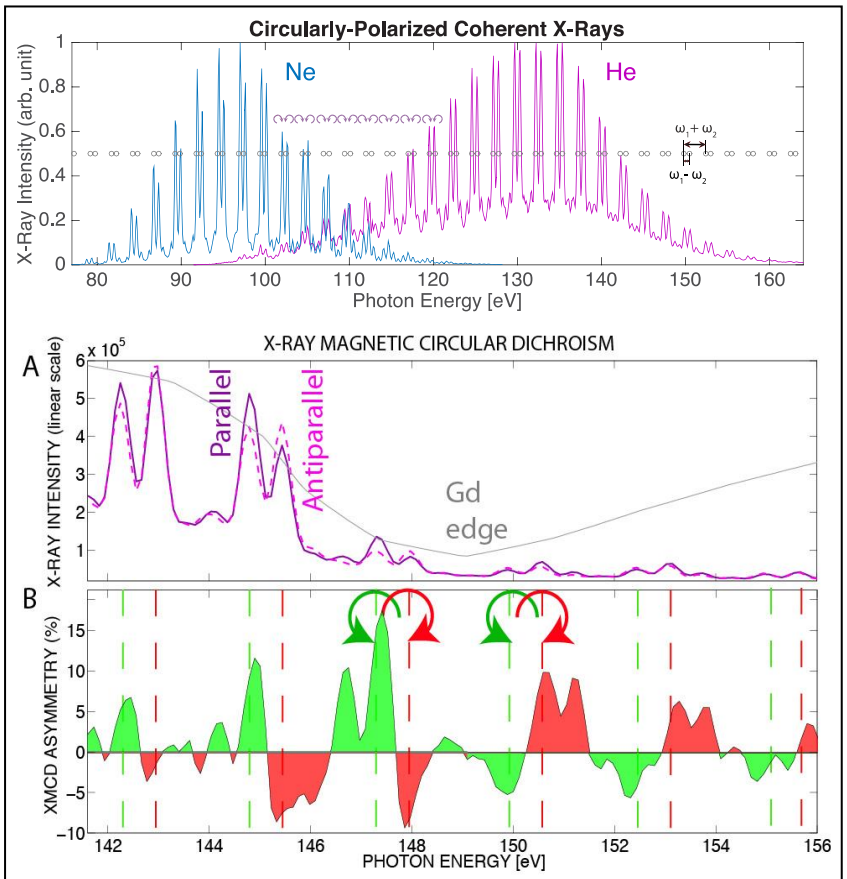


Fig. 1. First circular soft X-ray HHG and tabletop XMCD. (top) Circular soft X-ray HHG produced by combining circularly polarized 0.8 μm and 1.3 μm lasers of opposite helicities in a high pressure waveguide. (lower) HHG spectra through a Gd/Fe multilayer as the direction of magnetization is reversed. Strong magnetic asymmetry of opposite signs for left and right circularly-polarized HHG enables XMCD at the N edge of Gd.

(ii) Recent Progress

Bright Circularly Polarized High Harmonics and Tabletop XMCD [1-3]: For decades, high harmonic sources were limited to either linear or slightly elliptical polarization. Although studies of ultrafast phenomena have been highly fruitful for in-plane transition metals, another class of magnetic materials that exhibit out-of-plane magnetic anisotropy is becoming increasingly interesting for many applications. Fortunately, in recent work we demonstrated that we can now generate circularly polarized HHG spanning the EUV and soft X-ray regions, to photon energies ≈ 160 eV. Figure 1 plots the first circular soft X-ray HHG and tabletop XMDC measurements enabled by combining circularly polarized 0.8 μm and 1.3 μm lasers of opposite helicities in a high-pressure gas-filled waveguide. In collaboration with the Cohen group at Technion and the Fullerton/Shpyrko groups at UCSD, we can now access materials with intrinsic perpendicular magnetic anisotropy (e.g. 4f elements such as Gd, with an N edge near 145 eV) that exhibits a strong magnetic asymmetry, confirming that ultrafast magnetic effects can be studied in 4f elements.

Nondestructive measurement of the evolution of layer-specific mechanical properties in sub-10nm bilayer films [4]: In recent work, we used short wavelength extreme ultraviolet light to independently measure the mechanical properties of disparate layers within a bilayer film for the first time, with single-monolayer sensitivity. We showed that in Ni/Ta nanostructured systems, while their density ratio is not significantly changed from that expected in bulk, their elastic properties are significantly modified: the nickel softens while tantalum stiffens relative to their bulk counterparts. In particular, the presence or absence of the Ta capping layer influences the mechanical properties of the Ni film. This non-destructive nano-mechanical measurement technique represents the first approach to date able to distinguish the properties of composite materials well below 100 nm in thickness. This capability is critical for understanding and optimizing the strength, flexibility and reliability of materials in a host of nanostructured electronic, photovoltaic and thermoelectric devices.

Stoner vs. Heisenberg: Ultrafast exchange reduction and magnon generation during laser-induced demagnetization [7]: In recent work, we used time-, energy-, and angle-resolved ultrafast extreme ultraviolet (EUV) transverse-MOKE to extract the dynamically-changing magneto-optic response across the entire $M_{2,3}$ absorption edge of a Co film

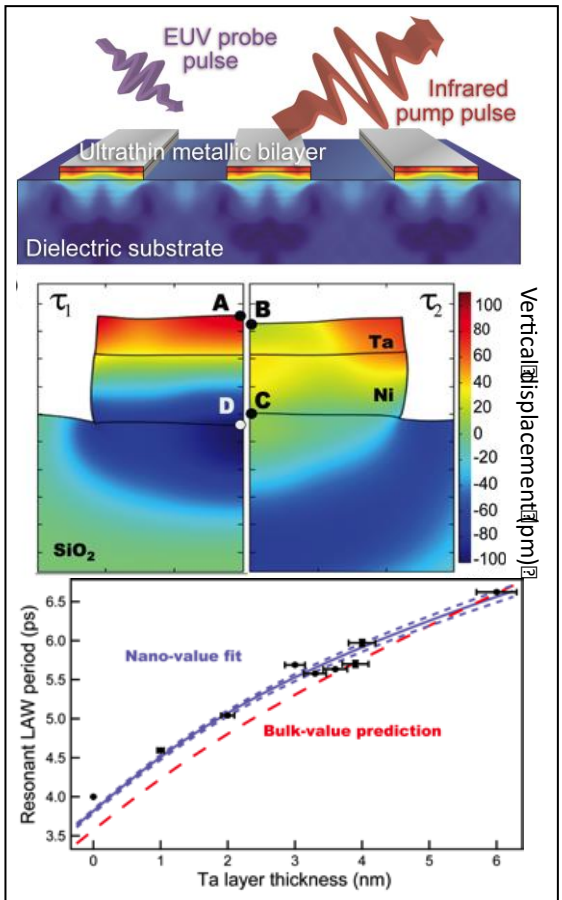


Fig. 2. EUV acoustic nanometrology for extracting nanoscale mechanical properties. (top) A series of Ni-Ta bilayers, with a constant 10nm of Ni and a Ta capping layer between 0 and 6nm, are excited by an 800nm pump pulse. The change in EUV diffraction is used to extract the mechanical properties of the bilayer. (bottom) Resonant LAW periods of the bilayer structures clearly are not well matched by predictions using bulk material parameters (dashed red). Instead, a least-squares optimization algorithm fits the data in order to extract the effective nanoscale longitudinal velocities of the Ni and Ta layers.

after excitation with a femtosecond laser pulse. This allowed us to explicitly identify the dominant mechanisms that contribute to ultrafast demagnetization. Since EUV MOKE probes the entire demagnetization response of the 3d bands, this provides a complete data set, which we can compare with first principles magneto-optical calculations. We find that both longitudinal and transverse processes contribute to ultrafast demagnetization in Co on timescales up to several picoseconds. Surprisingly, the magnon contribution to ultrafast demagnetization is dominant on very short 700 fs timescales, while the reduction in exchange splitting persists to several picosecond timescales. Finally, this work demonstrates that each of these mechanisms has a particular magneto-optical "fingerprint" that makes identification possible, as suggested forty years ago by Erskine and Stern. They proposed that in principal, measuring the EUV magneto-optic response across the entire $M_{2,3}$ absorption edge would contain all the spin-dependent information about the electronic structure in the conduction band. In our work, we demonstrate that this is possible even for dynamically out-of-equilibrium materials.

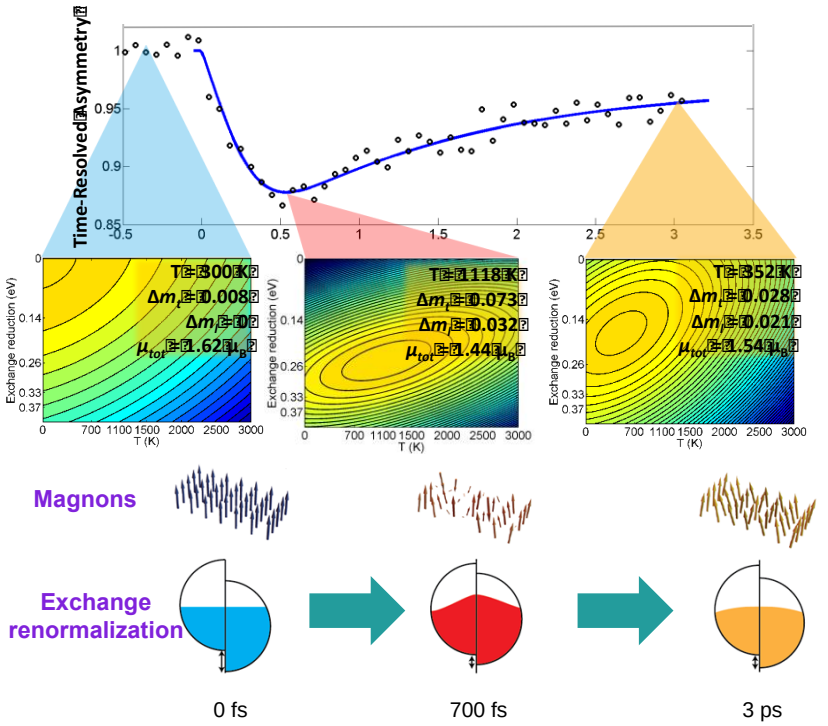


Fig. 3. Microscopic mechanisms responsible for ultrafast demagnetization for Co films on an insulating substrate. At 700 fs, demagnetization is due to magnons Δm_t (2/3), exchange reduction Δm_l (1/4 signal), and Fermi smearing Δm_e (1/10). By 3 ps, there are equal contributions from magnons and exchange reduction. The timescales for excitation and relaxation of both processes are similar. Note that the insulating substrate inhibits fast spin currents.

(iii) Ongoing and Future Plans

Time- and Polarization-Resolved EUV magneto-optic Kerr effect (MOKE) [10]: We are exploring a new approach for extracting the dynamic magneto-optic tensor, that will enable us to increase the dynamic range and sensitivity of the measurement, enabling us to achieve better time resolution for exploring coupled charge and spin dynamics in magnetic materials. A paper that discusses this work is currently in preparation.

Spin-, time-, and angle-resolved photoelectron spectroscopy [5, 6, 9]: Capturing the dynamic electronic band structure of a correlated material is a powerful capability for uncovering the complex couplings between the electronic and structural degrees of freedom. When combined with ultrafast laser excitation, new phases of matter can result, since far-from-equilibrium excited states are instantaneously populated. In recent work in collaboration with Kaiserslautern and just published in Nature Communications,[5] we uncovered a general relation between ultrafast non-equilibrium electron dynamics and the size of the characteristic energy gap in a

correlated electron material. We showed that carrier multiplication via impact ionization can be one of the most important processes in a gapped material, and that the speed of carrier multiplication critically depends on the size of the energy gap. In the case of the charge-density wave material 1*T*-$TiSe_2$, our data indicated that carrier multiplication and gap dynamics mutually amplify each other, which explains – *on a microscopic level* - the extremely fast response of this material to ultrafast optical excitation.

More recently in collaboration with Kaiserslautern and Julich,[9] we used time- and spin-resolved photoelectron spectroscopy to capture how the electronic properties of Cobalt change in real time after excitation with an ultrashort laser pulse. This allows us to uncover for the first time that demagnetization induces large transient changes spanning the entire conduction band of Cobalt. We showed that the loss of magnetization is not only found around the Fermi-level, where the states are affected by the laser excitation, but reaches deep into the electronic bands. We find that the ferromagnetic-paramagnetic phase transition cannot be explained by a loss of the exchange splitting of the spin-polarized bands, but instead shows rapid band mirroring after the excitation, which is a clear signature of efficient ultrafast magnon generation.

Finally, we explored many-body electron-electron interactions, which are among the fastest processes in materials, playing prominent roles in strongly-correlated electron systems and quantum materials. In recent years, these interactions have become accessible to direct time-domain studies by using femtosecond lasers. However, to date such measurements have been limited to the femtosecond time scales that are characteristics of interactions involving low-energy electrons. In recent work we showed that by using sequences of attosecond pulses produced by high harmonic generation, we can observe and distinguish many-body electron-electron interactions that occur on attosecond timescales during the photoemission process.[6] We extract the time delays associated with photoemission from occupied bands in Ni(111) and Cu(111) into free-electron final states, using photoemission selection rules to isolate the contributions from individual initial bands. This allows us to show that photoemission from the *d* band of Cu is delayed by ~100 attoseconds relative to photoemission from the same band of Ni. We attribute this difference to the fact that the *d* band in Ni is not fully occupied, resulting in enhanced electron-electron scattering during photoemission.

Coherent EUV Magnetic Scattering [11]: We recently demonstrated resonant magnetic scattering of coherent, linearly polarized XUV light with 15 nm thick Gd/Fe multilayers provided by our collaborators, Oleg Shpyrko and Ian McNulty at the University of San Diego and ANL. The magnetic sample exhibits a serpentine domain structure in zero applied field. Such a domain structure is known to yield purely magnetic diffraction peaks for the case of coherent forward X-ray scattering. The XUV HHG scatter signal was measured at 54.9 eV that corresponds with the *M*-edge for Fe. These results agree very well with both MFM data and L-edge resonant scattering data in terms of both average domain size and angular distribution. These preliminary, unpublished data are very promising for our ongoing development of coherent, lensless magnetic imaging via either holographic or ptychographic methods with linearly polarized as well as the recently developed circular polarized HHG beams.

Other plans: Dynamic spectroscopy and scattering of magnetic materials (collaborator John Freeland, ANL); Dynamic XMCD spectroscopy of Gd at the *N* absorption edges (collaborators Oleg Shpyrko and Erik Fullerton (UCSD).

(iv and v) References that report list of published and submitted papers since 2015

1. "Generation of bright circularly-polarized extreme ultraviolet high harmonics for magnetic circular dichroism spectroscopy", 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, Nature Photonics **9**, 99–105 (2015).

2. "Bright Circularly Polarized Soft X-Ray High Harmonics for X-Ray Magnetic Circular Dichroism," T. Fan, P. Gychtol, R. Knut, C. Hernández-García, D. Hickstein, C. Gentry, C. Hogle, D. Zusin, K. Dorney, O. Shpyrko, O. Cohen, O. Kfir, L. Plaja, A. Becker, A. Jaron-Becker, T. Popmintchev, M. Murnane, H. Kapteyn, PNAS **112**, 14206 (2015). 10.1073/pnas.1519666112
3. "Helicity-selective phase-matching and quasi-phase matching in generation of circularly polarized high-order harmonics: Towards chiral attosecond pulses", O. Kfir, P. Grychtol, E. Turgut, R. Knut, D. Zusin, A. Fleischer, E. Bordo, T. Fan, D. Popmintchev, T. Popmintchev, H. Kapteyn, M. Murnane, O. Cohen, Invited Paper, Journal of Physics B: At. Mol. Opt. Phys. **49**, 123501 (2016).
4. "Nondestructive measurement of the evolution of layer-specific mechanical properties in sub-10nm bilayer films," K. Hoogeboom-Pot, E. Turgut, J. Hernandez-Charpak, J. Shaw, H. Kapteyn, M. Murnane, D. Nardi, Nano Letters **16** (8), pp 4773–4778 (2016). DOI: 10.1021/acs.nanolett.6b00606
5. "Carrier multiplication and gap dynamics in the femtosecond response of a strongly correlated electron material," S. Mathias, S. Eich, J. Urbancic, S. Michael, A. Carr, A. Stange, T. Popmintchev, T. Rohwer, M. Wiesenmayer, A. Ruffing, S. Jakobs, S. Hellmann, P. Matyba, C. Chen, L. Kipp, M. Bauer, H. Kapteyn, H. Schneider, K. Rossnagel, M. Murnane, M. Aeschlimann, Nature Communications **7**, 12902 (2016). doi:10.1038/ncomms12902.
6. "Influence of the Material Band Structure on Attosecond Many-Body Electron-Electron Interactions in Transition Metals," C. Chen, Z. Tao, A. Carr, P. Matyba, T. Szilvási, M. Piecuch, S. Emmerich, M. Keller, D. Zusin, M. Rollinger, W. You, S. Mathias, U. Thumm, M. Mavrikakis, M. Aeschlimann, P. Oppeneer, H. Kapteyn, M. Murnane, Postdeadline paper, International Conference on Ultrafast Phenomena, Santa Fe, NM, July 2016; *also under review* (2016).
7. "Heisenberg vs. Stoner: Magnon Generation and Exchange Renormalization during Ultrafast Demagnetization," E. Turgut, P. Grychtol, J. Shaw, R. Knut, D. Zusin, D. Legut, K. Carva, H. Nembach, S. Mathias, T. Silva, P. Oppeneer, M. Murnane H.C. Kapteyn, *submitted* (2016).
8. "Controlling the distribution of virtual bound states in Permalloy (Fe0:2Ni0:8) by Cu alloying," R. Knut, E. Delczeg, J. Shaw, H. Nembach, P. Grychtol, D. Zusin, C. Gentry, E. Turgut, H. Kapteyn, M. Murnane, D. Arena, O. Eriksson, O. Karis, T. Silva, *submitted* (2016).
9. "Band-structure evolution during the ultrafast ferromagnetic-paramagnetic phase transition in Cobalt," S. Eich, M. Plötzing, M. Rollinger, S. Emmerich, R. Adam, C. Chen, H. C. Kapteyn, M. Murnane, L. Plucinski, D. Steil, B. Stadtmüller, M. Cinchetti, M. Aeschlimann, C. Schneider, S. Mathias, *submitted* (2016).

Papers in Preparation

10. "Measuring the magneto-optical constant across the entire M-edge in a simple photon in – photon out reflection geometry", D. Zusin et al., *in prep*. (2016).
11. "Imaging of buried magnetic domains using linearly polarized bright high harmonics from Ti:Sapphire laser," D. Popmintchev, B. Zhang, D. Zusin, J. Shaw, H. Nembach, M. Chen, J. Siqueira, C. Mancuso, F. Dollar, S. Brown, A. Hankla, I. McNulty, S. Dietze, O. Shpyrko, T. Silva, P. Grychtol, T. Popmintchev, M. Murnane, H. Kapteyn, *in prep*. (2016).

Element specific atomic arrangement in binary and ternary alloy nanosized catalysts in as-prepared and active state

DOE-BES Award: DE-SC0006877
PI: Valeri Petkov, Dept. Physics
Central Michigan University
Mt. Pleasant, MI-48859
Phone: (989) 774 3395; e-mail: petko1vg@cmich.edu
Co-PI: Chuan-Jian Zhong, Dept. Chemistry and Mat. Science
SUNY Binghamton, NY-13902
Phone: (607) 777 4605; e-mail: cjzhong@binghamton.edu

Research scope:

This project supports the Office of Basic Energy Sciences (X-ray scattering) mission through the application and advancement of cutting-edge x-ray scattering techniques for determining the atomic-level structure of nanosized catalysts vital for the development of clean energy conversion and storage technologies. In particular, our research activities involve: i) design, synthesis and optimization of metallic nanosized catalysts, ii) structure studies on metallic nanosized catalysts in as-prepared state by *ex-situ* high-energy x-ray diffraction (HE-XRD) and atomic pair distribution function (PDF) analysis, iii) element-specific structure studies on metallic nanosized catalysts by resonant HE-XRD and atomic PDF analysis, iv) structure studies on metallic nanosized catalysts in active state by *in-situ* and *in-operando* HE-XRD and atomic PDF analysis, v) modeling the 3D atomic structure of metallic nanosized catalysts using Molecular Dynamics and reverse Monte Carlo simulations guided by experimental PDF data and vi) using the obtained structure knowledge as a rational basis for optimizing the nanosized catalysts studied. Note, here the terms “alloy” and “intermetallic” are used to describe any mixture of distinct metallic species, irrespective of the degree of their mixing and way of mixing.

Present work: The group of Prof. Zhong (SUNY) synthesized and characterized catalytically several families of nanosized intermetallics, including Pt-Au and Pt-Ni nanowires, Pd-Ni nanotetrahedrons, Au@PtNi core-shell particles, Pd-Sn, Pt-Ni-Cu and Pt-V-Co nanoalloys. The intermetallics are supported on substrates found useful in catalysis such as graphene nanosheets, fine carbon, silica and titania powders. The intermetallics showed excellent catalytic properties for chemical reactions (e.g. hydrogen oxidation and oxygen reduction eactions) driving proton exchange membrane (PEMFC) and direct alcohol (DAFC) fuel cells, oxidation of carbon monoxide, propane, and others.

The most promising of the nanosized catalysts listed above were characterized by *ex situ* synchrotron HE-XRD and atomic PDF analysis. Results will be presented at the PIs’ meeting.

In February, 2016 we, that is the group of Prof. Petkov (CMU), conducted grazing incidence atomic PDF studies at Sector 12, APS. Selected results will be presented at the PIs’ meeting.

In the summer of 2016 we conducted *in operando* atomic PDF studies on nanosized catalysts as they function at the cathode of an operating PEMFC. We collected both HE-XRD data (2D Dexela CMOS detector) and EDS spectra (Vortex detector) thus following the concurrent evolution of the chemical composition, size, atomic-scale structure and functionality of the nanosized catalysts. Also, we took data at several locations across the Membrane Electrode Assembly (MEA) of the PEMFC thus obtaining information about both the progress of the catalytic reaction and mass transport across the MEA during the PEMFC operation. For the

purpose we used an x-ray beam (~ 90 keV energy) collimated down to 20 x 40 μm. Studies we carried out at Sector 1, APS. Selected results will be presented at the PIs' meeting.

Also, in the summer of 2016 we conducted combined *in situ* atomic PDF and Diffuse Reflectance Infrared Fourier Transform Spectroscopy studies on nanosized catalysts in reactive atmosphere, including oxygen, carbon monoxide and propane. The catalysts were studied at temperature ranging from room to 300 C. Studies were carried out at Sector 11, APS. Preliminary results will be presented at the PIs' meeting.

We analyzed several data sets from resonant HE-XRD studies on Fe@Pt core-shell particles and Pd-Au/Pt nanoalloys. Data sets were obtained at Sector 6, APS (Pd K edge) and Sector 1, APS (Au & Pt K edges). 3D structure models of the respective samples were built by Molecular Dynamics (MD) and refined by reverse Monte Carlo (RMC) simulations guided by the element-specific atomic PDFs. Structure models were used to compute the electronic structure of Au-Pd nanoalloys, in particular the width and energy position of the *4d*-electron band of Pd and *5d*-electron band of Au surface atoms. The electronic structure (*5d*-electron band) of surface Pt atoms in Fe@Pt core-shell particles was also computed and used to assess the catalytic properties of the NPs. Selected results will be presented at the PIs' meeting.

We continued developing improved potentials for metals and alloys confined to nanoscale dimensions, in particular the Quantum-corrected Sutton-Chen potential. Potentials are needed in the MD simulations. Also, we continued developing code for RMC simulations under non-periodic boundary conditions. The latter are a must in modeling the 3D structure of finite size, free surface nanosized metals and alloys. Selected results will be presented at the PIs' meeting.

Near future activities: We will continue developing advanced nanosized catalysts and study the relationship between their atomic-scale structure and functionality aiming at improving the latter by modifying the former on a rational basis provided by HE-XRD/PDFs *resonant, ex situ*, *in situ* and *in operando* experiments coupled to 3D structure modeling.

We will continue collaborating with staff scientists at Sectors 1 and 12, APS, in an effort to develop grazing incidence PDF studies to a user-friendly level. The effort requires some instrumental development. We hope APS will help in this respect.

We will carry out resonant HE-XRD experiments (Sector 1), *in operando* PEMFC and DAFC experiments (Sectors 1 and 11, APS) and *in situ* PDF&DRIFTS experiments (Sector 11, APS).

We will continue our effort in modeling the 3D structure of nanosized metallic catalysts and using the structure models for computing the electronic structure of the catalysts, thus assessing the trajectories of catalytic reactions taking place the catalysts' surface. The effort is very involved computationally (MD + RMC + DFT). To facilitate it we applied for and were granted computing time (2 million hours) at the 10-petaflops IBM Blue Gene/Q system (MIRA) at the Argonne Leadership Computing Facility.

Materials Structure Analysis by BCDI and PDF

I. K. Robinson, S. J. L. Billinge and E. S. Bozin

Condensed Matter Physics & Materials Science Department, Brookhaven National Laboratory

Program Scope

Our program uses NSLS-II, currently the brightest synchrotron in the world, and other DOE facilities to merge the strengths of two powerful, emerging X-ray techniques for structure analysis of nano-materials. Bragg Coherent Diffraction Imaging (BCDI) can image individual nanoparticles with sub-nanometer resolution in 3D, revealing information about local nano-scale domain structures; the atomic Pair Distribution Function (PDF) method yields sub-angstrom resolution structural information on nanometer length-scales from powders (ensembles of nanoparticles). The PDF yields rich information about local atomic arrangements whereas BCDI shows how the domains of different arrangements arrange in space. Both methods are being applied to study Grand Challenge science problems, as well as being under active development. To date, these approaches have not been combined in a systematic way to study the multi-scale structure on the same materials systems, but this is a major goal of this program. We recently extended PDF analysis to study local magnetic correlations and this will allow similar studies of charge, spin and orbital degrees of freedom. Furthermore, we are developing the applications of both methodologies applied to nanomaterials in thin layer format, which makes them then also suitable for time-resolved experiments by avoiding laser shadowing.

The methods are sensitive to magnetic, charge-density-wave and orbital-ordered materials under active exploration in the wider Condensed Matter Physics and Materials Science Department at BNL. These are material systems with symmetry broken ground-states. On warming, or in the presence of quenched disorder, the ordering mechanisms often leads to local structural correlations and domain formation. Characterizing these structures on multiple length-scales using PDF and BCDI together is critical for a full understanding of the physics giving rise to them and for potentially exploiting them in devices. We will exploit the use of X-ray resonances to enhance signals from charge-ordered states, notably at the CSX beamline of NSLS-II. Many of the symmetry broken states begin with a lifting of orbital degeneracies on 3d, 4d or 5d ions, a concept we refer to in general as Orbital Degeneracy Lifting (ODL). We aim to study how the entire hierarchy of effects where ODL results in a symmetry lowering at the ionic site itself, which may then form into locally ordered symmetry broken domains, or orbital molecules. Then we will investigate how these domains evolve into the long-rang ordered structures seen by conventional approaches. We believe that many of the physical properties of the materials, such as transport, magnetic and electric polarization, depend sensitively on the local domain structures, how they arrange, and their dynamics, yet do not require the order to be long-range in nature. Nano-scale characterizations are therefore at the center of efforts needed to understand the physics of **real** nano-structured materials. Where necessary, we are augmenting these structural results using techniques sensitive to structural and domain dynamics, for example, inelastic neutron/x-ray scattering and x-ray photon correlation spectroscopy (XPCS), respectively, using DOE national facilities.

Recent Progress

1. Phase Domain Structure of Manganites.

Nanocrystals of $La_{0.5}Ca_{0.5}MnO_4$ were studied using BCDI at the 34-ID-C beamline of APS. It was intended to establish the feasibility for low temperature imaging of the orbital-ordered domains, but even the bulk crystal peaks revealed interesting new structure. A typical BCDI data set consists of a 3D series of diffraction images passing through the center of the Bragg peak is obtained while “rocking” the sample through a fraction of a degree at a coherent diffraction X-ray beamline [1]. The diffraction

pattern is the 3D Fourier transform of the crystal shape, typically a set of fringes a compact solid object and streaks attributed to its prominent facets and internal defects [2]. Once the BCDI diffraction pattern is inverted [3], the strain is mapped in the resulting complex real-space 3D image as the phase of the complex number at each location. This phase $\Delta\varphi$ corresponds to a projection of the local crystal displacement vector **u,** according to the simple relation, $\Delta\varphi = \mathbf{Q}\cdot\mathbf{u}$, where **Q** is the momentum transfer vector of the Bragg peak measured.

Preliminary images show massive strain effects. Inversion of the BCDI diffraction patterns [3] gives images of these crystals containing a mosaic of domains, which are laterally shifted with respect to each other. The shifts, which are less than a unit cell in magnitude, show up as phase shifts in the range $-\pi<\varphi<\pi$ and are conveniently represented on a color wheel. This is a little like traditional picture of mosaic spread, except that the domains are only shifted (translated) and not rotated. The behavior has not been noted before, except in the general language of "microstrain" used to explain the pattern of broadening seen in powder diffraction, which can be explored through explicit modeling of the PDFs.

Rather than the small surface distortions seen before, whole blocks inside the crystal have different (real space) phase. Nanometer-sized blocks of crystal are laterally shifted with respect to each other and acquire different phases with in-grown planar defects separating these blocks. We identify this preliminary result as a new form of crystal mosaic disorder. Further investigation is planned to discover whether these phase domains are fundamental in nature or coupled to the crystal growth and subsequent treatment to prepare nanomaterials. Nanomaterials are frequently able to stabilize and promote out-of-equilibrium states of matter in the form of core-shell or epitaxial structures.

In the near future we will use the CSX facility of NSLS-II to image LCMO crystals at ½-order or fractional-order reflections on resonance at the Mn L-edge [4,5]. The orbital and magnetic cross sections are around 10^{-6} of the charge signal [4], so we will expect a weak but detectable signal from the orbital ordering domains, which will be compared with the structural domains.

2. Revisiting the Metal-Insulator transition in CMR Manganites

The insulating state of the manganites in the low and intermediate doping range ($0<x<0.5$) is a classic ODL state. At x=0 Jahn-Teller effects break the symmetry at the Mn site resulting in a long-range-ordered LRO symmetry-broken antiferromagetic insulator. However, doping holes into the system produces a disordered array of undistorted (non-ODL) sites that quickly break up the long-range orientational order of the ODL sites. PDF reveals that the ODL sites persist locally even though they are not seen crystallographically. However, when the sample passes through an insulator-metal (IM) transition with increased doping at around x=0.2 at low temperature the local ODL state is quenched and the MnO_6 octahedra become regular, even locally. For a long time this transition was thought to be percolative in nature, with a large percentage of the sample remaining in the ODL state, but the IM transition occurring when there was a percolating metallic pathway of undistorted metallic material through a matrix of ODL material. However, we recently showed [7] that in high-quality samples there is a very fast loss of ODL material at the transition that essentially rules out the percolative picture and requires a reassessment of the nature of this transition in this ubiquitous of spin-charge-lattice correlated material.

3. Dimerization transitions in iridium chalcogenides

In iridium chalcogenides, the metal-insulator ($CuIr_2S_4$) and metal-metal ($IrTe_2$) transitions ODL on $Ir^{3.5+}$ leave dramatic structural footprints and play an essential role in the displayed properties. The ODL results in observable symmetry lowering in the tetrahedral/triangular Ir sublattices which then form metal-metal bonds between pairs of iridium ions at low temperature that move together as dimers (diatomic orbital molecules) that are presumably spin singlets. X-ray based PDF analysis reveals that in both systems Ir-dimers disappear in the high temperature metallic states. In $CuIr_2S_4$,

although the dimers disappear on all lengthscales, the local ODL state persists deep into the high temperature metallic regime, with short-range orbital order limited only to the nearest Ir neighbors – resembling orbital liquid-like state. This implies that the MIT proceeds on cooling via crystallization of such orbital molecules into an orbital lattice with simultaneous formation of long range ordered dimers [8]. In $IrTe_2$ dimerization occurring on upon entering the low temperature metallic state affects only a small fraction of Ir-Ir contacts, which causes enormous local structural distortions around the affected sites. Bond valence analysis indicates that appreciable bond charge disproportionation at Ir sites leads to the dimerized state, with ligand hole localization being a likely prerequisite for this process [9].

Future Plans

The planned future approach is to merge the strengths of the Bragg Coherent Diffraction Imaging (BCDI) to study the domain structure and Pair Distribution Function (PDF) methods to look at the short range correlations. Our combined approach, applied to the same samples in the same in situ sample environments addresses the properties of nanoparticles with complementary information coming from the two approaches. Rationalization of these results will lead to new understanding of the underlying materials physics. This will also require development of some in house laboratory capabilities, for example to produce high-quality nanoparticles in uniform "thin layer" sample formats for precise laser excitation free from shadowing effects.

While a number of nanosized crystals appear to be perfect when imaged by BCDI, in the sense that the crystal planes pass right through the crystal without defects, there is a rising number of examples where this is not true. Especially common among oxides, there are nanocrystals which give speckled diffraction patterns instead of ideal single peak lineshapes when they are illuminated by a coherent X-ray beam. We plan to investigate the occurrence of this new phase domain mosaic behavior, initially at the level of systematically varying the degree of crystal perfection in a number of ways and measuring the result in the 3D images, for example in LCMO where bulk, charge and orbital ordering can all be monitored independently though different Bragg peaks.

This information can provide insight in PDF studies of nanoparticles, where single-phase models often give unsatisfactory fits. It can be very difficult to infer what distortions to put into the structural models to account for the residual signal. These residuals are presumably coming from interfacial structures and minority phases at the particle surfaces. Combining BCDI and PDF to build realistic multiscale hierarchical models for nanoparticles holds great promise for understanding these details.

We aim to look at laser-induced materials phase transformations in the time domain, using XFELs to the extent they are available to users. In parallel, we will attempt these experiments using the Brookhaven Ultrafast Electron Diffraction (UED) facility, which has recently been incorporated into the Accelerator Test Facility. We have already learned how to correct the electron diffraction data for background and dynamical effects in order to obtain electron PDF (ePDF) distributions [6], whose time domain evolution will be explored using pump-probe methods.

In order to gain more understanding of the ODL phenomenon, its relevance for the materials properties, as well as its ubiquity, we propose to systematically explore the ODL aspects in a broad class of TMCs. While such TMCs are seemingly unrelated/distinct from the standpoint of the displayed properties, they do have a common thread: partially filled d-orbital sector, and high symmetry crystal structures in the high-T regime. Material classes to be investigated include (a) 3D and 2D chalcogenides exhibiting exotic electronic/magnetic transitions, such as Ir and Ti based spinels, (b) pyroxenes exhibiting long range orbital-ordered ground states, (c) perovskites, such as Sr-doped "113"-manganites exhibiting electronic transitions and (d) stannates, such as $(A)_3B_4Sn_{13}$ (A=Sr/Ca, B=Rh,Ir), exhibiting structural QCPs, where nanoscale signatures of the ODL states (nanoscale

symmetry breaking) would be mapped out in (x, T, t) phase space by changing the electron filling (doping), temperature and optical excitation.

Last but not least, we will continue our technique development of BCDI and PDF. We are extending PDF methods to the study of short-range ordered magnetic structures with so-called magnetic PDF (mPDF) [7,10]. We are also extending PDF analysis to thin-layers, which are thin-films made up of fine-grained polycrystals or nanoparticles, that we call thin-layers [11]. This involves a multi-group collaboration, supported by the FWP in collaboration with Kirsten Jensen, a post-doc funded by the Villum Foundation in Denmark. These developments will be leveraged in the future plans, along with our earlier developments of electron PDF (ePDF) analysis [12] which is vital for our plans to develop ultrafast electron (UED) and X-ray methods.

References

[1] Ian Robinson and Ross Harder, Coherent Diffraction Imaging of Strains on the Nanoscale, Nature Materials 8 291-298 (2009)

[2] J. N. Clark, J. Ihli, A. S. Schenk, Y-Y Kim, A. N. Kulak, J. M. Campbell, G. Nisbit, F. C. Meldrum and I. K. Robinson, Three-dimensional imaging of dislocation propagation during crystal growth and dissolution, Nature Matls. 14 780 (2015)

[3] J. R. Fienup, Phase retrieval algorithms: a comparison, Appl. Opt. 21 2758-69 (1982)

[4] C. S. Nelson, J. P. Hill, Doon Gibbs, F. Yakhou, F. Livet, Y. Tomioka, T. Kimura and Y. Tokura, PRB 66 134412 (2002)

[5] E. Dagotto, Science, 309 257-262 (2005)

[6] M. Abeykoon E. S. Bozin, W-G Yin, G Gu, J. P. Hill, J. M. Tranquada and S. J. L. Billinge, Z. Kristallogr. 227 248 (2012)

[7] M. Shatnawi, E. S. Bozin, J. F. Mitchell and S. J. L. Billinge, Non percolative nature of the metal-insulator transition and persistence of local Jahn-Teller distortions in the rhombohedral regime of La1-xCaxMnO3, Phys. Rev. B 93, 165138 (2016).

[8] E. S. Bozin, M. Abeykoon, Y. S. Hor, J. F. Mitchell and S. J. L. Billinge (in preparation).

[9] R. Yu, M. Abeykoon, H.D. Zhou, W. G. Yin and E. S. Bozin (in preparation).

[10] B. A. Frandsen, M. Brunelli, K. Page, Y. J. Uemura, J. B. Staunton and S. J. L. Billinge, Verification of Anderson Superexchange in MnO via Magnetic Pair Distribution Function Analysis and ab initio Theory, Phys. Rev. Lett. 116, 197204 (2016).

[11] K. M. Jensen, A. B. Blichfeld, S. R. Bauers, S. R. Wood, E. Dooryhée, D. C. Johnson, B. B. Iversen and S. J. L. Billinge, Demonstration of thin film pair distribution function analysis (tfPDF) for the study of local structure in amorphous and crystalline thin films, IUCrJ. 2, 481-489 (2015).

[12] M. Abeykoon, H. Hu, L. Wu, Y. Zhu and S. J. L. Billinge , Calibration and data collection protocols for reliable lattice parameter values in electron pair distribution function studies, J. Appl. Crystallogr. 48, 244-251 (2015).

Publications FY16

[1] P. Juhás, C. L. Farrow, X. Yang, K. R. Knox, and S. J. L. Billinge, "Complex modeling: a strategy and software program for combining multiple information sources to solve ill posed structure and nanostructure inverse problems," Acta Crystallographica Section A 71, 562 (2015)

[2] X. Liu, M. P. M. Dean, Z. Y. Meng, M. H. Upton, T. Qi, T. Gog, Y. Cao, J. Q. Lin, D. Meyers, H. Ding, G. Cao, and J. P. Hill, "Anisotropic softening of magnetic excitations in lightly electron-doped Sr_2IrO_4," Phys. Rev. B 93, 241102(R) (2016).

[3] M. Shatnawi, E. S. Bozin, J. F. Mitchell, S. J. L. Billinge, "Nonpercolative nature of the metal-insulator transition and persistence of local Jahn-Teller distortions in the rhombohedral regime of $La_{1-x}Ca_xMnO_3$", Phys. Rev. B 93 165138 (2016) DOI: 10.1103/PhysRevB.93.165138

[4] Benjamin A. Frandsen, Michela Brunelli, Katharine Page, Yasutomo J. Uemura, Julie B. Staunton and Simon J. L. Billinge, "Verification of Anderson Superexchange in MnO via Magnetic Pair Distribution Function Analysis and ab initio Theory", Phys. Rev. Lett. 116 197204 (2016)
DOI: 10.1103/PhysRevLett.116.197204

[5] P.M. Duxbury, L. Granlund, S.R. Gujarathi, P. Juhas, ,S.J.L.Billinge, "The unassigned distance geometry problem" Discrete Applied Mathematics 204 117-132 (2016)
DOI: 10.1016/j.dam.2015.10.029

[6] Kirsten M. Ø. Jensen, Pavol Juhás, Marcus A. Tofanelli, Christine L. Heinecke, Gavin Vaughan, Christopher J. Ackerson, Simon J. L. Billinge,"Polymorphism in magic-sized Au144(SR)60 clusters", Nat.Commun. 7 11859 (2016)
DOI: 10.1038/ncomms11859

[7] Benjamin A. Frandsen, Zizhou Gong, Maxwell W. Terban, Soham Banerjee, Bijuan Chen, Changqing Jin, Yasutomo J. Uemura and Simon J. L. Billinge, "Local atomic and magnetic structure of dilute magnetic semiconductor (BaK)(ZnMn)2As2", Phys. Rev. B 94, 094102 (2016)
DOI: 10.1103/PhysRevB.94.094102

[8] Maxwell W. Terban, Eugene Y. Cheung, Paul Krolikowski and Simon J. L. Billinge, "Recrystallization phase composition and local structure of amorphous lactose from the total scattering pair distribution function", Cryst. Growth Des. 16, 210–220 (2015)
DOI: 10.1021/acs.cgd.5b0110

[9] H. Ryu, K. Wang, M. Opacic, N. Lazarevic, J. B. Warren, Z. V. Popovic, E. S. Bozin, and C. Petrovic, "Sustained phase separation and spin glass in Co-doped $K_xFe_{2-y}Se_2$ single crystals," Phys. Rev. B 92, 174522 (2015) DOI: 10.1103/PhysRevB.92.174522

[10] X. Huang, W. Yang, R. Harder, Y. Sun, M. Lu, Y. S. Chu, I. K. Robinson and H-K Mao, "Deformation twinning of a silver nanocrystal under high pressure", ACS Nano Letters 15, 7644-7649 (2015)

[11] H. Yan, X. Huang, K. Lauer, W. Xu, E. Nazaretski, U. Wagner, C. Rau, M. Yusuf, I. K. Robinson and Y. S. Chu, "Multimodality hard-x-ray imaging of a chromosome with nanoscale spatial resolution", Nature Scientific Reports 6 20112 (2015)

[12] E. S. Božin, A. Huq, Bing Shen, H. Claus, W. K. Kwok, and J. M. Tranquada, "Charge-screening role of c-axis atomic displacements in $YBa_2Cu_3O_{6+x}$ and related superconductors" Phys. Rev. B 93, 054523 (2016) DOI: 10.1103/PhysRevB.93.054523

[13] Zhijun Xu, J. A. Schneeloch, Jinsheng Wen, E. S. Božin, G. E. Granroth, B. L. Winn, M. Feygenson, R. J. Birgeneau, Genda Gu, I. A. Zaliznyak, J. M. Tranquada, and Guangyong Xu, "Thermal evolution of antiferromagnetic correlations and tetrahedral bond angles in superconducting $FeTe_{1-x}Se_x$," Phys. Rev. B 93, 104517 (2016) DOI: 10.1103/PhysRevB.93.104517

[14] M. P. M. Dean, Y. Cao, X. Liu, S. Wall, D. Zhu, R. Mankowsky, V. Thampy, X. M. Chen, J. Vale, D. Casa, Jungho Kim, A. H. Said, P. Juhas, R. Alonso-Mori, M. Glownia, A. Robert, J. Robinson, M. Sikorski, S. Song, M. Kozina, H. Lemke, L. Patthey, S. Owada, T. Katayama, M. Yabashi, Yoshikazu Tanaka, T. Togashi, J. Liu, C. Rayan Serrao, B. J. Kim, L. Huber, C.-L. Chang, D. F. McMorrow, M. Först, and J. P. Hill, "Ultrafast energy and momentum resolved dynamics of magnetic correlations in photo-doped Mott insulator Sr_2IrO_4", Nature Materials 15, 601–605 (2016)

[15] G. Fabbris, M. Hücker, G. D. Gu, J. M. Tranquada and D. Haskel, "Combined single crystal polarized XAFS and XRD at high pressure: probing the interplay between lattice distortions and electronic order at multiple length scales in high Tc cuprates", High Pressure Research, 36, 348-359 (2016) http://dx.doi.org/10.1080/08957959.2016.1198905

[16] S. Calder, J.G. Vale, N.A. Bogdanov, X. Liu, C. Donnerer, M.H. Upton, D. Casa, A.H. Said, M.D. Lumsden, Z. Zhao, J.-Q. Yan, D. Mandrus, S. Nishimoto, J. van den Brink, J.P. Hill, D.F. McMorrow & A.D. Christianson, "Spin-orbit-driven magnetic structure and excitation in the 5d pyrochlore $Cd_2Os_2O_7$", Nature Communications 7 11651 (2016)
DOI: 10.1038/ncomms11651

[17] V. Khanna, R. Mankowsky, M. Petrich, H. Bromberger, S. A. Cavill, E. Mohr-Vorobeva, D. Nicoletti, Y. Laplace, G. D. Gu, J. P. Hill, M. Forst, A. Cavalleri, and S. S. Dhesi, "Restoring interlayer Josephson coupling in $La_{1.885}Ba_{0.115}CuO_4$ by charge transfer melting of stripe order", Physical Review B 93, 224522 (2016)

[18] A. Wang, D. Graf, L. Wu, K. Wang, E. Bozin, Y. Zhu and C. Petrovic, "Interlayer electronic transport in $CaMnBi_2$" Phys. Rev. B 94, 125118 (2016)
DOI: 10.1103/PhysRevB.94.125118

[19] H. Ryu, M. Abeykoon, E. Bozin, Y. Matsumoto, S. Nakatsuji and C. Petrovic, "Multiband electronic transport in α-$Yb_{1-x}Sr_xAlB_4$ (x = 0 0.19) single crystals", J. Phys: Condens. Mat. 28, 425602 (2016) DOI:10.1088/0953-8984/28/42/425602

[20] Hyejin Ryu, Kefeng Wang, M. Opacic, N. Lazarevic, J. B. Warren, Z. V. Popovic, E. S. Bozin and C. Petrovic, "Sustained phase separation and spin glass in Co-doped $K_xFe_{2-y}Se_2$ single crystals", Phys. Rev. B 92, 174522 (2015)

Advancing High Pressure Materials Science at the Advanced Photon Source

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

Pressure profoundly alters matter and materials. The development of ultrahigh-pressure devices, to compress samples to sustained multimegabar pressures together with synchrotron x-ray techniques to probe material properties in situ, has enabled the exploration of novel properties of materials at extreme conditions. This collaborative project focuses on three thrust areas, (1) hydrogen and alkali metals, (2) magnetic and superconducting materials, and (3) enabling x-ray techniques. These activities are based on focused and cohesive collaborations between the HPCAT beamline scientists (led by Shen) and two scientists (Mao and Struzhkin) and their high-pressure research groups at the Carnegie Institution of Washington.

Hydrogen and alkali metals: The hydrogen research has been leading the advancement of modern science and development of new energy applications. Our goals are (1) to conduct fundamental investigations on hydrogen crystal structures and electronic band structures that are directly related to the metallization of elemental hydrogen, and (2) to extend the hydrogen research to address the fundamental problems in high-pressure physics related to alkali metal-insulation transition and phase relations of the first column elements, namely, hydrogen, lithium and sodium. We have studied synchrotron x-ray diffraction of H_2 to the near record of 160 GPa, and Raman and infrared spectroscopy of hydrogen to the near record pressure of 358 GPa. Several hydrogen rich compounds, such as $(Ar(H_2)_2$, $Xe(H_2)_{10}$, have been studied with Raman and x-ray diffraction to multi-megabar pressures. We have discovered unexpected pressure-induced chemistry that water reacts with iron oxide to form iron peroxide FeO_2 and release hydrogen, implying the Earth's deep lower mantle a big hydrogen generator. We will continue to study hydrogen, hydrogen rich systems, and alkali metals at higher pressures, to determine the crystal structure of hydrogen above 200 GPa, and to perform inelastic x-ray scattering experiments on hydrogen, Li, Na above 100 GPa for the evolution of electronic structures at megabars.

Magnetic and superconducting materials: Pressure is not only an important means to decouple several competing interactions for understanding the nature of superconductivity, but also significantly enhances materials superconductivity with higher T_c. We have discovered new polyhydride materials under pressure as precursors of conventional high-T_c superconductors. Superconductivity and charge-density wave competition has been studied in dichalcogenides and cuprates using pressure as a tuning parameter. Colossal magnetoresistance in $LaMnO_3$ has been uncovered by high pressure. We will continue to explore high-T_c superconducting materials with predicted high T_cs. We aim to establish the universality of phonon, magnon, electron, and lattice anomalies in the vicinity of the critical points by comparing to our previous extensive results in Bi-based materials.

Enabling techniques: We have developed several high-pressure synchrotron techniques tailored for the proposed research. These include generating pressures over 400 GPa, high-pressure multigrain crystallography, tight collimation for megabar x-ray spectroscopy, double stage configuration for >120 GPa in a large volume press suitable for weak scattering materials (liquid-H_2,-Li, -Na), high-pressure coherent diffraction imaging, and time-resolved studies with dynamic compression and decompression. We will continue to optimize the anvil design, x-ray micro probes, and optical probes to increase sample size and to further suppress background scattering. The newly developed spectroscopy system will be optimized for measuring band-gap of hydrogen at multi-megabar pressures. Spin and magnetic ordering properties of novel superconducting materials will be probed by x-ray emission, nuclear forward scattering techniques with <5 micron x-ray beams.

Electronic and Magnetic Properties of Quantum Materials

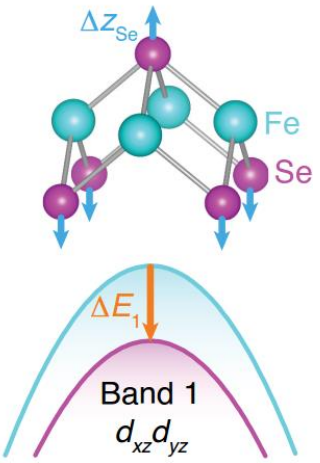
Z.X. Shen, T.P. Devereaux, D.H. Lu, R. G Moore, P. S. Kirchmann, M. Hashimoto, B. Moritz, and J. A Sobota

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 cuprates and Fe-based superconductors) and materials with strong spin-orbit interactions (such as topological insulators and transition metal dichalcogenides). The main activity is synchrotron-based ARPES, with complementary techniques such as laser-based ARPES, time-resolved ARPES, 2PPE ARPES and spin-resolved ARPES being actively pursued.

We continue our vision to address frontier science problems through advanced instrumentation, material synthesis and theory development. Since the last contractor's meeting, we have made major strides in commissioning the new beamline 5-2 at SSRL, the first 11 eV ps laser for spectroscopy experiment, and two MBE systems for oxides and chalcogenides. We are also making good progress in developing an efficient spin spectrometer to match the unique 11 eV laser. In addition, we have also actively engaged in LCLS experiments, as well as contributing to the scientific program development for LCLS-II. This aspect is strongly synergetic with x-ray scattering/spectroscopy FWP led by Tom Devereaux and others in SIMES and beyond.



Combining time-resolved X-ray diffraction and photoemission spectroscopy measures the absolute electron-phonon coupling strength.

The BES program support has enabled two unique aspects. The first is the long term sustained support which permits us to systematically tackle truly challenging scientific problems of scale. Our continued progress in understanding the electronic phase diagram of cuprate and iron based superconductors illustrated this. The second is a synergetic effort that optimally connects among different aspects of the FWP. Our recent experiment on the electron-phonon lock-in is a good example. In this case, high-quality MBE films permitted time-resolved x-ray scattering and time-resolved photoemission experiments with sufficient accuracy to directly measure the deformation potential of an unconventional superconductor. Comparison with theory provides the most compelling experimental evidence for enhanced electron-phonon coupling by electron-electron interaction. All these experimental results are under review now.

We will update the following recent progresses at this meeting: i) updates on synchrotron based experiments on electronic phase diagrams of superconductors, as well as an update on beamline commissioning; ii) energy gap structure and interface role for superconductivity in FeSe/STO, as well as MBE system commissioning and other material platforms; iii) time-resolved photoemission emission experiments, combined effort of time-resolved photoemission experiment and time resolved x-ray scattering at LCLS, as well as the development of spin-resolved photoemission experimental effort; iv) complimentary theoretical efforts.

Recent Progress

I Synchrotron ARPES study of copper and iron based superconductors

Over the past decade, one of our focuses has been in understanding the complex cuprate phase diagram, particularly from the perspective of the energy gaps, as further highlighted in recent papers [1-2]. Our new study revealed that, in deeply overdoped Bi2212 beyond the pseudogap regime, the superconducting gap follows that of a weak coupling superconductor with a simple d-wave BCS gap, suggesting that the mean field picture applies. Paradoxically, such canonical fermionic picture is in contrast with the more unconventional bosonic picture suggested by a recent superfluid measurement. In addition, we observed an intertwined growth of both superconducting and pseudogap with decreasing doping, synchronized with the increase visibility of electron-phonon coupling feature. This suggests that electron-phonon coupling plays an intimate role in the complex relationship between superconductivity and pseudogap. We further propose that composite multi-channel superconductivity may pose as a generic new route to the realization of higher Tc.

1) M. Hashimoto, I. M. Vishik, R.-H. He, T. P. Devereaux, Z.-X. Shen, "Energy Gaps in High-Transition-Temperature Cuprate Superconductors", *Nat Phys* **10**, 483 (2014).
2) M. Hashimoto, E. A. Nowadnick, R.-H. He, I. M. Vishik, B. Moritz, Y. He, K. Tanaka, R. G. Moore, D. Lu, Y. Yoshida, M. Ishikado, T. Sasagawa, K. Fujita, S. Ishida, S. Uchida, H. Eisaki, Z. Hussain, T. P. Devereaux, Z.-X. Shen, "Direct Spectroscopic Evidence for Phase Competition between the Pseudogap and Superconductivity in $Bi_2Sr_2CaCu_2O_{8+\delta}$", *Nat Mater* **14**, 37 (2015).

A distinct feature of iron based superconductor is its multi-orbital nature. This influences the role of electronic correlation, as well as the presence of various electronic phases. Understanding these phases and their transitions in the phase diagram as the role of orbital is the theme of our study here [3-7]. Progress has been made in studying the nematic phase in FeSe compounds, one of the important competing phases in iron based superconductors [6, 7]. Without the complexities induced by co-existing long-range magnetic order, the electronic signature of nematicity has been clearly delineated. It is characterized by a distinctive orbital anisotropy in both d_{xz}/d_{yz} and d_{xy} bands. The origin of such anisotropy holds the key to a microscopic understanding of the nematicity. A related work further reveals a strong underlying correlation

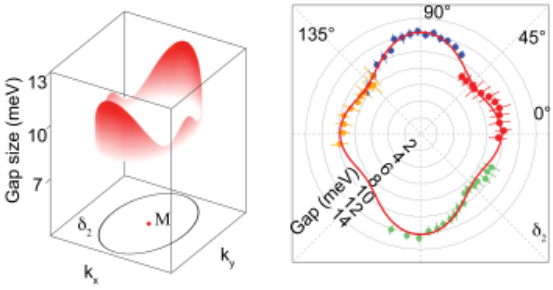
among superconductivity, inter-pocket scattering, and nematic fluctuation in a holistic phase diagram of electron-doped FeSe superconductors [7].

3) M. Yi, Z.-K. Liu, Y. Zhang, R. Yu, J. Zhu, J. J. Lee, R. G. Moore, F. Schmitt, W. Li, S. Riggs, J.-H. Chu, B. Lv, J. Hu, M. Hashimoto, S.-K. Mo, Z. Hussain, Z. Mao, C.-W. Chu, I. R. Fisher, Q. Si, Z.-X. Shen, D. H. Lu
Observation of universal strong orbital-dependent correlation effects in iron chalcogenides
Nature Communications 6, 7777 (2015).
4) M. Yi, M. Wang, A. F. Kemper, S. K. Mo, Z. Hussain, E. Bourret-Courchesne, A. Lanzara, M. Hashimoto, D. H. Lu, Z. X. Shen, R. J. Birgeneau
Bandwidth and Electron Correlation-Tuned Superconductivity in $Rb_{0.8}Fe_2(Se_{1-z}S_z)_2$
Phys. Rev. Lett. 115, 256403 (2015).
5) Z.-K. Liu, M. Yi, Y. Zhang, J. Hu, R. Yu, J. Zhu, R. He, Y. Chen, M. Hashimoto, R. G. Moore, S.-K. Mo, Z. Hussain, Q. Si, Z. Mao, D. H. Lu, Z.-X. Shen
Experimental observation of incoherent-coherent crossover and orbital dependent band renormalization in iron chalcogenide superconductors
Phys. Rev. B 92, 235138 (2015).
6) Y. Zhang, M. Yi, Z.-K. Liu, W. Li, J. J. Lee, R. G. Moore, M. Hashimoto, N. Masamichi, H. Eisaki, S. -K. Mo, Z. Hussain, T. P. Devereaux, Z.-X. Shen, D. H. Lu
Distinctive momentum dependence of the band reconstruction in the nematic state of FeSe thin film
Phys. Rev. B 94, 115153 (2016).
7) Z. R. Ye, C. F. Zhang, H. L. Ning, W. Li, L. Chen, T. Jia, M. Hashimoto, D. H. Lu, Z.-X. Shen, Y. Zhang
Simultaneous emergence of superconductivity, inter-pocket scattering and nematic fluctuation in potassium-coated FeSe superconductor
arXiv:1512.02526.

In strong collaboration with SSRL, we continue our effort to improve the beamline for this program and other users. The new undulator branch line BL5-2, complementary to the existing branch line BL5-4, has been fully commissioned. The performance of the new beamline meets or exceeds the design specification, including a resolving power of 40,000 and a small beam spot size of 32μm (H) × 5.4μm (V) with a wide photon energy range and polarization control. Meanwhile, the new ARPES end station with a 6-axes sample manipulator has also been commissioned. The new beamline and end station was opened to general users in June 2016. We have also designed and constructed the sophisticated sample transfer system to connect the ARPES end station with the MBE thin film growth chambers to enable the in-situ characterization of thin films fabricated by MBE, opening a wide possibility of new science. The first in-situ ARPES measurement was carried out this year.

II MBE-ARPES Study of Quantum Materials in Confined Geometry

Quantum systems in confined geometries continue to be a rich playground for discoveries.



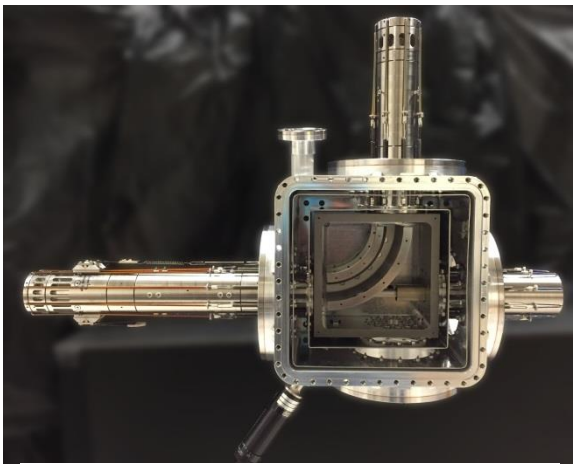
The MBE-ARPES combination permits us to explore a number of interesting topics [8-13]. Our breakthrough discovery of shadow bands in our ARPES spectrum of monolayer FeSe on SrTiO3, indicative of unusual electron-phonon coupling, continues to lead our understanding of the enhancement of superconductivity in this material system. Further in-depth studies have revealed the intertwined roles of the electron orbitals and the cross-interface coupling between the film and the substrate and how it relates to other materials in the iron pnictide family. Careful high resolution ARPES investigations unravel the anisotropy in the superconducting gap, demonstrating orbital dependent pairing and placing strong constraints on the symmetry of the order parameter in monolayer FeSe [9]. Our investigations are developing into a coherent picture where two factors are necessary to enhance superconductivity in this multi-orbital system: charge transfer and electron-phonon coupling. These ingredients are not necessarily linked to FeSe and provide a pathway to develop new superconductors with enhanced properties. We will continue to develop superconducting films of different material systems to learn how to control the electronic structure for maximum Tc enhancement.

8) Y. T. Cui, R. G Moore, A. M. Zhang, Y. Tian, J. J Lee, F. T Schmitt, W. H. Zhang, W. Li, M. Yi, Z. K. Liu, M. Hashimoto, Y. Zhang, D. H. Lu, T. P Devereaux, L. L. Wang, X. C. Ma, Q. M. Zhang, Q. K. Xue, D. H. Lee, and Z. X. Shen, Interface Ferroelectric Transition near the Gap-Opening Temperature in a Single-Unit-Cell FeSe Film Grown on Nb-DopedSrTiO3Substrate. Physical Review Letters 114, 037007 (2015).
9) Y. Zhang, J. J. Lee, R. G. Moore, W. Li, M. Yi, M. Hashimoto, D. H. Lu, T. P. Devereaux, D. H. Lee, and Z. X. Shen, Superconducting Gap Anisotropy in Monolayer FeSe Thin Film. Physical Review Letters 117, 117001 (2016).
10) Y. Zhang, M. Yi, Z. K. Liu, W. Li, J. J. Lee, R. G. Moore, M. Hashimoto, M. Nakajima, H. Eisaki, S. K. Mo, Z. Hussain, T. P. Devereaux, Z. X. Shen, and D. H. Lu, Distinctive orbital anisotropy observed in the nematic state of a FeSe thin film. Physical Review B 94, 115153 (2016)
11) M. Yi, Z. K. Liu, Y. Zhang, R. Yu, J. X. Zhu, J. J. Lee, R. G. Moore, F. T. Schmitt, W. Li, S. C. Riggs, J. H. Chu, B. Lv, J. Hu, M. Hashimoto, S. K. Mo, Z. Hussain, Z. Q. Mao, C. W. Chu, I. R. Fisher, Q. Si, Z. X. Shen, and D. H. Lu, Observation of universal strong orbital-dependent correlation effects in iron chalcogenides. Nature Communications 6, 7777 (2015).
12) S. L. Yang, J. A. Sobota, D. Leuenberger, A. F. Kemper, J. J. Lee, F. T. Schmitt, W. Li, R. G. Moore, P. S. Kirchmann, and Z. X. Shen, Thickness-Dependent Coherent Phonon Frequency in Ultrathin FeSe/SrTiO3 Films. Nano Letters 15, 4150-4154 (2015).
13) W. Li, M. Claassen, Cui-Zu Chang, B. Moritz, T. Jia, C. Zhang, S. Rebec, J. J. Lee, M. Hashimoto, D. H. Lu, R. G. Moore, J. S. Moodera, T. P. Devereaux, and Z. X. Shen, Origin of the low critical observing temperature of the quantum anomalous Hall effect in V-doped (Bi, Sb)2Te3 film, Scientific Reports 6, 32732 (2016).

III Time and/or Spin resolved Photoemission program

We focused our time-resolved studies on the coherent response of bosons in charge density wave systems [14,15] and unconventional Fe-based superconductors [16-18] using both ultrafast ARPES and x-ray diffraction to obtain complete information on the interplay of electronic and

lattice degrees of freedom. We quantify the electron-phonon coupling strength in high quality MBE-grown thin FeSe films by combining x-ray diffraction to track the light-induced coherent lattice motion, while photoemission monitors the related changes of the electronic bands. Extracting oscillatory responses at a single phonon frequency defines a high-precision 'coherent lock-in' measurement of the electron-phonon coupling in the THz regime. Comparison with theory reveals a strong enhancement of the coupling strength in FeSe due to correlation effects. As the electron-phonon coupling impacts superconductivity exponentially, the uncovered enhancement highlights the significance of the cooperative interplay of electron-electron and electron-phonon interactions. In addition, we have investigated the scattering rates in correlated material systems, and clarified the relationship between scattering dynamics and population dynamics [19].



Photograph of the electrostatic lens system of the spin-resolved time-of-flight spectrometer during assembly.

On spin physics, we are developing a scientific program to address the rich physics associated with electron spins. Our earlier work demonstrated that topological states can be optically excited on ultrafast timescales. We have expanded these studies by using circularly polarized light to drive spin-selective excitations. These experiments not only demonstrate a means of spin manipulation via optical control, but also provide a measure of spin lifetimes and depolarization pathways in topological materials. In addition, we collaborated with Prof. Alessandra Lanzara to directly probe the spin-polarization of these transiently populated states [20]. We discovered an unoccupied spin-polarized surface resonance related to the material's topological phase transition, which is undetectable in photoemission measurements without both spin and time resolution.

In parallel, we have made progress building a high-efficiency TOF based spin-resolved photoelectron spectrometer (see figure), taking advantage of the time structure of modern lasers. This spectrometer will be coupled with an 11eV laser source to permit direct measurement of electron spin polarization over a broad range of momentum-space [21]. Its time-of-flight detection scheme is well-suited to integration with pulsed ultrafast light sources, a critical capability for extending our work on spin-dynamical phenomena in spin-textured materials. Based on the success of the 11 eV ps laser, we are making progress on designing and building a femtosecond 11eV laser than can reach a significant fraction of the Brillouin zone in most quantum materials and in Fe-based superconductors specifically. This will also be useful for other material systems.

14) D. Leuenberger, J. A. Sobota, S.-L. Yang, A. F. Kemper, P. Giraldo-Gallo, R. G. Moore, I. R. Fisher, P. S. Kirchmann, T. P. Devereaux, and Z.-X. Shen *Classification of Collective*

Modes in a Charge Density Wave by Momentum-Dependent Modulation of the Electronic Band Structure; Physical Review B **91** (2015) 201106(R)
15) R. G. Moore, W. S. Lee, P. S. Kirchman, 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. Hays, P. Hering, T. Benson, J.-H. Chu, T. P. Devereaux, I. R. Fisher, Z. Hussain, and Z.-X. Shen*Ultrafast resonant soft x-ray diffraction dynamics of the charge density wave in $TbTe_3$*;Phys. Rev. B **93** (2016) 024304
16) S.-L. Yang, J. A. Sobota, D. Leuenberger, A. F. Kemper, J. J. Lee, F. T. Schmitt, W. Li, R. G. Moore, P. S. Kirchmann, and Z.-X. Shen; *Thickness-Dependent Coherent Phonon Frequency in Ultrathin FeSe/$SrTiO_3$ Films*; Nano Lett. **15** (2015) 4150
17) S. Gerber, K. W. Kim, Y. Zhang, D. Zhu, N. Plonka, M. Yi, G. L. Dakovski, D. Leuenberger, P. S. Kirchmann, R.G. Moore, M. Chollet, J.M. Glownia, Y. Feng, J.-S. Lee, A. Mehta, A. F. Kemper, T. Wolf, Y.-D. Chuang, Z. Hussain, C.-C. Kao, B. Moritz, Z.-X. Shen, T.P. Devereaux, and W.-S. Lee; *Direct Characterization of Photoinduced Lattice Dynamics in $BaFe_2As_2$*; Nature Comms. **6** (2015) 7377
18) S. Gerber, S.-L. Yang, D. Zhu, H. Soifer, J. A. Sobota, S.Rebec, J. J. Lee, T. Jia, B. Moritz, C. Jia, A. Gauthier, Y. Li, D. Leuenberger, Y. Zhang, L. Chaix, W. Li, H. Jang, J.-S. Lee, M. Yi, G. L. Dakovski, S. Song, J. M. Glownia, S. Nelson, K. W. Kim, Y.-D. Chuang, Z. Hussain, C.-C. Kao, R. G. Moore, T. P. Devereaux, W.-S. Lee, P. S. Kirchmann, and Z.-X. Shen; *Femtosecond electron-phonon lock-in via photoemission and x-ray free-electron laser*; Science (under review)
19) S.-L. Yang, J. A. Sobota, D. Leuenberger, Y. He, M. Hashimoto, D. H. Lu, H. Eisaki, P. S. Kirchmann, and Z.-X. Shen; *Inequivalence of Single-Particle and Population Lifetimes in a Cuprate Superconductor*; Phys. Rev. Lett. **114** (2015) 247001
20) C. Jozwiak, J.A. Sobota, K. Gotlieb, A.F. Kemper, C.R. Rotundu, R.J. Birgeneau, Z. Hussain, D.-H. Lee, Z.-X. Shen, A. Lanzara; Spin-Polarized Surface Resonances Accompanying Topological Surface State Formation; Nature Communications 7, 13143 (2016)
21) Y. He, I. M. Vishik, M. Yi, S.-L. Yang, Z. Liu, J. J. Lee, S. Chen, S. N. Rebec, D. Leuenberger, A. Zong, C. M. Jefferson, R. G. Moore, P. S. Kirchmann, A. J. Merriam, and Z.-X. Shen; *Invited Article: High resolution angle resolved photoemission with tabletop 11 eV laser*; Rev. Sci. Instrum. **87** (2016) 011301

IV Theory

Theory program of this FWP is closely integrated with the experiments, as reflected in many of the papers above where theoretical model is critical to interpret the experimental data. In addition, there is also the aspect of theory that develops codes and provides insights base on model systems, whose focus falls broadly into two categories: strongly correlated materials investigated through numerical simulations of model Hamiltonians, with a particular emphasis on spectroscopy, and non-equilibrium dynamics in simple models, which may be captured by pump-probe photoemission and x-ray techniques. We have continued in-house development of our own charge-transfer hybridization, full atomic multiplet (CTHFAM) code, which links ab initio materials modeling methods to our small cluster, exact diagonalization (ED) codes. With additional algorithm improvements, including the Paradeisos index mapping algorithm to reduce

memory requirements, the ED codes now can handle model simulations with several billion elements in the effective Hilbert space.

We have continued to refine our state-of-the-art determinant quantum Monte Carlo (DQMC) codes [22-24], significantly improving computational efficiency, for simulating single- and multi-particle response functions in models of correlated materials. Utilizing clusters with rectangular geometries, which inherently break C4 rotational symmetry, we recently have studied formation of a stripe phase in multi-orbital Hubbard models of the cuprate high-temperature superconductors. Stripe phases, or charge and spin density waves (CDW or SDW), appear ubiquitously upon charge carrier doping Mott/charge transfer insulators from both x-ray and neutron scattering experiments. In particular, CDWs appear across a wide doping range in the cuprates, in close proximity to the pseudogap and superconducting phases. Ground state numerical studies using the density matrix renormalization group (DMRG) show the formation of static stripes near 1/8th hole doping in a three-orbital Hubbard model of the cuprates. Limited to high temperatures by the fermion sign problem in DQMC, we have demonstrated the existence of fluctuating spin domains with extremely short correlation lengths and without signatures of charge ordering across a very wide doping range. Additionally, we studied the magnetic excitation spectrum for these models in the vicinity of the antiferromagnetic wave vector to reveal hints of the "hourglass" dispersion – incommensurability of the soft magnetic excitations as a function of doping. These findings cast a new light on the intertwined orders that emerge from the normal state in cuprates and they provide a novel perspective on the nature of the pseudogap and phase diagram. We will continue to refine these simulations, including coupling to vibrational degrees of freedom representing oxygen phonons, to better understand the stability of these fluctuating spin domains. These studies also will benefit from a new collaboration established with T. Maier, Center for Nanophase Materials Science (CNMS), ORNL, to study the charge and spin response of the Hubbard model using DCA++ code base, allowing simulations down to significantly lower temperatures than currently accessible by DQMC.

To make direct spectroscopic comparisons that require materials specificity, we utilize commercially available first principles codes [25-27] or our own CTHFAM. Benchmark CTHFAM simulations currently are underway on transition metal monoxides. Through a collaboration with the group of K. Gaffney, SSRL, the CTHFAM code has been used to study metal center-ligand spin crossover complexes with potential applications in spintronics or data storage. The results help to better characterize the effect of different ligands on magnetic properties in these complexes. In another collaboration with W. Yang, ALS, LBNL, and the group of W. Chueh, Stanford/SIMES, the CTHFAM code is being used to simulate the electronic states and x-ray spectra of transition metal oxide battery materials. These simulations highlight changes in the x-ray spectra which can be linked to structural morphology during the charging cycle due to lithiation/delithiation, with the ultimate goal of guiding materials design for

improved battery performance.

In the area of non-equilibrium dynamics, we have investigated pump-probe dynamics in the single-particle spectra of models with electron-phonon coupling, in particular for s-wave superconductors and using approximations for d-wave superconductors [28-30]. We find strong amplitude mode (Higgs) oscillations in the spectra, self-energies, and anomalous propagators, which are uniform in momentum space and locked to the effective gap maximum as a function of time. The results highlight the possibility of using photoemission to hunt for these oscillations, as has been done in CDW materials. At the same time, we have used our ED codes and Krylov time evolution to investigate the non-equilibrium dynamics in model systems with competing interactions. In a model system tuned near the cross-over transition between Mott and Peierls phases, we highlight the development of an effective momentum dependence in the charge dynamics driven by the interplay between the electronic and vibrational degrees of freedom [31]. Using a similar approach, we will investigate "photoinduced" phase transitions in correlated models, including "photoinduced" superconductivity, beyond effective bandwidth control.

22) Y. F. Kung, C.-C. Chen, Yao Wang, E. W. Huang, E. A. Nowadnick, B. Moritz, R. T. Scalettar, S. Johnston, and T. P. Devereaux, "Characterizing the three-orbital Hubbard model with determinant quantum Monte Carlo," Physical Review B 93, 155166 (2016) (Editors' Suggestion)
23) Y. F. Kung, E. A. Nowadnick, C.J. Jia, S. Johnston, B. Moritz, R. T. Scalettar, and T. P. Devereaux, "Doping evolution of spin and charge excitations in the Hubbard model," Physical Review B 92, 195108 (2015)
24) E. A. Nowadnick, S. Johnston, B. Moritz, and T. P. Devereaux, "Renormalization of spectra by phase competition in the half-filled Hubbard-Holstein model," Physical Review B 91, 165127 (2015)
25) J.F. He, C.F. Zhang, N. J. Ghimire, T. Liang, C.J. Jia, J. Jiang, S.J. Tang, S. Chen, Y. He, S.-K. Mo, C. C. Hwang, M. Hashimoto, D.-H. Lu, B. Moritz, T. P. Devereaux, Y.L. Chen, J. F. Mitchell, and Z.-X. Shen, "Distinct electronic structure for the extreme magnetoresistance in YSb," arXiv:1607.07855 [cond-mat.str-el]
26) X.S. Liu, Y. J. Wang, B. Barbiellini, H. Hafiz, S. Basak, J. Liu, T. Richardson, G.J. Shu, F.C. Chou, T.-C. Weng, D. Nordlund, D. Sokaras, B. Moritz, T. P. Devereaux, R. Qiao, Y.-D. Chuang, A. Bansil, Z. Hussain, and W.L. Yang, "Why LiFePO 4 is a safe battery electrode: Coulomb repulsion induced electron-state reshuffling upon lithiation," Physical Chemistry Chemical Physics 17, 26369-26377 (2015)
27) W. T. Hong, K. A. Stoerzinger, B. Moritz, T. P. Devereaux, W. Yang, and Y. Shao-Horn, "Probing LaMO 3 metal and oxygen partial density of states using x-ray emission, absorption, and photoelectron spectroscopy," Journal of Physical Chemistry C 119, 2063-2072 (2015)
28) B. Nosarzewski, B. Moritz, J. K. Freericks, A. F. Kemper, and T. P. Devereaux, "Amplitude mode oscillations in pump-probe photoemission spectra from a d-wave superconductor," arXiv:1609.04080 [cond-mat.supr-con]
29) A. F. Kemper, M. A. Sentef, B. Moritz, T. P. Devereaux, J. K. Freericks, "Review of the theoretical description of time-resolved angle-resolved photoemission spectroscopy in electron-phonon mediated superconductors," arXiv:1609.00087 [cond-mat.supr-con]

30) A. F. Kemper, M. A. Sentef, B. Moritz, J. K. Freericks, and T. P. Devereaux, “Direct observation of Higgs mode oscillations in the pump-probe photoemission spectra of electron-phonon mediated superconductors,” Physical Review B 92, 224517 (2015)
31) Y. Wang, B. Moritz, C.-C. Chen, C.J. Jia, M. van Veenendaal, and T. P. Devereaux, “Using non-equilibrium dynamics to probe competing orders in a Mott-Peierls system,” Physical Review Letters 116, 086401 (2016)

Nanoscale X-ray Imaging and Dynamics of Electronic and Magnetic Materials

PI: Oleg Shpyrko, University of California San Diego

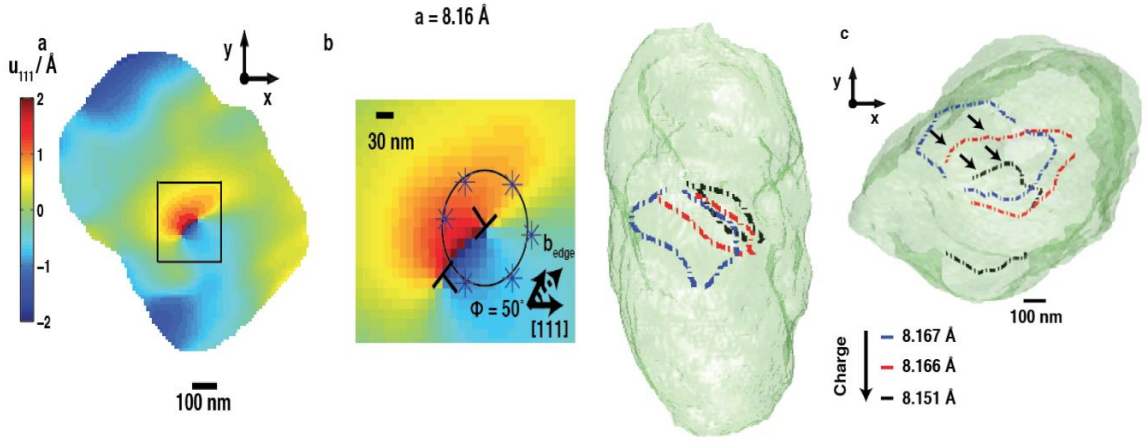
Program Scope

The overarching theme of our research is the development and application of coherent x-ray scattering and imaging methods, which will serve as frontier of modern materials physics research at the major synchrotron facilities.

The common thread among these areas of research is the development and application of coherent x-ray methods to study complex materials, their structure, and dynamics, we pursue the research directions lie at the intersection of materials physics research, energy sciences, condensed matter physics, and materials science.

Recent Progress

Key Highlight: Among major scientific challenges related to energy storage materials is detailed understanding of nanoscale processes involved in ionic diffusion, as well as deterioration of battery electrodes that happens over many cycles. Repeated charge and discharge cycles



Coherent X-ray Diffractive Imaging reconstructions of complex electron density showing the formation of a dislocation pair (a) and (b), as well as motion of dislocation cores upon cycling (c). Adapted from Ulvestad et al, Science 348 (6241), 1344-1347 (2015)

involving intercalation and extraction of ions a can lead to inhomogeneous distribution of strain, nucleation of topological defects and structural phase transformations in the electrode, leading to degradation of battery performance.

We have used coherent x-ray scattering and in particular Coherent X-ray Diffractive Imaging (CXDI) experiments on operando lithium battery devices during charge/discharge. [9,12] The approach of CXDI is a lens less alternative to lens-based techniques – the diffraction pattern

formed by scattering a coherent x-ray beam from a sample is inverted numerically to form an image of the object. By removing the need for the optics, the spatial resolution achievable is no longer limited by the quality of the optical elements, but by the highest spatial frequencies measured in the x-ray diffraction pattern.

The basic principle of these studies is to apply CXDI in Bragg reflection geometry. The technique is extremely sensitive to the periodic arrangement of atoms and slight variations thereof. Applying in-situ CXDI we reveal three-dimensional (3D) displacement field evolution of a single $LiNi_{0.5}Mn_{1.5}O_4$ nanoparticle in a coin cell battery under operando conditions during charge/discharge cycles. We also performed three-dimensional imaging of dislocation dynamics in individual battery cathode nanoparticles under operando conditions using Bragg coherent diffractive imaging. [9] Dislocations are static at room temperature and mobile during charge transport. During the structural phase transformation, the lithium-rich phase nucleates near the dislocation and spreads inhomogeneously. [9]

Additionally, we have performed a number of measurements that investigate strain and defect formation in nanostructures, such as twin domain defects in gold nanocrystals [10], mechanisms of growth of gold nanocrystals [4], imaging of defects in biophotonic crystals [3] and in-situ studies of effects of radiation pressure [1], and avalanching dynamics due to catalytic processes in palladium nanocrystals [5]. We have performed pump-probe studies at XFEL (LCLS, SLAC) that lead to discovery of photoinduced enhancement in CDW amplitude in Chromium [2] (also supported by pump-probe measurements at APS [11]). We have also performed numerical/theoretical calculations and simulations regarding the proposals of using the coherent properties of the beam to achieve the ultimate temporal [7] and spatial [8] resolution at the next generation of light sources, as well as participated in development and applications of tabletop coherent x-ray sources [6].

Future Plans

We plan to continue carrying out CXDI measurements of in-situ or operando processes in energy storage, catalytic, photonic, electronic and other devices and materials. Additionally, we plan to keep exploring the novel non-equilibrium states that can be created by ultrafast optical excitations, at new x-ray facilities such as LCLS.

References/Publications:

1. "Observation of x-ray radiation pressure effects on nanocrystals" J. W. Kim, A. Ulvestad, S. Manna, R. Harder, E. Fohtung, A. Singer, L. Boucheron, E. E. Fullerton and O. G. Shpyrko, J. Appl. Phys. **120**, 163102 (2016)

2. "Photoinduced Enhancement of the Charge Density Wave Amplitude"**,** A. Singer, S. K. K. Patel, R. Kukreja, V. Uhlíř, J. Wingert, S. Festersen, D. Zhu, J. M. Glownia, H. T. Lemke, S. Nelson, M. Kozina, K. Rossnagel, M. Bauer, B. M. Murphy, O. M. Magnussen, E. E. Fullerton, and O. G. Shpyrko, Phys. Rev. Lett. 117, 056401 (2016)

3. “Domain morphology, boundaries, and topological defects in biophotonic gyroid nanostructures of butterfly wing scales”, Andrej Singer, Leandra Boucheron, Sebastian H. Dietze, Katharine E. Jensen, David Vine, Ian McNulty, Eric R. Dufresne, Richard O. Prum, Simon G. J. Mochrie and Oleg G. Shpyrko, Sci. Adv. 2 (6), 1600149 (2016)
4. “Synthesis of single-crystalline anisotropic gold nano-crystals via chemical vapor deposition”, Sohini Manna, Jong Woo Kim, Yukiko Takahashi, Oleg G. Shpyrko and Eric E. Fullerton, J. Appl. Phys. 119, 174301 (2016)
5. “Avalanching strain dynamics during the hydriding phase transformation in individual palladium nanoparticles”, A. Ulvestad, M. J. Welland, S. S. E. Collins, R. Harder, E. Maxey, J. Wingert, A. Singer, S. Hy, P. Mulvaney, P. Zapol & O. G. Shpyrko, Nature Communications 6, 10092 (2015)
6. “Bright circularly polarized soft X-ray high harmonics for X-ray magnetic circular dichroism”, Tingting Fan, Patrik Grychtol, Ronny Knut, Carlos Hernández-García, Daniel D. Hickstein, Dmitriy Zusin, Christian Gentry, Franklin J. Dollar, Christopher A. Mancuso, Craig W. Hogle, Ofer Kfir, Dominik Legut, Karel Carva, Jennifer L. Ellis, Kevin M. Dorney, Cong Chen, Oleg G. Shpyrko, Eric E. Fullerton, Oren Cohen, Peter M. Oppeneer, Dejan B. Milošević, Andreas Becker, Agnieszka A. Jaroń-Becker, Tenio Popmintchev, Margaret M. Murnane, Henry C. Kapteyn, Proc. Natl. Acad. Sci. U S A 112, 14206 (2015)
7. “A new method for studying sub-pulse dynamics at synchrotron sources”, J. Wingert, A. Singer and O. G. Shpyrko J. Synchrotron Rad. 22, 1141, (2015)
8. “Coherent diffractive imaging: towards achieving atomic resolution”, S. H. Dietze and O. G. Shpyrko, J. Synchrotron Rad. 22, 1498 (2015)
9. “Topological defect dynamics in operando battery nanoparticles”, A. Ulvestad, A. Singer, J. N. Clark, H. M. Cho, J. W. Kim, R. Harder, J. Maser, Y. S. Meng and O. G. Shpyrko, Science 348 (6241), 1344-1347 (2015)
10. “3D Imaging of Twin Domain Defects in Gold Nanoparticles”, Andrew P. Ulvestad, Jesse Clark, Ross Harder, Ian K. Robinson and Oleg G. Shpyrko Nano Lett.,15 (6), 4066 (2015)
11. “Condensation of collective charge ordering in Chromium”, A. Singer, M. J. Marsh, S. H. Dietze, V. Uhlíř, Y. Li, D. A. Walko, E. M. Dufresne, G. Srajer, M. P. Cosgriff, P. G. Evans, E. E. Fullerton, and O. G. Shpyrko, Phys. Rev. B 91, 115134 (2015)
12. “In-situ strain evolution during a disconnection event in a battery nanoparticle”, Andrew Ulvestad, Jesse Clark, Andrej Singer, David Vine, Hyung-Man Cho, Ross Harder, Ying Shirley Meng and Oleg Shpyrko, Physical Chemistry Chemical Physics 17, 10551 (2015)

Understanding Mesoscale Nonequilibrium Heterogeneity by Multimodal X-ray Imaging

Haidan Wen, Advanced Photon Source, Argonne National Laboratory

Program Scope

Heterogeneities in correlated matter are by nature comprised of separate yet connected regions with distinct properties, usually in the length scales of tens of nm to μm. This project is targeted at understanding and controlling mesoscale heterogeneity and bridge the knowledge gap from atomistic to macroscopic length scales as a material evolves in time. The approach to achieve this goal is to develop an in-situ, multimodal, spatiotemporally resolved imaging system at the Advanced Photon Source (APS) using suitable ultrafast terahertz, optical and x-ray radiation (Fig. 1). Snapshots of localized material properties with distinct structural, electronic, and optical characteristics will be captured simultaneously and correlated unambiguously. Quantitative correlation of heterogeneous properties in both space and time will provide crucial information with which to understand and subsequently harness the mesoscale properties of materials with new and enhanced functionalities. The developed methodology and instrumentation will be generalizable for use at other large-scale synchrotron x-ray facilities and free electron lasers.

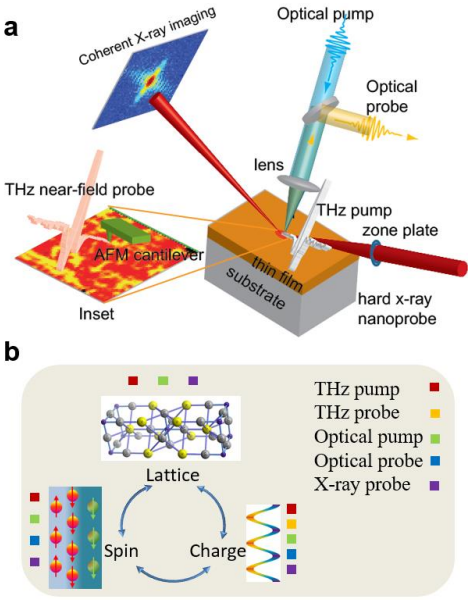


Figure 1 (a) Multimodal, spatiotemporally resolved imaging using THz, optical and x-ray pump-probe techniques. (b) The interaction of multiple degrees of freedom in correlated materials. The colored squares represent techniques that will be employed for studying a particular degree of freedom.

Recent Progress

This project is funded by DOE Early Career Research Program (FWP:52038) starting on Aug, 15th, 2016. The first-stage design of the proposed instrument is completed. The integration of a scanning near-field optical microscope (SNOM) on a time-resolved hard x-ray nanodiffraction beamline is achieved by modifying a commercial available SNOM that allows the spatial clearance for the incident and diffracted x-ray beam. The customized SNOM is in the process of manufacturing and is scheduled to be delivered by the end of 2016. A partner user proposal has been submitted to the APS for requesting the beamtime.

Toward the proposed *in-situ* multimodal imaging platform, we have recently developed time-resolved hard x-ray diffraction microscopy (TXDM) technique and applied it to various material science problems.

In the first example, we directly visualize the structural phase progression in a VO_2 film upon photoexcitation (Fig.2a)[1]. The sub-μm spatial and sub-ns time resolution allows us to reveal the structural phase progression during the photo-induced phase transition. The inhomogeneous structural phase transformation that develops from nucleation sites and subsequent progresses laterally can be understood by a displacive lattice motion from the unstable high-energy monoclinic phase into a metastable rutile phase. The visualization of phase transformation with

time-resolved x-ray imaging technique enables the study of nanoscale structural phase transition and separation in correlated materials in the time domain.

In the second example, we demonstrate that the THz field enhanced by metasurfaces can create a highly inhomogeneous strain profile, directly characterized by TXDM technique[2]. Meta-surface-enhanced terahertz fields provide an important tool to control the material properties not only on ultrafast time scales but also on nanometer length scales. The transient lattice strain and its evolution are imaged in a $BaTiO_3$ film upon localized THz field excitation (Fig.2b). The maximum of the strain is located close to the edge of the gold meta-surface where the THz field is maximally enhanced. By comparing the evolution of the strain profile with molecular dynamics simulation (data not shown), we found that an in-plane ballistic phonon transport occurs within 100 ps on the length scale of 200 nm upon THz excitation, while the out-of-plane heat transport dominates the strain recovery on longer time scales. The ultrafast and localized THz field excitation controllable by meta-surface design open up opportunities for transient spatial engineering of nanoscale structural states for new functionalities.

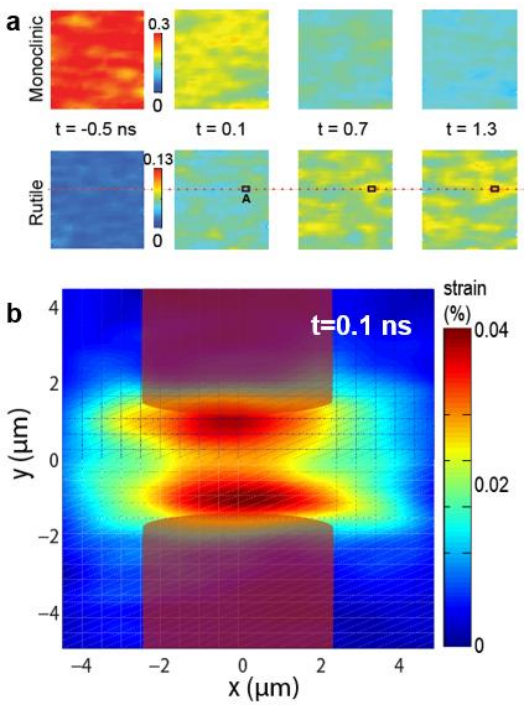


Figure 2 Time-resolved x-ray diffraction imaging: (a) 2D maps of diffraction intensity from monoclinic and rutile phases in photoexcited VO_2 thin films at various delay. (b) 2D map of strain profile in a 90 nm $BaTiO_3$ film on $NdSrO_3$ substrate at 100 ps after THz field excitation.

Future Plans

The first phase (2017-2018) of the ECRP project is to enable time-resolved *in-situ* SNOM and x-ray diffraction microscopy measurement at room temperature. In 2017, leveraging the support from the APS, we plan to redesign the endstation and x-ray optics at the 7ID-C beamline for enhanced mechanical stability and x-ray beam quality. Meanwhile, the installation and testing of the customized SNOM will be performed. The integration of SNOM on the 7ID-C beamline is planned in the summer of 2017. Initial static characterization of ferroelectric domains and phase separation in strained VO_2 films will be performed in the fall of 2017. In 2018, we will develop time-resolved SNOM and integrate the time-resolved optical and x-ray probe capability on the beamline. Initial dynamical characterization of conducting domain walls in ferroelectric thin films will be performed.

References:

1. Zhu, Y. *et al.* Mesoscopic structural phase progression in photo-excited VO_2 revealed by time-resolved x-ray diffraction microscopy. *Scientific Reports* **6,** 21999 (2016).
2. Zhu, Y. *et al.* Imaging metasurface-enhanced terahertz-ferroelectric interaction by time-resolved hard x-ray diffraction microscopy. *in prep.*

Ultrafast Control of Emerging Electronic Phenomena in 2D Quantum Materials

Principle Investigator: Prof. Xiaodong Xu, Department of Physics, Department of Material Science and Engineering, University of Washington, Seattle, WA 98195

Co-PI: Prof. Di Xiao, Department of Physics, Carnegie Mellon University, Pittsburg, PA
Dr. Haidan Wen, Physicist, Argonne National Lab, Chicago, IL
Prof. Nuh Gedik, Department of Physics, MIT

Program Scope

This team project is a collaboration between PI Xiaodong Xu at U. Washington, Di Xiao at Carnegie Mellon, Nuh Gedik at MIT, and Haidan Wen at Argonne National Lab. The objective of this proposal is to combine both theoretical and experimental efforts to investigate emerging ultrafast phenomena in novel two-dimensional (2D) quantum materials - monolayer transition metal dichalcogenides (TMDs) and their heterostructures. We employ a wide range of state-of-the-art ultrafast technologies involving terahertz, optical, x-ray, and electron pulses to investigate 2D quantum materials. Advanced large-scale x-ray user facilities such as the Advanced Photon Source (APS) and the Linac Coherent Light Source (LCLS) play crucial roles of advancing this research program.

Recent Progress

1. *Optical Study of 2D valley excitons dynamics and their strong coupling with phonons*

(a) In solid state systems, spontaneous anti-Stokes emission describes the scattering of low-energy incident photons to higher energy by absorbing energy quanta of lattice oscillations (optical phonons), while Stokes emission refers to the conjugate process of adding phonons to the lattice. The efficiency of these processes can be enhanced by a large optical transition strength in the light-matter interaction, or by realizing doubly resonant conditions, meaning both incident and emitted photons are in resonance with electronic transitions whose energy spacing matches an optical phonon.

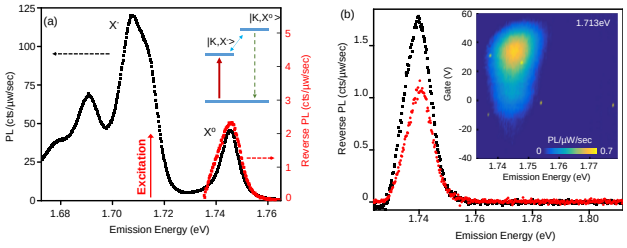


Figure 1. Excitonic luminescence up conversion via doubly resonant anti-Stokes. (**a**) Superposition of PL spectrum for 1.96 eV excitation (black) and 1.715 eV excitation (red), indicated by the red arrow. Inset: doubly resonant up-conversion scheme. (**b**) Polarization resolved reverse PL spectra with excitation 30 meV below neutral exciton with circularly polarized excitation. Inset: Up conversion PL intensity plot as a function of gate and emission energy. Excitation: 1.713 eV, 30 meV below neutral exciton.

Here, the Xu group found a unique excitonic doubly resonant anti-Stokes process in monolayers, which has not be observed in any solid state system[1]. In particular in monolayer WSe_2, we found that the

negatively charged exciton (X-) has a binding energy of 30 meV matching the A_1` optical phonon, i.e. X- plus an $A_1$` phonon is nearly energy degenerate with the neutral exciton (Xo), resulting in a unique excitonic doubly resonant condition (Inset, Fig. 1a). Take advantage of this unique doubly-resonant condition in monolayer WSe_2, we observed spontaneous anti-Stokes scattering from the negatively charged exciton to neutral exciton. The black data of Fig. 1a shows the standard PL spectrum near intrinsic doping levels with 1.96 eV excitation. The spectrum consists of Xo and X- peaks. Remarkably, when exciting 30 meV below the Xo resonance, nearly resonant with X-, we find significant exciton emission (Fig. 1a, red data, hereafter we name it as reverse PL). The reverse PL possesses the same line shape and peak energy as Xo obtained in standard PL. The up-conversion is also valley selective and gate tunable (Fig. 1b).

(b) The Xu group investigate the role of exciton-phonon interaction in exciton dynamics using the model system of monolayer[2] $MoSe_2$. Performing photoluminescence excitation (PLE) spectroscopy, we observe that the neutral exciton PL intensity (Fig. 2a), as well as its linewidth, oscillates as a function of excitation energy with a period matching that of the longitudinal acoustic phonon at the M point, LA(M). Nested within the oscillations are fine structures, with linewidths one order of magnitude smaller than that of ordinary PL, originating from resonant Raman scattering. Using time-resolved PLE, shorter rise-times are measured for excitation resonant with multiple LA(M) phonon modes, a result of faster exciton formation via emission of a small number of these high energy phonons (Fig. 2b). Conversely, fast decay of bright exciton states is observed for off resonance excitation (Fig. 2c). This is attributed to the elevated lattice temperature arising from the emission of long wavelength (small *k*-vector) acoustic phonons in the exciton formation process, which facilitates the subsequent exciton recombination process. Our results clearly show that phonons near the LA(M) mode play an important role in electron-phonon coupling and hot-carrier cooling in monolayer $MoSe_2$, suggesting the involvement of intermediate indirect excitonic states (i.e. Q-valley electrons) in the formation of K-valley excitons. The prevailing involvement of acoustic phonons, rather than of optical phonons, also implies that the deformation potential coupling dominates over Fröhlich coupling, although the converse is normally expected.

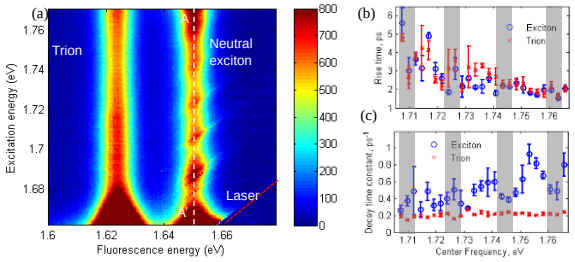


Figure 2 | Electron-phonon coupling on the exciton dynamics (**a**) PLE spectra of monolayer $MoSe_2$ taken at 5 K. (**b**) Excitation frequency-dependent rise-times of trion (crosses) and neutral exciton (circles) extracted from a series of streak camera measurements. Shaded regions indicate phonon resonances obtained from (**a**). (**b**) Excitation frequency-dependent decay rate, γ, of trion (crosses) and neutral exciton (circles).

(c) Bloch-Siegert shift in monolayer WS_2: Coherent light-matter interaction can be used to manipulate the energy levels of atoms, molecules and solids. When light with frequency ω is detuned away from a resonance ω_0, repulsion between the photon-dressed (Floquet) states can lead to a shift of energy resonance. The dominant effect is the optical Stark shift ($\propto 1/(\omega_0 - \omega)$,

Fig 3a), but there is an additional contribution from the so-called Bloch-Siegert shift ($\propto 1/(\omega_0 + \omega)$, Fig 3b). Bloch-Siegert shift is an important and delicate marvel of quantum electrodynamics (QED). Due to its delicate nature, the Bloch-Siegert shift has so far never been observed in solids. What makes it more challenging to observe is that it has always been inseparable from the optical Stark effect.

Here, we discover an exceptionally large Bloch-Siegert shift in monolayer WS_2. Our discovery presents three groundbreaking highlights. First, this is the *first observation* of Bloch-Siegert shift in any extensive condensed matter systems. Second, the shift (10 meV) is *five orders of magnitude larger* than those found in atomic systems. This remarkably large shift arises from strong interaction between light and excitons in monolayer WS_2. Third, for the first time, the Bloch-Siegert shift *can be separated entirely* from the optical Stark shift. Since these two effects are time-reversed partners of each other, they can in principle be separated by breaking time-reversal symmetry. We achieve this by utilizing the valley selection rules in monolayer WS_2, a unique feature in solids that is not present in atoms. That is, by using intense circularly polarized light in the infrared, we can control the Bloch-Siegert shift to emerge only at one valley and the optical Stark shift at the other valley.

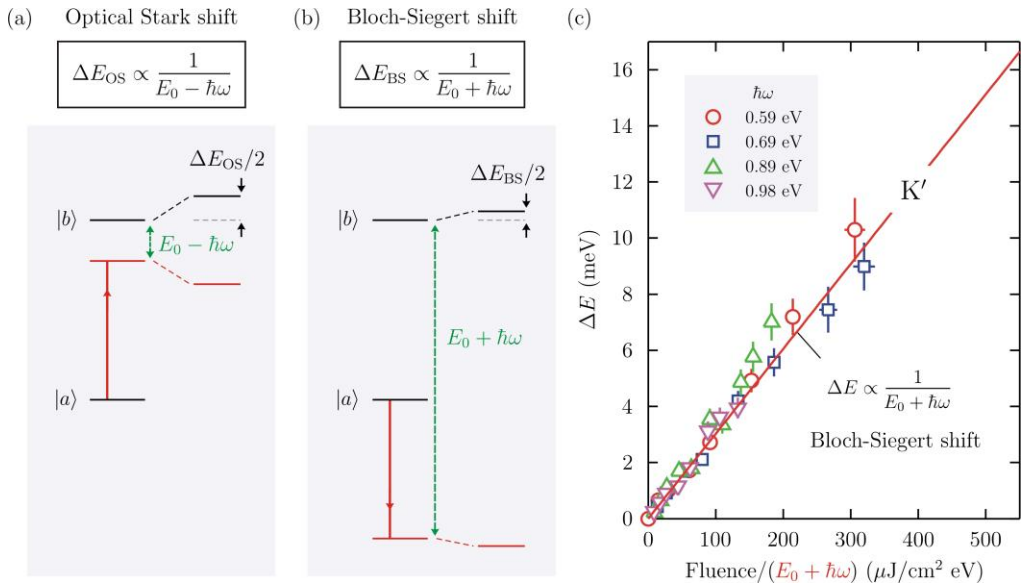


Figure 3. Observation of Bloch-Siegert shift in monolayer WS_2. (a) Energy diagram for optical Stark shift, inversely proportional to the energy separation $(E_0 - \hbar\omega)$ between state $|b\rangle$ (black) and Floquet state of $|a\rangle$ (red). **(b)** Energy diagram for Bloch-Siegert shift, inversely proportional to the energy separation $(E_0 + \hbar\omega)$ between state $|b\rangle$ (black) and the *reversed* Floquet state of $|a\rangle$ (red). **(c)** Fluence and detuning dependences of the Bloch-Siegert shift at K' valley, induced using cross-circularly polarized pump pulses.

(d) The low-energy charge carriers in 2D TMDs behave like massive Dirac fermions with nonzero Berry phase. This electron Berry phase can propagate to composite particles such as excitons and trions, which opens the door to engineering topological photonic states. The Xiao group theoretically discovered a fine energy splitting of 2D p-exciton state resulted from Berry phase effect, a unique property of high angular momentum excitons in 2D quantum materials[3].

Specifically, this splitting is determined by the Berry curvature flux through the ***k***-space area spanned by the relative motion of the electron-hole pair in the exciton wave function. This result reveals the importance of the Berry phase in exciton physics and calls for a thorough investigation of its effect on interacting phenomena.

(e) THz spin dynamics in antiferromagnets: The spin dynamics in typical antiferromagnets fall into the terahertz range, and therefore could be potentially used to generate terahertz signals. The Xiao group considered the current-induced dynamics of insulating antiferromagnets in a spin Hall geometry (Fig. 4). Sufficiently large in-plane currents perpendicular to the Néel order trigger spontaneous oscillations at frequencies between the acoustic and the optical eigenmodes[4]. The direction of the driving current determines the chirality of the excitation. When the current exceeds a threshold, the combined effect of spin pumping and current-induced torques introduces a dynamic feedback that sustains steady-state oscillations with amplitudes controllable via the applied current. This findings open a route towards terahertz antiferromagnetic spin-torque oscillators. The experimental realization and characterization of the spin-torque oscillator is planned in Wen group.

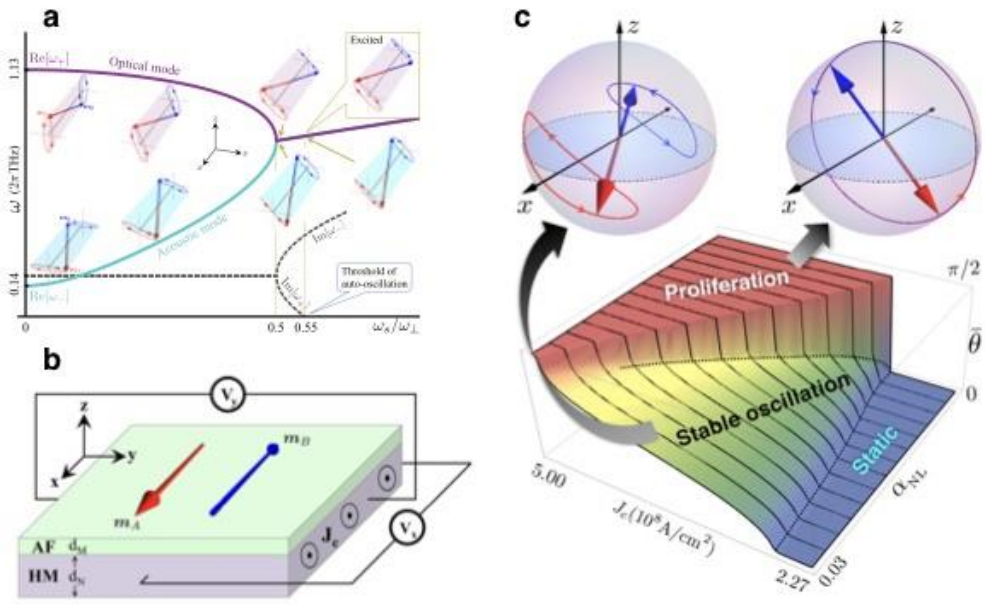


Figure 4 Terahertz antiferromagnetic spin-Hall nano-oscillator. (**a**) Evolution of the eigenfrequencies and th eigenmodes of an antiferromagnets with an increasing spin-transfer torque. (**b**) An insulating antiferromagnets/heavy metal heterostructure (**c**) Phase diagram of a spin-Hall nano-oscillator as a function of the applied current density and the feedback strength.

2. *Investigation of structural and electronic correlation using ultrafast x-ray and ultrafast electron diffraction techniques*

We have achieved significant advances of the structural studies of TMDs on three forefronts. (a) Investigation of electronic and structural correlation of TMD heterostructures using newly developed in-situ photoluminescence (PL) and full-field x-ray diffraction microscopy technique

by our team at the Advanced Photon Source; (b) Systematic studies of ultrafast structural dynamics of TMDs from bulk to monolayers by ultrafast x-ray diffraction and spectroscopy using LCLS and APS; (c) investigation of TMDs by ultrafast electron diffraction techniques.

(a) *In-situ* photoluminescence (PL) and full-field x-ray diffraction microscopy at the APS. In order to understand the interplay of lattice structure and electronic properties of TMD heterostructures, Wen and Xu directly measured the lattice structure and the corresponding PL spectra with a sub-micrometer spatial resolution, revealing a strong correlation of PL intensity and lattice parameters. Although various theoretical predictions was made, no systematic experiemtal studies yet performed. The spatially resolved lattice spacing of TMD heterostructures are quantitatively measured by the full-field x-ray diffraction microscopy, while the electronic properties are characterized by the *in-situ* photoluminescence microscopic probe capability built by Xu group at the APS, as recently developed by under the support of this grant. The localized buried structural configuration along the out-of-plane in TMD heterostructures are revealed for the first time. Correlating the structural variation with the electronic properties of the film shown as the PL intensity and frequency variation, we found that the larger the interlayer spacing of a bilayer heterostructure yields a blue shift of the PL peak from monolayer exciton and weaker PL intensity from the bilayer exciton. The quantitative analysis allows a direct comparison between the theory and experiments. The in-situ optical and x-ray imaging capability opens opportunity to monitor interlayer spacing of heterostructures with in-situ applied stress or electric field. This technique can be further developed by introducing an optical excitation, enabling ultrafast x-ray diffraction studies with real-space imaging capability.

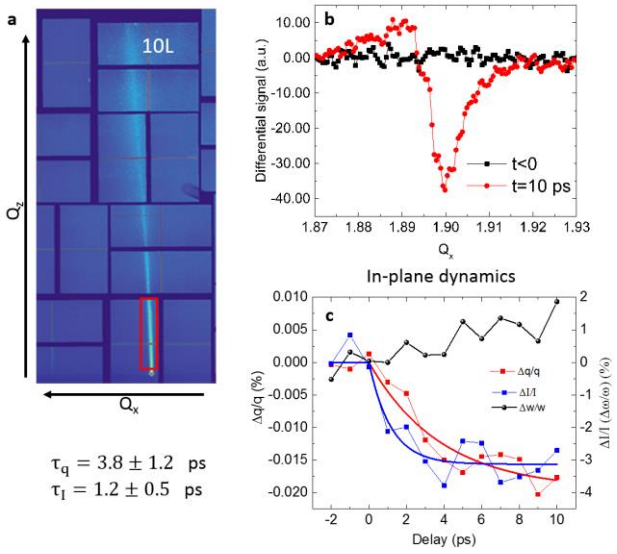


Figure 5 Ultrafast x-ray diffraction measurements of a monolayer WSe_2 at the LCLS. (**a**) X-ray off-specular diffraction of (10L) rod of a monolayer WSe_2 . The red box indicates the region of interests for extracting plot in b and c. (**b**) The differential intensity as projected to the Q_x-axis in the red box in a) shows a diffraction peak position shift and the reduction of diffraction intensity at t=10 ps, in comparison of the differential intensity of the ground state before optical excitation (t<0). (**c**) The extracted change of peak position, width and diffraction intensity of 10L rode as a function of time. The left shows the fitting results of the rise times associated with the changes in the diffraction position and intensity.

(b) Ultrafast x-ray diffraction measurements at LCLS. Our team led by Wen has performed a successful ultrafast optical pump and x-ray probe experiment at the XPP hutch of the LCLS. A series TMD samples with different thickness down to the monolayer limit have been systematically studied, which is only made possible by the intense and ultrafast x-ray pulses at the LCLS. In

monolayer WSe_2, we found that the in-plane expansive strain develops in 3.8 ps, significantly faster than the expected in-plane strain wave propagation (Fig. 5). This result indicates a short range structural roughness or rippling that effectively confines the mechanical deformation. On-going analysis of time-dependent crystal truncation rods may reveal ultrafast structural dynamics along the out-of-plane direction that is challenging to be obtained by other means. In exfoliated bulk WSe2 layers, we observed ultrafast structural factor modulation that arises within 1 ps upon optical excitation as a result of reduction of W-Se bond length in the unit cell, in agreement with the ultrafast x-ray absorption spectroscopy measurement at the APS. A compressive out-of-plane strain develops as a result from ultrafast photodoping that modifies van der Waals interaction in multilayer TMDs, in contrast to an expansion as expected from heating.

(c) Ultrafast electron diffraction experiment. In addition to X-ray studies, we have just started the direct measurement of structural dynamics of monolayer TMDs by using Ultrafast Electron Diffraction (UED) led by Prof. Gedik. Electrons scatter about a million times more strongly than X-rays, which will enable the measurement of diffraction pattern of monolayer of TMDs. We have obtained the static electron diffraction image of exfoliated WSe2, prepared in PI Xu's group. Sharp diffraction peaks are observed, indicating that the sample probed by the electron pulse is mostly single-domain.

Future Plans

We will continue the investigation of spin and valley dynamics, and the role of phonons in 2D semiconductors and heterostructures.

(a) The Xu group will investigate the interfacial phonon coupling at van der Waals interface, while the Nuh group will probe the coupling dynamics by non-degenerate ultrafast pump-probe spectroscopy.

(b) The Wen and Xu group plan to investigate ultrafast spin dynamics across 2D heterostructures interfaces including ferromagnetic-metal, antiferromagnetic-metal and antiferromagnetic-TMD interfaces, with theoretical investigations by the Xiao group. Preliminary data from Wen group has shown that the THz emission spectroscopy, as the THz radiation is generated when the spin current cross the ferromagnetic-metal interface, is an effective probe of ultrafast spin dynamics. Based on the theoretical investigation by Xiao group, the initial study will be concentrated on the experimental demonstration of ferromagnetic spin-Hall oscillator and the corresponding dynamics.

(c) Gedik group will study intervalley scattering using time and angle resolved photoemission spectroscopy. We have demonstrated 30 meV energy resolution using high-harmonic generation based light source. We will use this system to directly visualize intervalley scattering dynamics in various sample structures developed in the Xu group.

References

1. Excitonic Luminescence Up-Conversion in a 2D Semiconductor, A. M. Jones, Hongyi Yu, John R. Schaibley, Jiaqiang Yan, David G. Mandrus, Takashi Taniguchi, Kenji Watanabe, Hanan Dery, Wang Yao, Xiaodong Xu, ***Nature Physics***, 12, 323–327 (2016).
2. Phonon-assisted oscillatory exciton dynamics in monolayer $MoSe_2$, Colin M. Chow, Hongyi Yu, Aaron M. Jones, John R. Schaibley, Michael Koehler, David G. Mandrus, R. Merlin, Wang Yao, Xiaodong Xu, submitted (2016).
3. J. Zhou, W.-Y. Shan, W. Yao, and D. Xiao, "Berry phase modification to the energy spectrum of excitons", ***Phys. Rev. Lett.*** 115, 166803 (2015).
4. R. Cheng, D. Xiao, and A. Brataas, "Terahertz Antiferromagnetic Spin Hall Nano-Oscillator", ***Phys. Rev. Lett.*** 116, 207603 (2016).

Publications

1. John R. Schaibley, Pasqual Rivera, Hongyi Yu, Kyle L. Seyler, Jiaqiang Yan, David G. Mandrus, Takashi Taniguchi, Kenji Watanabe, Wang Yao, and Xiaodong Xu, Directional Interlayer Spin-Valley Transfer in 2D Heterostructures, ***Nature Communications*** in press (2016).
2. Qingjun Tong, Hongyi Yu, Qizhong Zhu, Yong Wang, Xiaodong Xu, Wang Yao, Topological mosaic in Moiré superlattices of van der Waals heterobilayers, ***Nature Physics*** in press (2016).
3. Andreas V. Stier, Nathan P. Wilson, Genevieve Clark, Xiaodong Xu, and Scott A. Crooker, Probing the Influence of Dielectric Environment on Excitons in Monolayer WSe2: Insight from High Magnetic Fields, ***Nano Letters*** DOI: 10.1021/acs.nanolett.6b03276, (2016).
4. John R. Schaibley, Hongyi Yu, Genevieve Clark, Pasqual Rivera, Jason S. Ross, Kyle L. Seyler, Wang Yao & Xiaodong Xu, Valleytronics in 2D materials, ***Nature Reviews Materials*** 1, Article number: 16055 (2016).
5. Zhe Fei, M. Scott, D. J. Gosztola, J. J. Foley, J. Yan, D. G. Mandrus, H. Wen, P. Zhou, D. W. Zhang, Y. Sun, J. R. Guest, S. K. Gray, W. Bao, G. P. Wiederrecht, X. Xu, Nano-optical imaging of exciton polaritons inside WSe2 waveguides, ***Phys. Rev. B*** (2016);
6. Fucai Liu, Lu You, Kyle L. Seyler, Xiaobao Li, Peng Yu, Junhao Lin, Xuewen Wang, Jiadong Zhou, Hong Wang, Haiyong He, Sokrates T. Pantelides, Wu Zhou, Pradeep Sharma, Xiaodong Xu, Pulickel M. Ajayan, Junling Wang, Zheng Liu., Room-temperature ferroelectricity in CuInP2S6 ultrathin flakes, ***Nature Communications*** Article number: 12357 doi:10.1038/ncomms12357 (2016).
7. Evolution of the Valley Position in Bulk Transition-Metal Chalcogenides and their Mono-Layer Limit, Hongtao Yuan, Zhongkai Liu, Gang Xu, Bo Zhou, Sanfeng Wu, Dumitru Dumcenco, Kai Yan, Yi Zhang, Sung-Kwan Mo, Pavel Dudin, Victor Kandyba, Mikhail Yablonskikh, Alexei Barinov, Zhi-Xun Shen, Shoucheng Zhang,Ying-Sheng Huang, Xiaodong Xu, Zahid Hussain, Harold Y. Hwang, Yi Cui, and Yulin Chen, ***Nano Letters*** DOI: 10.1021/acs.nanolett.5b05107 (2016).

8. Akshay Singh, Galan Moody, Kha Tran, Marie Scott, V. Overbeck, G. Berghäuser, John Schaibley, Edward J. Seifert, Dennis Pleskot, N. M. Gabor, J. Yan, David G. Mandrus, Marten Richter, Ermin Malic, Xiaodong Xu, Xiaoqin Li, "Trion Formation Dynamics in Monolayer Transition Metal Dichalcogenides", ***Phys. Rev. B*** 93,041401(R) (2016).
9. Excitonic Luminescence Up-Conversion in a 2D Semiconductor, A. M. Jones, Hongyi Yu, John R. Schaibley, Jiaqiang Yan, David G. Mandrus, Takashi Taniguchi, Kenji Watanabe, Hanan Dery, Wang Yao, Xiaodong Xu, ***Nature Physics***, 12, 323–327 (2016).
10. Valley-Polarized Exciton Dynamics in a 2D Semicondcutor Heterostructure, Pasqual Rivera, Kyle Seyler, Hongyi Yu, John Schaibley, Jiaqiang Yan, D. G. Mandrus, Wang Yao, Xiaodong Xu, ***Science*** 351,688-691 (2016).
11. R. Cheng, S. Okamoto, and D. Xiao, "Spin Nernst effect of magnons in collinear antiferromagnets", **Phys. Rev. Lett.** (in press)
12. T. Suzuki, R. Chisnell, A. Devarakonda, Y.T. Liu, W. Feng, D. Xiao, J.W. Lynn, and J.G.Checkelsky, "Large anomalous Hall effect in a half-Heusler antiferromagnet", **Nature Phys.** (2016) (advanced online publication).
13. R. Cheng, J.-G. Zhu, and D. Xiao, "Dynamic feedback in ferromagnet/spin-Hall heterostructures", **Phys. Rev. Lett.** 117, 097202 (2016).
14. R. Cheng, D. Xiao, and A. Brataas, "Terahertz Antiferromagnetic Spin Hall Nano-Oscillator", ***Phys. Rev. Lett.*** 116, 207603 (2016).
15. R. Cheng, M. W. Daniels, J.-G. Zhu, and D. Xiao, "Antiferromagnetic Spin Wave Field-Effect Transistor", ***Sci. Rep.*** 6, 24223 (2016).
16. J. Zhou, W.-Y. Shan, W. Yao, and D. Xiao, "Berry phase modification to the energy spectrum of excitons", ***Phys. Rev. Lett.*** 115, 166803 (2015).
17. M. Sui, G. Chen, L. Ma, W.-Y. Shan, D. Tian, K. Watanabe, T. Taniguchi, X. Jin, W. Yao, D. Xiao, Y. Zhang, "Gate-tunable topological valley transport in bilayer graphene" **Nature Phys.** 11, 1027 (2015).
18. Galan Moody, Chandriker Kavir Dass, Kai Hao, Chang-Hsiao Chen, Lain-Jong Li, Akshay Singh, Kha Tran, Genevieve Clark, Xiaodong Xu, Gunnar Bergauser, Ermin Malic, Andreas Knorr, Xiaoqin Li, "Intrinsic Exciton Linewidth in Monolayer Transition Metal Dichalcogenides", ***Nature Communications*** 6:8315 | DOI: 10.1038/ncomms9315 (2015).
19. Xiaomu Wang, Mitch Jones, Kyle Seyler, Vy Tran, Yichen Jia, Hua Zhao, Han Wang, Li Yang, Xiaodong Xu, and Fengnian Xia, "Highly Anisotropic and Robust Excitons in Monolayer Black Phosphorus", ***Nature Nanotechnology*** doi:10.1038/nnano.2015.71 (2015).
20. Kyle L. Seyler, John R. Schaibley, Pu Gong, Pasqual Rivera, Sanfeng Wu, Aaron Mitchell Jones, Jiaqiang Yan, David G. Mandrus,Wang Yao, Xiaodong Xu, "Valley Selective Monolayer Second-Harmonic Generation Transistor", ***Nature Nanotechnology*** doi|10.1038/nnano.2015.73 (2015).
21. John R. Schaibley, Todd Karin, Hongyi Yu, Jason S. Ross, Pasqual Rivera, Aaron M. Jones, Marie Scott, Jiaqiang Yan, D. G. Mandrus, Wang Yao, Kai-Mei Fu, Xiaodong Xu,

"Population Pulsation Resonances of Excitons in Monolayer MoSe2 With sub 1 μeV Linewidths", ***Physical Review Letters*** 114, 137402 (2015).

22. R. Cheng, M. W. Daniels, J. Zhu, and D. Xiao, “Ultrafast switching of antiferromagnets via spin-transfer torque”, ***Phys. Rev. B*** 91, 064423 (2015).
23. W.-Y. Shan, J. Zhou, and D. Xiao, “Optical generation and detection of pure valley current in monolayer transition-metal dichalcogenides”, ***Phys. Rev. B*** 91, 035402 (2015).
24. F. Xia, H. Wang, D. Xiao, M. Dubey, and A. Ramasubramaniam, “Two-dimensional material nanophotonics”, ***Nature Photon.*** 8, 988 (2014).
25. Pasqual Rivera, John R. Schaibley, Aaron M. Jones, Jason S. Ross, Sanfeng Wu, Grant Aivazian, Philip Klement, Nirmal J. Ghimire, Jiaqiang Yan, D. G. Mandrus, Wang Yao, Xiaodong Xu, "Observation of Long-Lived Interlayer Excitons in Monolayer MoSe2-WSe2 Heterostructures", ***Nature Communication*** 6, 7472 (2015).
26. Grant Aivazian, Zhirui Gong, Aaron M. Jones, Rui-Lin Chu, J. Yan, D. G. Mandrus, Chuanwei Zhang, David Cobden, Wang Yao, Xiaodong Xu, "Magnetic Control of Valley Pseudospin in Monolayer WSe2", ***Nature Physics*** 11, 148 (2015).

Author Index

Participant List

Name	Organization	Email
Abbamonte, Peter	University of Illinois, Urbana-Champaign	abbamont@illinois.edu
Averitt, Richard	University of California, San Diego	raveritt@ucsd.edu
Basov, Dmitri	Columbia University	db3056@columbia.edu
Billinge, Simon	Columbia Univ./Brookhaven National Lab	sb2896@columbia.edu
Bozin, Emil	Brookhaven National Laboratory	bozin@bnl.gov
Chakhalian, Jak	Rutgers University	jak.chakhalian@rutgers.edu
Chiang, Tai	University of Illinois	tcchiang@illinois.edu
Chueh, William	Stanford University	wchueh@stanford.edu
Davenport, James	US Department of Energy	james.davenport@science.doe.gov
Dean, Mark	Brookhaven National Laboratory	mdean@bnl.gov
Devereaux, Tom	Stanford University	tpd@stanford.edu
Dzero, Maxim	Kent State University	mdzero@kent.edu
Evans, Paul	University of Wisconsin, Madison	pgevans@wisc.edu
Fadley, Charles	University of California, Davis/LBNL	fadley@physics.ucdavis.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
Gleason, Arianna	LANL/Stanford University	ariannag@stanford.edu
Gopalan, Venkatraman	Pennsylvania State University	Vgopalan@psu.edu
Hancock, Jason	University of Connecticut	jason.hancock@uconn.edu
Hasan, M. Zahid	Princeton University	mzhasan@princeton.edu
Hashimoto, Makoto	SLAC National Accelerator Laboratory	mhashi@slac.stanford.edu
Hastings, Jeffrey	University of Kentucky	todd.hastings@uky.edu
Heinz, Tony	SLAC National Accelerator Laboratory	tony.heinz@stanford.edu
Highland, Matt	Argonne National Laboratory	mhighland@anl.gov
Hilton, David	University of Alabama, Birmingham	dhilton@uab.edu
Hone, James	Columbia University	jh2228@columbia.edu
Hruszkewycz, Stephan	Argonne National Laboratory	shrus@anl.gov
Hussain, Zahid	Lawrence Berkeley National Laboratory	zhussain@lbl.gov
Jiang, Hong-Chen	SLAC National Accelerator Laboratory	hongchen777@gmail.com
Kaindl, Robert	Lawrence Berkeley National Laboratory	rakaindl@lbl.gov
Kapteyn, Henry	JILA/University of Colorado	Kapteyn@jila.Colorado.EDU
Karaiskaj, Denis	University of South Florida	karaiskaj@usf.edu
Kevan, Stephen	Lawrence Berkeley National Laboratory	SDKevan@lbl.gov
Kirchmann, Patrick	SLAC National Accelerator Laboratory	kirchman@slac.stanford.edu
Lanzara, Alessandra	University of California, Berkeley/LBNL	alanzara@lbl.gov

Lee, Wei-Sheng	University of California, Berkeley/LBNL	leews@slac.stanford.edu
Lessner, Eliane	US Department of Energy	Eliane.Lessner@science.doe.gov
Lin, Yu	SLAC National Accelerator Laboratory	lyforest@stanford.edu
Lindenberg, Aaron	Stanford Univ./SLAC National Accelerator Lab	aaronl@stanford.edu
Luo, Jin	The State University of New York, Binghamton	jluo@binghamton.edu
Mao, Hokwang	Carnegie Institution for Science	hmao@carnegiescience.edu
Mao, Wendy	Stanford Univ./SLAC National Accelerator Lab	wmao@stanford.edu
Martin, Lane	University of California, Berkeley	lwmartin@berkeley.edu
Millis, Andrew	Columbia University	ajm2010@columbia.edu
Moore, Robert	SLAC National Accelerator Laboratory	rgmoore@slac.stanford.edu
Moritz, Brian	SLAC National Accelerator Laboratory	moritzb@slac.stanford.edu
Murnane, Margaret	JILA/University of Colorado	murnane@jila.Colorado.EDU
Pechan, Michael	US Department of Energy	michael.pechan@science.doe.gov
Petkov, Valeri	Central Michigan University	petko1vg@cmich.edu
Reis, David	SLAC National Accelerator Laboratory	dreis@stanford.edu
Robinson, Ian	Brookhaven National Laboratory	irobinson@bnl.gov
Rondinelli, James	Northwestern University	jrondinelli@northwestern.edu
Roy, Sujoy	Lawrence Berkeley National Laboratory	sroy@lbl.gov
Shan, Jie	Pennsylvania State University	jus59@psu.edu
Shan, Shiyao	The State University of New York, Binghamton	sshan2@binghamton.edu
Shen, Guoyin	Carnegie Institution of Washington	gshen@ciw.edu
Shen, Zhixun	Stanford University	zxshen@stanford.edu
Shpyrko, Oleg	University of California, San Diego	oleg.shpyrko@gmail.com
Silva, Tom	National Institute of Standards and Technology	thomas.silva@nist.gov
Sobota, Jonathan	SLAC National Accelerator Laboratory	sobota@stanford.edu
Stephenson, Gregory	Argonne National Laboratory	stephenson@anl.gov
Struzhkin, Viktor	Carnegie Institution for Science	vstruzhkin@carnegiescience.edu
Thiyagarajan, Thiyaga	US Department of Energy	p.thiyagarajan@science.doe.gov
Trigo, Mariano	SLAC National Accelerator Laboratory	mtrigo@slac.stanford.edu
Wen, Haidan	Argonne National Laboratory	wen@aps.anl.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