X-ray Scattering
Principal Investigators' Meeting

Hilton Washington DC/Rockville Hotel
& Executive Meeting Center
Rockville, Maryland
December 5–6, 2018

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Foreword

This abstract book summarizes the scientific content of the 2018 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 December 5–6, 2018, at the Hilton Washington DC/Rockville in Rockville, Maryland, is the sixth 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 Washington DC/Rockville Hotel & Executive Meeting Center, 1750 Rockville Pike
Rockville, Maryland

December 5–6, 2018

Wednesday, December 5

7:00 – 8:00 **Breakfast** (poster setup, presentation loading on DOE computer)

8:00 – 8:40 **BES Welcome**
Linda Horton, BES
Helen Kerch, BES
Lane Wilson, BES

8:40 – 9:45 **Panel A**

Andrej Singer, Cornell (12 minutes)
Darrell Schlom, Kyle Shen, Nicole Benedek, John Harter

Ian Robinson, BNL (12 minutes)
Mark Dean, Robert Konik, Yimei Zhu, Pavol Juhas, Jing Tao, Ivan Bozovic Weiguo Yin

Naomi Ginsberg, UC–Berkeley (12 minutes)
David Limmer, Feng Wang, Dmitri Talapin

Z-X Shen, SLAC (12 minutes)
Jia Chunjing, Tanja Cuk, Georgi Dakovski, Tom Devereaux, Giulia Galli, Makoto Hashimoto, Matthias Hoffmann, Zahid Hussain, Patrick Kirchmann, Wei-Sheng Lee, Donghui Lu, Rob Moore, Brian Moritz, Jonathan Sobota, JoshuaTurner, Diling Zhu

Wendy Mao, SLAC (8-minute summary + 8-minute highlight)
Arianna Gleason, Yu Lin

9:45 – 10:50 Small group discussions at each panelist poster

10:50 – 11:55 **Panel B**

Zahid Hasan, Princeton (8 minutes)

Dmitri Basov, Columbia (8-minute summary + two 8-minute highlights)
James Hone, Michael Fogler, Rick Averitt, Andy Millis

Tai Chiang, Illinois UC (8 minutes)

Nuh Gedik, MIT (8 minutes)

Peter Abbamonte, Illinois UC (8 minutes)

Jason Hancock, Connecticut (8 minutes)
Maxim Dzero

11:55 – 1:00 Small group discussions at each panelist poster

1:00 – 2:00 ****Working lunch with discussions****

2:00 – 3:05 **Panel C**

Alessandra Lanzara, LBNL (8-minute summary + 8-minute highlight)
Robert Kaindl, Joel Moore

Margaret Murnane, Colorado (8-minute summary + 8-minute highlight)
Henry Kapteyn

Eric Fullerton, UC–San Diego (8-minute summary + two 8-minute highlights)
Tom Silva, Justin Shaw, Mark Hoefer, Hermann Durr, Oleg Shpyrko

Chuck Fadley, UC–Davis (8 minutes)

3:05 – 4:10 Small group discussions at each panelist poster

4:10 – 5:15 **Panel D**

Venkat Gopalan, Penn State (8-minute summary + two 8-minute highlights)
John Freeland, Aaron Lindenberg, Haidan Wen, Rick Averitt, Dmitri Basov, Roman Engel-Herbert, Jak Chakhalian, Lane Martin, Andy Millis, James Rondinelli, Long-Qing Chen

Oleg Shpyrko, UC–San Diego (8 minutes)

Valeri Petkov, Central Michigan (8 minutes)

Randy Headrick, Vermont (8 minutes)

Xiaodong Xu, Washington (8 minutes)

Denis Karaiskaj, South Florida (8 minutes)

5:15 – 6:20 Small group discussions at each panelist poster

6:20 – 6:30 End of day remarks, general discussion

Evening Working dinner, small group meetings, collaborative exchanges, additional discussion at posters

Thursday, December 6

7:00 – 8:00 **Breakfast** (poster setup, presentation loading on DOE computer)

8:00 – 9:05 **Panel E**

Mark P. M. Dean, BNL (8 minutes)
Joshua Turner, SLAC (8 minutes)
Haidan Wen, ANL (8 minutes)
Alexander Gray, Temple (8 minutes)
Brian Collins, Washington State (8 minutes)
Jing Tao, BNL (8 minutes)
Matthias Hoffmann, SLAC (8 minutes)
Todd Hastings, Kentucky (8 minutes)

9:05 – 10:10 Small group discussions at each panelist poster

10:10 – 11:15 **Panel F**

Z-X Shen, SLAC (8-minute summary + two 8-minute highlights)
Tom Devereaux, Makoto Hashimoto, Patrick Kirchmann, Donghui Lu, Rob Moore, Brian Moritz, Jonathan Sobota

Brian Stephenson, ANL (8-minute summary + two 8-minute highlights)
Stephan Hruszkewycz, Yue Cao, Jeff Eastman, Matt Highland, Hoydoo You

Robert Suter, Carnegie Mellon (8 minutes)
Guoyin Shen, ANL (8 minutes)

11:15 – 12:20 Small group discussions at each panelist poster

12:20 – 1:30 ****Working lunch with discussions****

1:30 – 2:30 **Panel G**

Aaron Lindenberg, SLAC (8-minute summary + two 8-minute highlights)
William Chueh, David Reis, Mariano Trigo

Xiaodong Xu, Washington (8-minute summary + two 8-minute highlights)
Haidan Wen, Nuh Gedik, Di Xiao

Keith Nelson, MIT (12 minutes)
Riccardo Comin, David Reis, Mariano Trigo, Rohit Prasankumar, James Freericks

2:30 – 3:35 Small group discussions at each panelist poster

3:35 – 4:40	**Panel H**
	Tom Devereaux, SLAC (8-minute summary + two 8-minute highlights) Z-X Shen, Zahid Hussain, Yi-De Chuang, Wei-Sheng Lee, Tony Heinz, HongChen Jiang, Aaron Lindenberg
	Ian Robinson, BNL (8-minute summary + two 8-minute highlights) Simon Billinge, Emil Bozin
	Steve Kevan, Sujoy Roy, LBNL (8 minutes)
	Paul Evans, Wisconsin (8 minutes)
4:40 – 5:45	Small group discussions at each panelist poster
5:45 – 6:30	General discussion on new opportunities
Evening	Working dinner, small group meetings, collaborative exchanges, additional discussion at posters

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Abstracts

Novel X-Ray Probes of Electronically Heterogeneous Quantum Materials

Peter Abbamonte
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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 studying the structure and dynamics of 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- and time-resolved soft x-ray spectrometers, particularly the new qRIXS instrument at the Advanced Light Source (ALS) and the SXR endstation at LCLS, enabling study of collective bosonic collective modes in these materials.

Recent Progress: *Ultrafast time-resolved x-ray scattering reveals diffusive charge order dynamics in $La_{2-x}Ba_xCuO_4$*

Charge order is universal among high-T_c cuprates but its relation to superconductivity is unclear. While static order competes with superconductivity, dynamic order may be favorable and even contribute to Cooper pairing. Using time-resolved resonant soft x-ray scattering at the SXR endstation at LCLS, we show that the charge order in prototypical $La_{2-x}Ba_xCuO_4$ exhibits transverse fluctuations at ps timescales. These sub-meV excitations propagate by Brownian-like diffusion and have an energy scale remarkably close to the superconducting T_c (Fig. 1). At sub-meV energy scales, the dynamics exhibit dynamic critical scaling, meaning they are governed

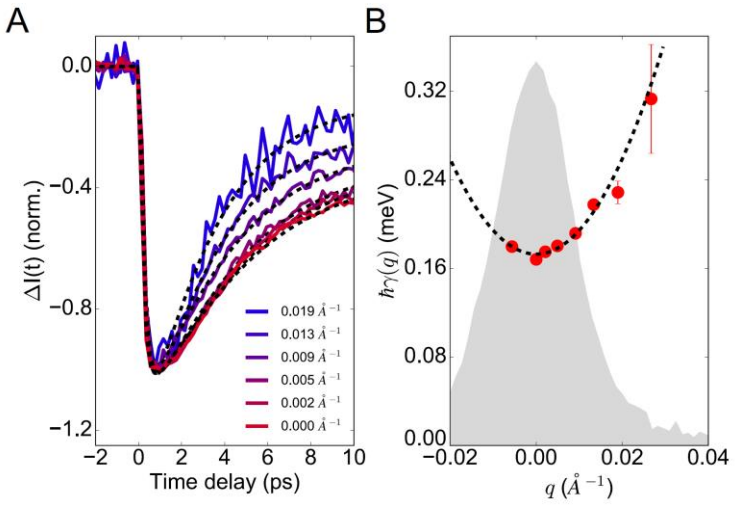

Figure 1 Collective modes of charge order in LBCO propagate diffusively. (A) (solid lines) Time traces of the energy-integrated charge order scattering for a selection of momenta, q, measured with respect to the charge order wave vector. The data are scaled to the same height and binned into 200 fs time steps to reduce counting noise in the plot. (dashed lines) Fits using a single exponential show the recovery time is highly momentum-dependent. (B) (red points) Exponential decay parameter, $\gamma(q)$, as a function of momentum. (shaded area) Lineshape of the unperturbed charge order reflection in equilibrium. The parabolic form of $\gamma(q)$ demonstrates that the collective excitations propagate diffusively.

by universal scaling laws defined by propagation of topological defects. Our results show that charge order in $La_{2-x}Ba_xCuO_4$ exhibits dynamics favorable to the in-plane superconducting tunneling, and establish time-resolved x-rays as a means to study excitations at energy scales inaccessible to conventional scattering techniques [##].

Observation of a Charge Density Wave Incommensuration Near the Superconducting Dome in $CuxTiSe_2$

X-ray diffraction was employed to study the evolution of the charge density wave (CDW) in Cu_xTiSe_2 as a function of copper intercalation in order to clarify the relationship between the CDW and superconductivity. The results show a CDW incommensuration arising at an intercalation value coincident with the onset of superconductivity at around $x = 0.055(5)$. Additionally, it was found that the charge density wave persists to higher intercalant concentrations than previously assumed, demonstrating that the CDW does not terminate inside the superconducting dome. A charge density wave peak was observed in samples up to $x = 0.091(6)$, the highest copper concentration examined in this study. The phase diagram established in this work (Fig. 2) suggests that charge density wave incommensuration may play a role in the formation of the superconducting state.

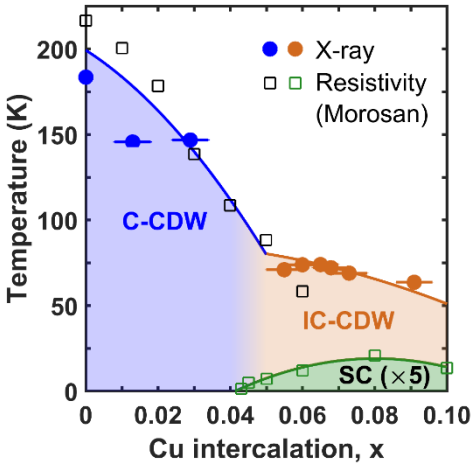

Figure 2 Phase diagram of CuxTiSe2 determined in our study. Superconductivity coexists with an incommensurate CDW, suggesting a connection to domain walls in the ordered phase.

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

In the future we intend to have an increased focus on studies of the dynamics of the charge order in these materials. In particular, we intend to study how the time scale of the diffusive dynamics described above correlates with superconductivity. This will involve time-resolved RIXS experiments at LCLS for LBCO crystals of different doping. We also intend to continue our studies of glassy order using synchrotron facilities, particularly the qRIXS instrument at ALS and beamline 13 at SSRL.

Publications (Oct. 2016 – present)

1. A. Kogar, G. A. de la Pena, Sangjun Lee, Y. Fang, S. X.-L. Sun, D. B. Lioi, G. Karapetrov, K. D. Finkelstein, J. P. C. Ruff, P. Abbamonte, S. Rosenkranz, Observation of a Charge Density Wave Incommensuration Near the Superconducting Dome in $CuxTiSe_2$, Phys. Rev. Lett. **118**, 027002 (2017)
2. Shichao Yan, Davide Iaia, Emilia Morosan, Eduardo Fradkin, Peter Abbamonte, Vidya Madhavan, Influence of Domain Walls in the Incommensurate Charge Density Wave State of Cu Intercalated 1T-$TiSe_2$, Phys. Rev. Lett. **118**, 106405 (2017)

3. W. B. Doriese, P. Abbamonte, B. K. Alpert, D. A. Bennett, E. V. Denison, Y. Fang, D. A. Fischer, C. P. Fitzgerald, J. W. Fowler, J. D. Gard, J. P. Hays-Wehle, G. C. Hilton, C. Jaye, J. L. McChesney, L. Miaja-Avila, K. M. Morgan, Y. I. Joe, G. C. O'Neil, C. D. Reintsema, F. Rodolakis, D. R. Schmidt, H. Tatsuno, J. Uhlig, L. R. Vale, J. N. Ullom, and D. S. Swetz, A practical superconducting-microcalorimeter X-ray spectrometer for beamline and laboratory science, Rev. Sci. Inst. 88, 053108 (2017)
4. Huihuo Zheng, Yu Gan, Peter Abbamonte, Lucas K. Wagner, Importance of σ Bonding Electrons for the Accurate Description of Electron Correlation in Graphene, Phys. Rev. Lett. 119, 166402 (2017)
5. Matteo Mitrano, Sangjun Lee, Ali A. Husain, Luca Delacretaz, Minhui Zhu, Gilberto de la Peña Munoz, Stella Sun, Young Il Joe, Alexander H. Reid, Scott F. Wandel, Giacomo Coslovich, William Schlotter, Tim van Driel, John Schneeloch, Genda D. Gu, Sean Hartnoll, Nigel Goldenfeld, Peter Abbamonte, Ultrafast time-resolved x-ray scattering reveals diffusive charge order dynamics in $La_{2-x}Ba_xCuO_4$, arXiv:1808.04847 (under review)

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

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

Program Scope

A goal of this program is to investigate nonequilibrium superconductivity and establish new experimental protocols to characterize enhanced transient and metastable changes to the superconducting state. Our team (Basov, Averitt, Hone, Fogler, Millis) is approaching the challenges of transient superconductivity under intense optical fields by rethinking the types of experimental observables that are best suited to elucidate the physics of light-induced effects.

Search for light-induced superconductivity. Our team explores light-induced transformations in unconventional high-Tc superconductors including $La_{2-x}Ba_xCuO_4$, $Bi_2Sr_2CaCu_2O_8$ and others subject to intense optical pump fields. We investigate the response of superconductors at nano- and meso-scales using novel instruments, structures, and theoretical modeling.

Strong light-matter interaction and interface superconductivity. We examine collective modes in superconductors at nano- and meso-scales under equilibrium and non-equilibrium conditions. We investigate methods for implementing strong and ultra-strong light-matter couplings including matamaterials, patterned structures and polaritonic effects.

Inhomogeneous superconductivity. Our team works on the development of novel experimental methods aimed at the exploration of electromagnetic phenomena that stem from static and photo-induced inhomogeneities in unconventional superconductors. We study real-space aspects at nano- and meso-scales, photo-voltage, and THz emission of inhomogeneous structures, including planar Josephson junctions under intense pumping.

Recent Progress

A. C-axis electrodynamics of $La_{1.885}Ba_{0.115}CuO_4$ and $La_{2-x}Sr_xCuO_4$.

We investigated the c-axis dynamics of prototypical cuprates. These combined experimental and theoretical studies: (i) provided access to the temporal evolution of the superconducting condensate in single crystals following photoexcitation and (ii) uncovered rich linear and non-linear Josephson junction physics with the potential to manipulate inter-layer phase coherence with locally tailored terahertz fields. We provide a brief summary of the results that have been submitted for publication.

A1.1 Photo-enhanced metastable c-axis electrodynamics in stripe ordered cuprate $La_{1.885}Ba_{0.115}CuO_4$ Evidence of transiently enhanced interlayer tunneling has been reported in several cuprates via selective phonon pumping and intense near infrared excitation. In these experiments, the c-axis Josephson plasma resonance (JPR) serves as a reporter of the interlayer

tunneling which scales with the superfluid spectral weight. Our effort has focused on near-infrared pump, THz probe experiments of $La_{2-x}Ba_xCuO_4$ (x = 0.115, T_c = 14K). We have chosen the x = 0.115 phase of $La_{2-x}Ba_xCuO_4$ to enable study of the stripe ordered region of the phase diagram, by initiating dynamics from within the superconducting state. We have observed a metastable phase that persists beyond 300 ps. This metastable state exhibits superconducting fluctuations well above the equilibrium T_c, with an increase in spectral weight that is consistent with photo-induced collapse of charge order.

Figure 1 shows experimental results for low fluence optical excitation (100 μJ/cm^2) obtained at an initial temperature of 7 K. Figure 1(a) shows the photoinduced reflectivity (blue curve at 10 ps, red curve at 300 ps), revealing a large reflectivity increase extending out to 1 THz, corresponding to an increase in the plasma frequency from ~0.2 to 0.9 THz. Figs. 1(b) and (c) show the loss function -Im(1/ε) (where $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is the c-axis dielectric response) which peaks at the plasma frequency. There is no sign of decay of the photo-induced state over the measured temporal window, indicating a metastable state that persists beyond 300 ps.

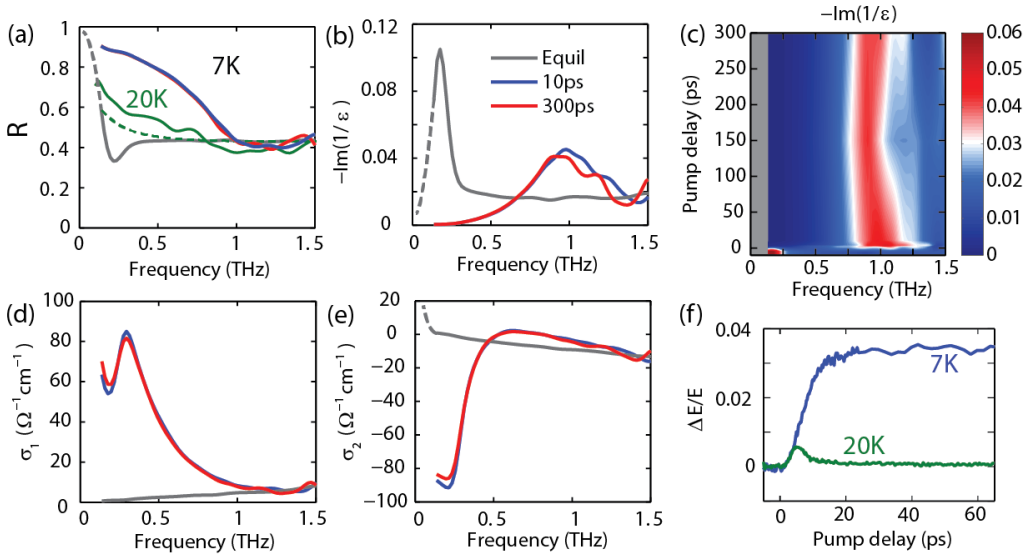

Figure 1: Extracted c-axis THz optical properties of LBCO at different pump-probe delays after photo-excitation with 100 μJ/cm^2 (colored) and at equilibrium (grey). All data has been taken at 7 K (well below T_C ~32 K) except for the green curves in panels a) and f) which were taken at 20 K. a) Reflectivity at 7 K before (grey) and after photo-excitation (colored) at different pump-probe delays. Plotted in green is the equilibrium (dotted) reflectivity and largest photo-induced change (solid) in reflectivity at 20 K. b) Loss function -Im(1/ε). Dashed grey line is below our resolution window and is a guide to the eye. (c) Spectral evolution of the loss function after photo-excitation. d)-e) Real and imaginary parts of the THz conductivity. f) Peak of ΔE/E THz transient electrical field after photo-excitation at 7 K and 20 K. Adapted from Publication [1].

Figure 1(d) and (e) display the associated c-axis optical conductivity ($\sigma = \sigma_1 + \iota\sigma_2$) highlighting an important observation. Namely, there is a peak in σ_1 at 0.3 THz signifying dissipation in the c-axis THz transport. In contrast, in equilibrium for a superconductor, σ_1 approaches zero (solid grey line in Fig. 1(d)). This peak in σ_1 in the photoinduced response is indicative of a metastable state that is inhomogeneous, with a small superconducting volume fraction co-existing with a Drude-like response. The solid green line in Fig. 1(a) shows the spectral response at 10 ps delay for a fluence of 100 $\mu J/cm^2$ taken at an initial temperature of 20K – that is, above T_c. There is an increase in the reflectivity, arguably with the development of a weak plasma edge. However, as shown in Fig. 1(f), the response is much smaller and shorter lived in comparison to dynamics initiated from the superconducting state. Notably, the emergence of a robust metastable state upon low fluence photo-excitation requires starting from the superconducting state.

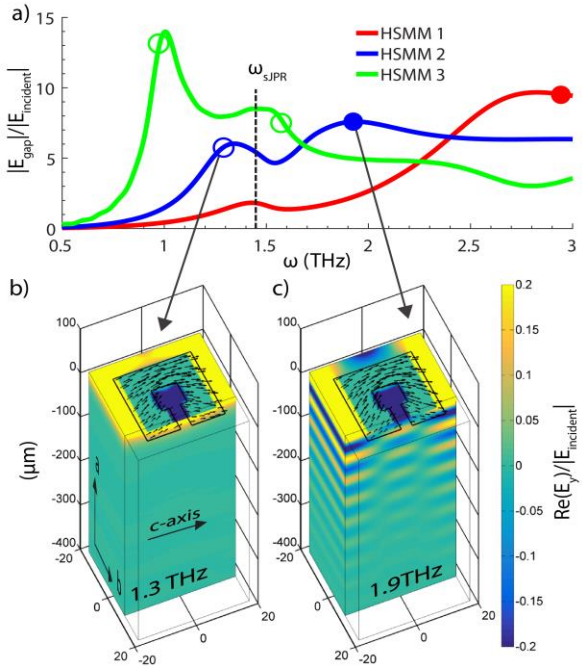

Figure 2: a) The field enhancements relative to the incident field at the SRR gap for each of the tested HSMM 1 (red), HSMM 2 (blue), and HSMM 3 (green). Open circles correspond to frequencies of local minima in experimental results while closed circles indicate local maxima. (Top) surface current densities (black arrows) and electric fields parallel to the c-axis (color) for HSMM 2 sampled at 1.3 b) and 1.9 THz c), corresponding to the circled features in the spectrum. Adapted from Publication [2].

A.1.2 Metamaterial Josephson Plasma Resonance (JPR) coupling in superconducting in $La_{2-x}Sr_xCuO_4$.

We investigated electromagnetic coupling between metasurface arrays of split ring resonators (SRRs) and the JPR of an in-plane c-axis $La_{2-x}Sr_xCuO_4$ single crystal (T_c = 32K). This is accomplished by applying a series metamaterial tapes where the LC resonance frequency (ω_{MM}) is swept through the JPR frequency (ω_{JPR} = 1.53THz). Far-infrared reflectivity measurements on these hybrid superconducting metamaterials (HSMMs) reveal anti-crossing behavior characteristic of strong light-matter coupling. Further, HSMMs with $\omega_{MM} > \omega_{JPR}$ provide a route to couple to hyperbolic waveguide modes in c-axis cuprate samples which will be important for our ongoing studies of nonlinear superconductivity under high field terahertz excitation. We expect that

HSMMs coupled with our near field capabilities will enable characterization (and possible control) of the direct superconducting hyperbolic waveguide modes.

Figure 2 shows the results of simulations building from our experimental measurements. This highlights the SRR nearfield coupling with LSCO, showing the local fields for resonances above and below the JPR longitudinal mode frequency. In particular, Fig. 2c shows the hyperbolic waveguide mode propagating into the LSCO crystal providing a route to drive nonlinear superconducting dynamics in a manner complementary to optical or mid-infrared excitation. Optimized metamaterial tapes have been designed and initial nonlinear experiments are in progress.

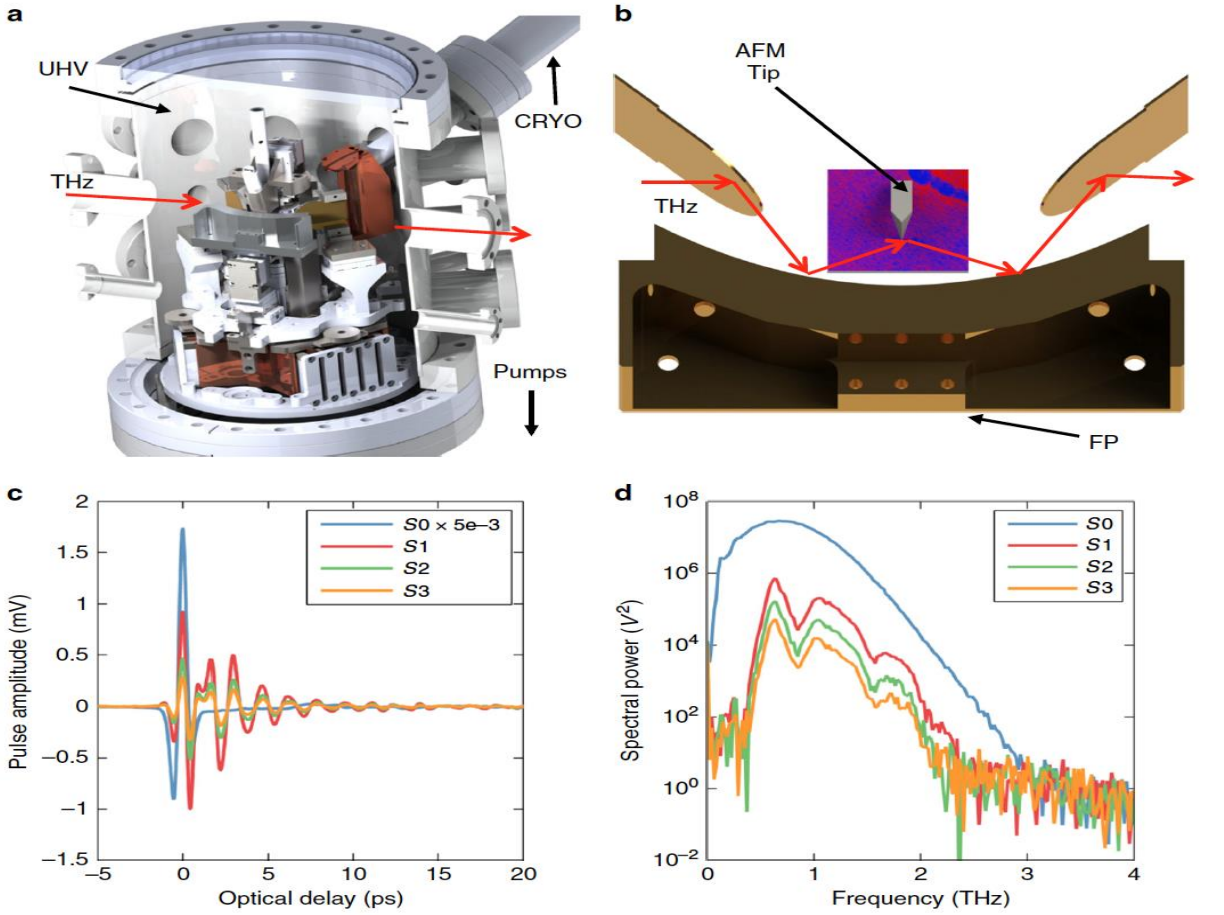

Figure 3. Schematic and typical performance of the THz-SNOM. a) Schematic of the THz-SNOM. b) Detail view of the SNOM inside the chamber. The same focusing parabola (FP) is used to both focus the THz pulse onto the tip (not shown to scale) and collect the tip-scattered light. c) Broadband THz pulse (blue, S0) and the near-field THz pulse measured in the system on gold in a dry-air purged environment. S1, S2, and S3 are the detected THz signal demodulated at the first, second, and third harmonic of the tip tapping frequency. d) Measured THz spectrum of the far-field pulse (blue) and the near-field spectrum for different harmonics, collected on gold. Adapted from Publication [3].

B. Nano-imaging at cryogenic temperatures.

In our recent paper (Publication [4]), we reported first of its kind imaging of propagating plasmon polaritions at cryogenic temperatures at infrared frequencies. We anticipate that this experimental breakthrough will open a new direction in the field of nano-optics and enable investigation of the charge response of correlated electron systems in previously inaccessible parameter ranges of frequency and momenta. Our approach utilized a scanned probe as an optical antenna that couples far- and near-field radiation. We used graphene as a model system to test our new technique. The low-T imaging discovered near-ballistic propagation of plasmons, with a record-high plasmonic Q-factor of 130. The measured temperature dependence of the Q-factor allowed us to refine the theoretical analysis of weakly- and non-dissipating propagating plasmons. Specifically, we resolved long-standing open questions in the field about the relative significance of the electron-phonon, electron-electron, and environmental plasmon scattering effects.

Another recent experimental advance pertains to commissioning of a nano-THz apparatus operating at cryogenic temperatures. This system is comprised of an ultra-fast near-infrared beamline coupled to an ultra-high vacuum cryostat. THz radiation is generated and detected using dipole antennas. Recently published results (Publications [3,5]) document the unique capabilities of this apparatus. Notably, samples and tips are exchanged using a load lock mechanism developed by our team without the need to break vacuum. Importantly, the THz frequency range is essential for studies of the electrodynamics of superconductors.

C. **Towards Auston switch based on high-Tc superconductors.**

An Auston switch refers to an optically gated antenna that can be used as an emitter of THz radiation. An Auston switch with a superconductor as an active element enables direct inquiry into non-equilibrium electrodynamics that is difficult or impossible to obtain from alternative experimental methods. Our emphasis during the first year of the program was on the fabrication of a suitable structure and on theoretical studies of Auston switch emission characteristics.

We have chosen to work with highly anisotropic $Ba_2Sr_2CaCu_2O_{8+x}$ (BSCCO) high-T_c superconductor. These readily exfoliable samples can be encapsulated with hBN to maintain the sample in pristine conditions. However, making electrical contacts to BSCCO is technically challenging, since this compound readily reacts with water molecules in air and forms an amorphous dead layer on the surface. To address this issue, our team has developed a process of making robust electrical contacts to BSCCO in a nitrogen-purged glovebox. The same glovebox is utilized for the assembly of the desired heterostructures. After many unsuccessful attempts, our team has developed a highly reliable procedure to fabricate robust ohmic contacts. We were able to execute this procedure with BSCCO microcrystals with thicknesses down to 35 nm. The data in Figure 4b reveal a clear superconducting transition at temperature near bulk T_c. This achievement

paves the way for designing and fabricating artificial vdW heterostructures with BSCCO serving as an active element.

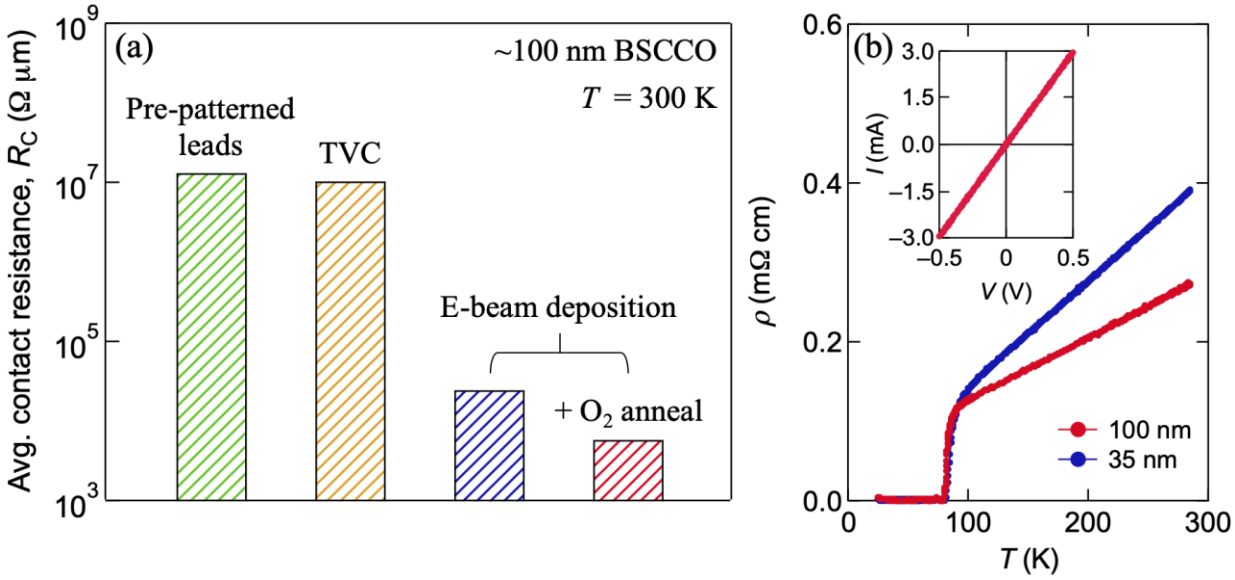

Figure 4. Making electrical contacts to $Ba_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO). a) Average contact resistance R_C for various contact methods utilized. b) Resistivity verses temperature curves for BSCCO flakes incorporating the optimized contact scheme. The inset shows the *I–V* characteristics between two contact leads showing an ohmic behavior.

D. Theory of transient electrodynamics of unconventional superconductors

Experimental work is conducted in close coordination with the theoretical investigations of transient superconductivity. We investigate dynamically driven changes in collective electronic behavior, including microscopic (Green's function-based) theories of driven electronic systems as well as computation of observables using semi-phenomenological (Ginzburg-Landau-based) approaches to computing the properties of nonequilibrium states of matter. Current areas of theoretical activity include: first-principles studies of the nonequilibrium state (Publications [6,9]) as an alternative, non-superconducting explanation of the transient superconductivity, Ginzburg-Landau, theoretical analysis of collective electronic properties of dynamically (Floquet)-driven materials, determination of the nano-optical response of Higgs, Carlson-Goldman and superconducting and plasmonic collective modes of equilibrium and driven superconductors, and further analysis of a design for an Auston switch [Fig.5] based on a dynamically switched current-driven superconducting region.

Theoretical studies of modeling of the transient dynamics of superconducting Auston switches with characteristics comparable to what is attainable in realistic structures are presented in Figure 4. These modeling results are most valuable for planning spectroscopy and nano-imaging

studies of BSCCO-based Auston switches that will be implemented by our team in Y2-Y3 of the program.

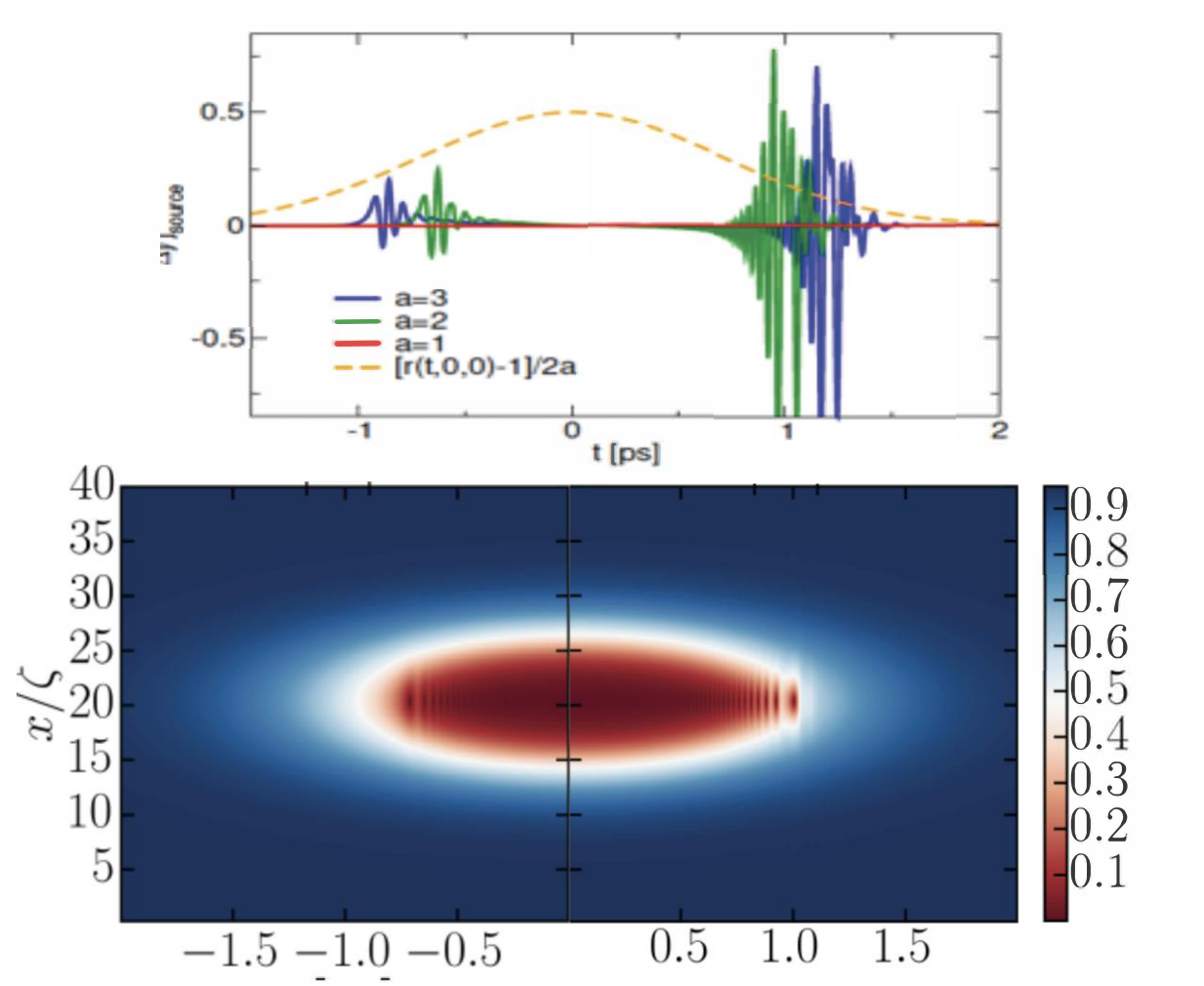

Figure 5. Auston switch from dynamical suppression of superconductivity in a segment of a superconducting region. Upper panel, oscillating current as function of time. Lower panel: false color representation of superconducting gap vs time (x axis, same as upper panel) and position (y axis). D. Kennes and A. Millis, unpublished.

In Publication [7] we theoretically studied various electron hydrodynamics phenomena suitable for investigation by near-field optical probes. Electron hydrodynamics has become a subject of active research following recent experiments with solid-state materials (GaAs, graphene, $MoCoO_2$) which discovered dc transport properties consistent with viscous flow. Near-field optics can, in principle, reveal both the frequency and the momentum dependence of the response. To guide future experiments Fogler studied this problem theoretically. He has shown that the response of an electron fluid to electromagnetic field is different from what is predicted by the usual kinetic

theory. Certain aspects of this response are universal. For example, a simple relation between the linear and the second-order nonlinear optical conductivities holds for a broad class of conductors and superconductors in the hydrodynamic regime. We made predictions regarding harmonics generation, photon drag, and collective mode spectra. These investigations improve our understanding of the light-matter interaction in diverse electron systems, including superconductors.

Millis in collaboration with Aleiner and DOE-supported graduate student G. Chiriaco have put forward a general theory of nonequilibrium quantum matter. Generalizing previous work on the zero resistance state of the two dimensional electron gas in crossed electric and magnetic fields, they demonstrated the fundamental importance of time-dependent entropy production, derived a novel mixed heat-plasmon collective mode and showed how the coupling of this mode to external electromagnetic fields could account for the essential features of the transient superconductivity (Publication [8]). Further work on the theory is in progress.

Future Plans

Our collaborative experimental-theory team is firmly on track towards fulfilling all or most of the ambitious goals outlined in our 2017 proposal. We plan to systematically investigate trends in the transient response of $La_{2-x}Ba_xCuO_4$ and related materials. The key nano-IR observable is the JPR resonance yielding a pronounced peak in the raw scattering amplitude data (Fig.1). Our team will investigate competing ground states in different classes of superconductors capitalizing on the information contained in transient observables. We plan to harness nano-IR and nano-THz methods to investigate superconductivity in ultra-thin samples of BSCO down to monolayer limit. These experiments will set the stage for the exploration of interface superconductivity in different classes of heterostructures. The proposed research will establish electromagnetic signatures of transient superconductivity across length scales.

We plan to theoretically investigate spontaneous parametric down conversion (SPDC). In photonics, this process is well known and is in fact utilized in certain light sources. We plan to study a similar effect for plasmons instead of photons. Specifically, we envision that SPDC in superconductors can convert THz photons into entangled plasmon pairs. We show that this can be realized in a thin film of any low-loss plasmonic material, including an exfoliated flake of a layered high T_c superconductor.

Finally, we plan to study interaction of plasmons with planar Josephson junctions (JJ) in YBCO. Arrays of such junctions in the normal state have been recently characterization by nano-infrared optics. At present, we are developing a novel THz beamline that will allow our team to to launch plasmons at the JJ and measure their reflection and transmission across the junction.

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N/A.

Publications

Since the inception of the award out team has published 11 articles, including 1 in *Nature*, 1 in *Nature Materials*, 1 in *Nature Physics*, 1 in *Nature Communications*, 2 in *Physical Review Letters*, 1 in *PNAS*. Several additional works have been submitted and are under review. Notably, 6 publications are co-authored by two or more co-investigators.

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

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Program Scope

We focus on electronic and atomistic effects in ultrathin films where quantum confinement and dimensional crossover may lead to novel properties and phenomena. Of interest are materials that exhibit charge density waves, nontrivial topological states, magnetic order, and superconductivity. We perform a systematic investigation of selected materials ranging from a single layer (2D limit), to multi-layers (transition regime), and to the bulk (3D limit). Also of interest are hybrid composite systems made of layers in different phases where proximity coupling, quantum coherence, interference, and entanglement may give rise to new effects.

Recent Progress

Major findings include: (1) discovery of a topological Dirac semimetal phase in strained Sn films, (2) dimensional effects on the charge density wave in $TiSe_2$ and a hidden electronic order, (3) discovery of a pseudogap in single layer $TiTe_2$, (4) an unusually large quantum spin Hall gap in single layer WSe_2, (5) a unique charge density wave gap symmetry in single layer VSe_2, (6) dynamic Floquet and two-phonon processes in WSe_2, and (7) proximity coupling induced superconductivity in the spin-polarized topological surface states of Bi_2Se_3.

Future Plans

We will continue the work on ultrathin films of various materials including charge density wave compounds, topologically nontrivial materials, superconductors, and magnetic crystals. We will also explore the physics of hybrid composite film systems made of proximity-coupled layers of different classes of materials. The static measurements thus far based on angle-resolved photoemission, x-ray diffraction, etc. will be complemented by time-resolved pump-probe measurements for a detailed understanding of the dynamics and driven behavior.

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Developing polarized resonant soft X-ray scattering to probe order at molecular interfaces

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Program Scope

The interactions and structures of organic small molecules and polymers on the nano-to-mesoscale drive materials properties and represent a critical realm for investigation of new technologies and medicines. However, traditional techniques to probe nanostructure suffer from poor resolution and/or contrast, resulting in little information or requiring laborious and potentially disruptive labeling. Near edge X-ray absorption fine structure (NEXAFS) spectroscopy can distinguish molecular species and bond orientation and has been demonstrated to be potentially powerful in revealing such information at a local level when paired with scattering. The objective of the program is to develop scattering models and analysis methods for resonant soft X-ray scattering (RSoXS) that enable the quantitative measurement of molecular identities, concentrations, relative orientations, and conformations within composite and hierarchical structures. In particular, local information of molecular orientation and conformation without crystallinity is a capability not possible with any other technique. Such models and methods will be immediately applied to better understand the ordering mechanisms of self-assembled molecular nanostructures and electronic devices such as fuel cells, transistors, and solar cells.

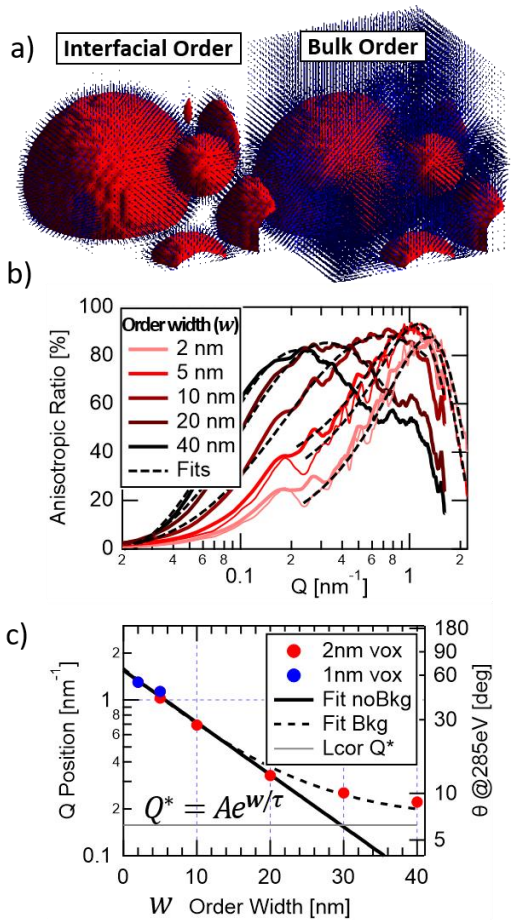

Figure 1: **Polarized scattering can resolve molecular orientation near interfaces.** a) Simulations of fullerene domains (Dia.=40±16nm, red spheres) surrounded by polymer (transparent) oriented (blue vectors) either at interfaces (within 2 nm) or in the bulk. b) Anisotropic ratio profiles $\boldsymbol{A} = (I_S - I_P)/(I_S + I_P)$, where $I_{S,P}$ are the S- and P-polarized scattering intensities. Each profile when alignment is confined to the width (w) of the interface is fit to a Gaussian. c) Quantitative exponential fit (black) between R and the peak position Q^* of the anisotropy independent of system size (vox).

Recent Progress

Three aims embody the program, each of which we report progress. ***Aim 1:*** *Establish a theoretical framework for resonant scattering.* We started with our recently developed spectral analysis that enables measurement of interfacial width between amorphous self-assembled block copolymer nanostructures.[1] Supported by this grant, we extended this analysis to semicrystalline polymers in blends with a fullerene to quantitatively measure the composition and volume

fraction of the mixed interface between the pure phases of organic photovoltaic devices. Combining this with a novel charge extraction probe, we revealed a quantitative causal relationship between charge generation and the mixed interfacial volume. The work has been submitted for publication (see below). ***Aim 2:*** *Determine spatial and statistical sensitivity limits or orientational ordering.* We have used our recently developed RSoXS simulation platform[2] to systematically probe the spatial sensitivity limits for orientational ordering at internal interfaces. Our initial work, shown in Figure 1, indicates that polarization dependent anisotropic X-ray scattering (PAXS) can quantitatively indicate the proximity of molecular alignment at the interface even in the presence of significant polydispersity in the nanostructures. This will be critical for organic devices as alignment at these junctions will govern excited state dyanmics. ***Aim 3:*** *Develop optical models for organic molecules that enable quantitative measurement of molecular conformation.* We have successfully used density functional theory calculations to model NEXAFS of a polymer specifically to determine the dipole moment of each transition. We have combined this information with a building blocks model of experimental angle-dependent NEXAFS measurements to create an optical tensor that accurately represents the molecule. The combination of an analytical model that matches experiment with individual dipole moments of each molecular bond is the first step to quantitatively describing conformation of macromolecules.

Future Plans

Moving forward, we have begun an investigation of a whether a scattering model beyond the Born approximation is necessary to quantitatively describe thick samples with refractive indices that significantly vary from that of vacuum. We believe an analytic form of the Wentzel-Kramers-Brillouin (WKB) may be possible solution, and plan to have a definitive determination of this hypothesis in the next year. We additionally plan in the next year to finish our simulation based study of sensitivity limits of orientation and move on to experimental demonstrations, primarily using reflectivity of controlled bilayered samples. Finally, in the next year we will demonstrate our newly developed tensor optical model to measurements of model molecular structures where the orientation and conformation is known.

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Probing excitations in complex oxide heterostructures

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Program Scope

Transition metal oxides exhibit numerous novel properties driven by complex inter and intra-layer correlations between their electrons. The microscopic origin of these properties is poorly understood. 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 can be used to further tune the properties of these systems.

Recent Progress

Our recent work builds on efforts to modify and probe magnetism in iridates and nickelates.

Magnetism and electron-phonon coupling in iridates: Due to spin-orbit coupling, the magnetic moments in iridates consist of "effective J" states in which spin and orbital angular momentum are combined. This causes novel coupling between structure and magnetism opening routes to modifying magnetism within heterostructures. $(SrTiO_3)_n$-$(SrTiO_3)_m$ superlattice heterostructures have been studied in collaboration with Jian Liu (University of Tennessee) with this aim in mind. Fig 1a) plots RIXS measurements of the magnetic dispersion that show changes in spin anisotropy driven by bond bending in differently stacked iridate heterostructures [1,2]. These magnetic interactions underlie our recent discovery of a giant magnetic response to applied magnetic field published in Nature Physics recently and shown in Fig. 1b) [3]. At the same time, we found multi-phonon excitations in these systems using O K-edge RIXS, which show that heterostructuring drives changes in the electron-phonon interaction through the Fröhlich mechanism [4]. Iridates heterostructures were reviewed in Ref. [5] and we followed

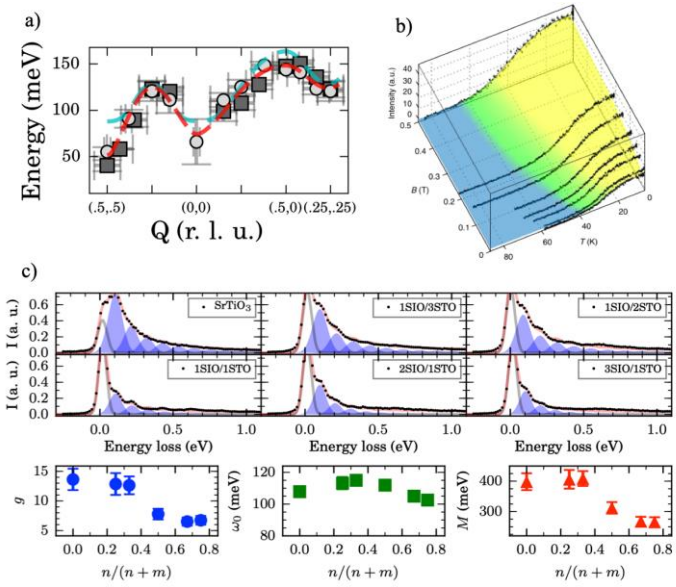

Figure 1: Modification of magnetic interactions and electron-phonon interactions in iridate heterostructures. (a) and (b) show the magnetic dispersion [1] and field-driven modification of magnetic order [3], respectively. c) Through analyzing multi-phonon excitations we extracted the electron phonon coupling matrix element, M, and how it changes with superlattice composition [4].

previous work on ultra-fast modification of magnetism in iridates [6] with a review of the wider considerations of time resolved RIXS [7].

Magnetic Helix in Nickelate-Manganite Heterostructures: One advantage of resonant x-ray probes is the ability to separately study magnetic interactions in different atomic layers. We recently exploited this to isolate the magnetic states of the nickelate layers within $(La_{2/3}Sr_{1/3}MnO_3)_9/(LaNiO_3)_3$ heterostructures, as neutron reflectivity experiments are overwhelmed by the strong Mn magnetic moments [8]. Figure 2 shows the ratio of scattering with circular right and circular left polarized x-rays multiplied by q_z^4, compared to various model magnetic structures. This establishes the c-axis helix structure (shown to the right) as the magnetic ground state [9]. Such a c-axis magnetic helix has not been shown to occur in other nickelate systems. Knowledge of this state is crucial for modeling the potential spintronic functionality of this system and may be important for designing emergent magnetism in heterostructures in general.

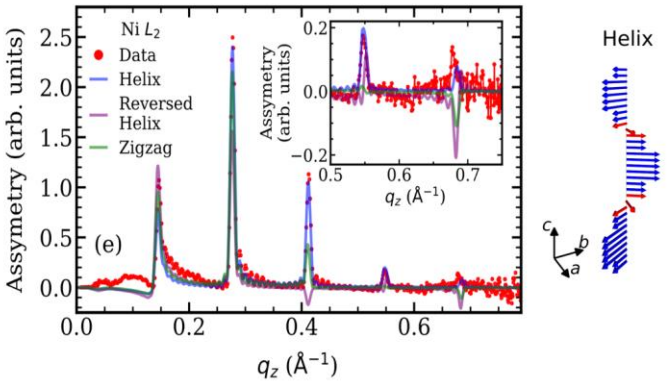

Figure 2: Discovery of a novel c-axis magnetic helix in $(La_{2/3}Sr_{1/3}MnO_3)_9/(LaNiO_3)_3$ superlattices [].

Future Plans

We plan to expand investigations of iridate heterostructures with a view to understanding the mixed Mott/Slater character of their insulating state and novel phenomenology arising for the way that this couples the magnetic order parameter to the charge gap. Investigations of topological excitations will be expanded following our recent detection of Weyl phonons in FeSe [10]. We plan to build on our recent observation of magnetic excitations in nickelates [11] exploring newly discovered high valance compounds and CDW excitations related to our recent studies of cuprates [12,13].

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Time-Resolved Soft X-ray Materials Science at the LCLS & ALS

Principal Investigator(s): T. P. Devereaux, Z.-X. Shen, Tony Heinz and A. Lindenberg.
Staff Scientists: Hongchen Jiang, Wei-Sheng Lee
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Overview:

This program connects concepts of ultrafast time-domain science with those for momentum- and energy-domain x-ray spectroscopy. The FWP consists of the single-investigator small group research (SISGR) program (Devereaux, Lee, Shen, Hussain, Chuang) on time-resolved soft x-ray materials science at the Linac Coherent Light Source (LCLS) and the Advanced Light Source (ALS), merged with ultrafast studies of 2D chalcogenide materials (Lindenberg, Heinz). The combined activities bring a synergy to explore how materials behave under extreme conditions, driving lattice and charge conformational changes by applying short pulses or high fields. The purpose of this research is to develop a world-class program on the dynamics of complex materials using the x-ray beamlines available at LCLS and other state-of-the-art synchrotrons to address the grand challenge problems of "emergence", non-equilibrium dynamics, and to probe model systems for deep insights on materials for energy conversion, transport and efficiency.

Theoretical calculations and simulations conducted in parallel with experimental progress will establish a formalism for describing non-equilibrium physics of strongly correlated and related materials and provide additional guidance to experiments. This activity requires the development of novel theoretical and computational tools and as well as the deployment of standard techniques designed to uncover the nature of the many-body state both in and out of equilibrium.

We have made substantial progresses on several research fronts to advance our understanding of complex materials through advanced x-ray based techniques coupled with advanced numerical simulations. These include LCLS- and synchrotron based experiments to further the study novel quantum materials and extend knowledge of time-domain based x-ray spectroscopy. In the following, we outline our progress through lists of bullets.

Progress in FY2018

LCLS-related activities:

- We have fully analyzed the results of our third pulsed magnetic experiment on YBCO at LCLS to investigate the onset of the CDW. We established that the onset of the CDW does not coincide with the onset of superconductivity, but with a putative quantum critical point inside the superconducting dome. We have submitted this result for publication.
- We have performed our first time-resolved RIXS measurement on CDW order 1T-$TiSe_2$. In this beamtime, the timePix detector developed by UC-Berkeley and ALS at Lawrence Berkeley Lab were used to upgrade SXR spectrometer to obtain high energy resolution. We successfully commissioned this detector at LCLS and were able to resolve particle-hole excitation associated with the charge density wave state in *1T*-$TiSe_2$. We are finalizing the analysis.
- The results of a recent combined LCLS/SSRL experiment were published in the fall of FY2018 probing ultrafast light-induced structural responses in TMDC materials. This work demonstrated a surprising light-induced modulation of the interlayer van der Waals interaction occurring on ultrafast time-scales. This work was published in Nano Letters. New measurements in FY18 were carried out at BL 10-2 at SSRL probing time-resolved phonon transport and interfacial coupling processes in 2D materials. This work is in preparation and will be submitted shortly.
- Analysis of data from the same LCLS run probing light-induced dynamics of monolayer WSe_2 was completed and this paper is now submitted for publication, showing how monolayer unit cell atomic-scale processes can be resolved on sub-picosecond time-scales via crystal truncation rod measurements.

RIXS activities:

- We have investigated the magnetic excitations in the heavily underdoped $La_{2-x}Sr_xCuO_4$ from x = 0.0019 to 0.08. The dispersion of magnetic excitations remains unchanged along both (0,0) - (π,0) and (0,0) - (π,π) directions, but the width and spectral weight exhibit a momentum dependent variation. We have also observed the dispersion of bimagnon using Cu *L*-edge RIXS. This result has been published [Chiax *et al.*, Phys. Rev. B **97**, 155144 (2018).]

- We have investigated zone-center excitations in electron-doped compounds, $La_{2-x}Ce_xCuO_4$. We discovered that these excitations exhibit strong dispersion along the *c*-axis, in addition to the *ab*-plane. Importantly, the dispersion along the c-axis indicates that interplanar Coulomb interaction drives the observed out-of-plane dynamics. This are the hallmark of acoustic plasmons. We have submitted this work for publication.
- We have performed high resolution RIXS experiments using the new instrument at Diamond light source (invited early science experiments). We have investigated CDW-phenomena in optimally doped Bi2212 superconducting cuprates. We confirmed that the CDW exists at this doping concentration and competes with superconductivity. Interestingly, enhanced phonon softening in the superconducting state occurs despite a reduction of the CDW, due in part to a competition with SC. We are finalizing our analysis and will prepare a manuscript for publication soon.
- We have performed RIXS measurement on a $LaNiO_2$ film from the Hwang FWP, produced by annealing high quality $LaNiO_3$ films. The formal Ni valence in this compound is d^9, raising an interesting question whether this system can behave like the cuprates. By tuning the incident photon energy across the Ni L_3-edge, we revealed a ground state configuration of the $LaNiO_2$ with significant weight of d^8 and d^7 components despite that the formal valence is d^9. We are finalizing an analysis and will prepare a manuscript for publication soon.

TMDC activities:

- We have discovered an exciting 2D topological insulator, or quantum spin hall state in *1T'* WTe_2 [Tang et al., Nature Physics 2017]. A quantum spin Hall insulator is an exciting example of a relativistic quantum material, where the helical edge state is robust against scattering by non-magnetic impurities. WTe_2 is more robust than previously known materials due to much larger energy gap.
- Heinz, Shen, and Lindenberg have collaborated on an effort probing for the first time the ultrafast charge transfer processes occurring within bilayer TMDC heterostructures as probed by THz emission spectroscopy. This work enables quantitative measurement of interfacial current flow on the sub-nm length and femtosecond time scales by recording the emitted EM radiation at terahertz frequencies. We find that charge relaxation and separation occur on a time scale of less than 100 fs, consistent with pump-probe measurements. Moreover, we use the unique phase-sensitivity and quantitative capabilities of this approach to unambiguously determine the direction of current flow and to demonstrate a charge transfer efficiency on the order of unity. This work has been submitted and is in review. Complementary work at UED has probed electron-phonon coupling time-scales in a range of TMDC systems.

Expected Progress in FY2019

- We will continue to use RIXS for the investigation of the rich physics in the cuprates. We plan to review comprehensive information of the CDW phenomena in Bi2212 superconducting cuprates. In addition, we will search for signatures of acoustic plasmons in hole-doped compounds, and their relation to high Tc superconductivity.
- We will start to explore RIXS and x-ray scattering measurements on strained samples. Different types of strain apparatus will be developed for RIXS and x-ray scattering experiments. In addition, we plan to collaborate with Hwang's group to explore strain effect on free-standing films.
- We will continue to utilize the *q*-RIXS endstation at ALS to perform energy-resolved resonant diffraction and momentum-resolved RIXS measurements on materials at both the *L*-edges of *3d* elements and oxygen *K*-edges.
- We have submitted new proposals for LCLS beamtime to carry out time-resolved *q*-RIXS experiments at LCLS. We proposed to use the TimePix detector to improve the resolution of the current RIXS instrument, such that preliminary time-resolved experiment on lower energy excitations can be investigated. The titles of submitted proposal is "Exploring light-induced effects on magnetic excitations in 1D cuprates via time-resolved RIXS".
- We will continue to use UED to probe ultrafast structural responses in the TMDC material system. THz emission spectroscopy will be used to provide complimentary probes of the electronic and phononic response of these materials on short time-scales.
- We will continue to work on 2D TMDCs, with focus on possible realization of exciton insulator state in $ZrTe_2$ and further exploration of ultrafast dynamics in semiconducting TMDC and TMDC heterostructures.

Expected Progress in FY2020

- Continue investigating the collective dynamics with high-resolution momentum RIXS measurement. RIXS instruments with energy resolution better than 50 meV are/will be operational in several synchrotron facilities in the world (e.g. ESRF, NSLS-II, and TPS). New discoveries enabled by these new instruments are expected. Thus, it is important to continue these efforts. These efforts are strategically important to the continuation of our FWP, as well as the development of a next generation time-resolved RIXS instrument at the LCLS-II that can fully utilize the self-seeded FEL and high-repetition rate.

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Structure and Dynamics of Exotic Ferroic Polarization Configurations

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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. The goals of our proposed work are: (1) To probe the atomic-scale structure of exotic ferroelectric domain configurations using x-ray coherent scattering and ultrafast diffraction, (2) To obtain insight into the dynamics of nanodomain configurations driven by electric fields and optical excitation, and (3) To discover and apply x-ray coherent scattering methods for nanostructures and interfaces.

Recent Progress

We have made significant progress in (i) probing, understanding, and manipulating nanoscale polarization domain configurations, (ii) observing ps-scale structural dynamics, and (iii) applying coherent x-ray nanobeam diffraction techniques incorporating dynamical diffraction.

i. Nanoscale polarization domain configurations and polarization dynamics

The competition of depolarization and domain wall energies leads to the spontaneous formation of polarization domain structures with nanoscale periodicity in ultrathin ferroelectrics and in ferroelectric/dielectric superlattices incorporating ultrathin ferroelectrics. The balance is extremely sensitive to external perturbations. We have discovered that above-bandgap optical radiation can alter this energetic balance and can lead to a transformation to a uniform polarization configuration in a ferroelectric/dielectric superlattice [P11]. Similarly, altering the mechanical boundary conditions via the formation of nanoscale patterns induces a preferred nanodomain orientation [P2].

Following those studies, we have recently begun a series of experiments at free-electron-laser (FEL) light sources to probe the coupling between optically induced electronic excitation and the distortion and transformation of the nanodomain pattern. Experiments at Pohang X-Ray FEL (Pohang XFEL), revealed the structural and domain dynamics illustrated in Fig. 1. Studies resolving the polarization in each component layer of a ferroelectric/dielectric superlattice will be conducted at LCLS in November 2018.

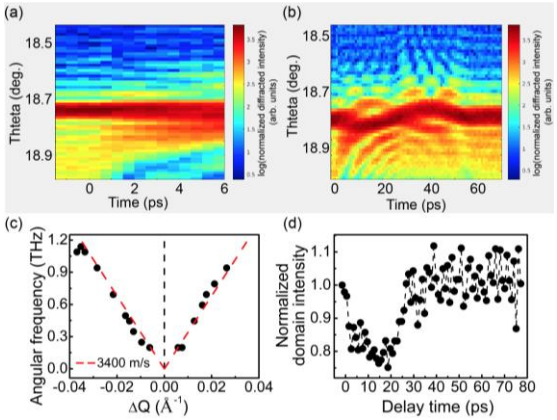

Fig. 1: **Optically induced nanodomain dynamics in a $PbTiO_3/SrTiO_3$ superlattice.** (a) Response of the 002 reflection in the first several ps following optical excitation, indicating the formation of an acoustic pulse. (b) Later-time regime, with an optically induced pulse followed by long-timescale lattice expansion. (c) Fourier analysis of the diffuse scattering has an angle/wavevector dependence corresponding to the acoustic phonon dispersion. (d) The intensity of domain diffuse scattering after optical excitation indicates that the acoustic transient distorts the domain pattern.

ii. Picosecond octahedral rotation in $BiFeO_3$

Oxygen octahedral tilts have a crucial role in

electrical and multiferroic properties, including ferroelectricity and long-range magnetic order. The octahedral tilt thus represents a key mechanism for the control of oxide properties because the magnitude and symmetry of tilts can be controlled by varying the composition, stress, or interface structure. Ultrafast methods for probing, manipulating, and ultimately engineering oxygen octahedral tilts (or tilt ordering) in ABO_3 perovskite materials and interfaces present a novel strategy for understanding how the tilt is related to functional properties such as optical nonlinearities, ferroelectricity, and ferromagnetism. The structural distortion of the octahedral rotation of in a $BiFeO_3$ thin film observed at the Pohang XFEL is shown in Fig. 2. We have also observed a sharp x-ray fluence threshold for x-ray-induced degradation in $BiFeO_3$ [R1].

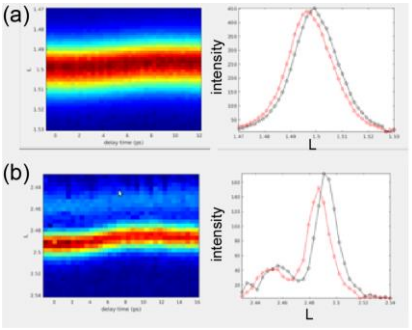

Fig. 2: **Octahedral Rotation Dynamics in $BiFeO_3$.** Intensity as a function of delay in the ps time regime following optical excitation of $BiFeO_3$ for (a) 0.5 0.5 1.5 and (b) 0.5 0.5 3.5 reflections. The intensity of each reflection varies due to the detailed scheme of the octahedral rotation.

iii. Nanobeam dynamical scattering: lattice-matched heterostructures and disorder in quantum devices.

We have developed dynamical diffraction analysis methods that will expand the range of thin film heterostructures that can be probed quantitatively using x-ray nanobeam diffraction. We have incorporated dynamical diffraction effects into simulations of the diffraction patterns produced in experiments using Fresnel zone plate focusing optics [P1, P3, P4]. The dynamical diffraction methods build on our earlier work in kinematical diffraction with convergent x-ray beams [P18, P19]. The kinematical simulations are available to the community through a web-based x-ray nanobeam diffraction simulation program [R2]. Initial nanobeam dynamical diffraction experiments have focused on structural problems in semiconductor quantum computing devices based on AlGaAs-GaAs heterostructures. This is an excellent model system because of it has an extremely defect density and is closely lattice matched. There is an excellent agreement between simulation and experiment, as in Fig. 3. Beyond their use as a model system, the experiments with AlGAs-GaAs also reveal that the the formation of metal gate electrodes leads mechanical distortions that are an important source of electronic disorder in quantum devices [P1,P4].

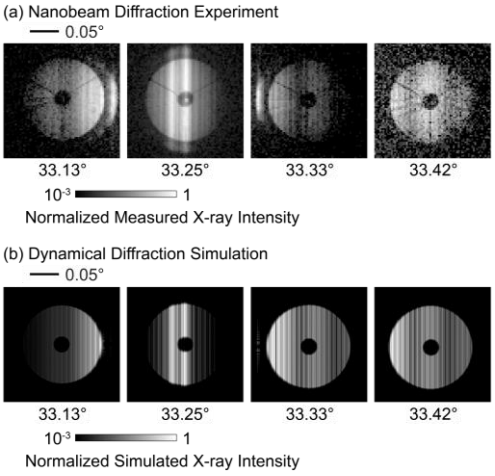

Fig. 3: **Nanobeam dynamical diffraction experiment and simulation.** (a) Observed and (b) simulated focused-beam dynamical diffraction patterns for a GaAs-AlGaAs heterostructure, at different values of the x-ray incident angle θ [P1].

Future Plans

We plan to use ultrafast and nanobeam coherent scattering studies to investigate the dynamics of complex three-dimensional polarization domain configurations and ultrafast photoinduced structural phase transformations. In order to prepare for the new opportunities that arise from the development of highly coherent storage-ring-based light sources (e.g. the upgraded ESRF in 2020) we have already conducted a series of nanobeam magnetic scattering experiments and coherent diffraction imaging studies of quasicrystals. Such studies are at the limits of present-day light sources but will become easily accessible for time-resolved and nanostructural studies at upgraded sources and FELs.

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Development of advanced photoemission and x-ray techniques and application to buried interfaces and quasi-2D quantum materials

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Program Scope

We have further developed hard x-ray photoemission and standing-wave soft- and hard- x-ray photoemission and resonant inelastic scattering and applied these techniques to interfaces and buried layers in complex oxide- and superconducting- heterostructures, and quasi 2D quantum materials.

Recent Progress

In past studies, we have shown that standing-wave XPS photoemission (SW-XPS) is a powerful tool for studying the depth dependence of various properties (atomic concentration, chemical and magnetic state, and valence electronic structure-including SW-ARPES). Particular emphasis is on measuring interface-specific properties, which can be critical determinants of behavior in many materials systems, including e.g. 2DEG formation. The SW is generated by Bragg reflection from a multilayer (ML), either as the sample itself, or on which the sample is grown, or more recently, by Bragg reflection from single-crystal/epitaxial systems to generate standing waves that scan through the unit cell.

Standing-wave x-ray photoemission and ARPES:

- Soft- and hard- x-ray ML SW-XPS has been applied to **a heterostructure 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, the LCO and STO contributions to the valence-band densities of states, and for the first time, the detailed built-in potential in the multilayer [1].
- Following earlier work in which hard x-ray ARPES (HARPES) was first demonstrated [Gray et al. Nature Materials 11, 957 (2012)], hard/tender x-ray Bragg reflection from single-crystal planes has been used to carry out SW-XPS, including HARPES, from **GaAs and the dilute magnetic semiconductor (Ga,Mn)As** [2]. 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 HARPES data**. These results are compared with LDA theory in the coherent potential approximation. A companion SW-HARPES study has also revealed new aspects of the electronic structure of **(Ga,Mn)P** [3].
- Soft x-ray SW-XPS based on Bragg reflection **from crystal planes** has been used to study **$Bi_2Sr_2CaCu_2O_{8+\delta}$**, with results permitting the determination of the composition of the different atomic planes, and decomposition of the valence-level density of states into **atomic-layer contributions** [4]. The results are compared to LDA theory, including for the first time the superstructure modulations along the crystallographic b axis. These results suggest broad applications to quasi-2D quantum materials such as topological insulators (Tis) and transition-metal dichalcogenides (TMDCs) (with Pickett, UCD).
- We have used variable-exit angle-resolved XPS (ARXPS) of core levels, together with other element-specific probes, to show that **the surface termination of $LaAlO_3$ grown on $SrTiO_3$** remains AlO_2 irrespective of the starting termination of the SrTiO3 substrate is TiO_2 or SrO [5] (with Ramesh, UCB)
- We have also used hard x-ray SW-XPS to determine the **interface composition in semiconductor InAs membrane stripes** [6**] (**with Javey, UCB).

Standing-wave RIXS:

- The SW technique has been applied for the first time to RIXS, for a **heterostructure of $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) and $La_{0.67}Sr_{0.33}MnO_3$ (LSMO)** [7], for which LSCO develops 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 they do not have the same

origin in depth, with quantitive analyses for example showing differences among dd, magnetic, and quasi-elastic excitations (with Ghinghelli and Braicovich, Milano & ESRF). Recent SW-XPS and SW-RIXS measurements on the **prototypical 2DEG system $LaAlO_3/SrTiO_3$** also have permitted quantitatively determining the 2DEG depth distribution near the interface (with Chuang, ALS).

Software development:

- We have also developed software for the interpretation of SW spectroscopy and photoemission in general, in particular a **Black Box optimizer program** for searching through sample geometries in SW studies that is 10-100 times faster than the current manual searches, and eliminates most/all of user biases in such searches [8] (with the CAMERA project, LBNL)
- An online program permits for the first time calculating **differential photoelectric cross sections for real atomic orbitals (e.g. $2p_x$, $3d_{z^2}$, $4f_{z^3}$,…)** for all atoms in the periodic table and photon energies from 100 to 10000 eV, with variable polarization excitation: http://bear.physics.ucdavis.edu/Xsections_test/ [9] (with Nemšák, ALS).

Invited contributions:

- Book chapter [10] and review article in SR News [11].

Future Plans

We will place special emphasis on further developing SW-RIXS, together with complementary SW-XPS and SW-ARPES, including applications to oxide heterostructuress and quasi-2D quantum materials.

Publications during the last two years: ten publications and one online program

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Ultrafast Electronic and Structural Dynamics in Quantum Materials

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Program Scope

The broad goal of this proposal is to probe and control quantum materials with light. To achieve this, we use and develop time resolved techniques to probe both electronic and structural dynamics in these systems. One of the current directions is to investigate different ways of using the coherent light-matter interaction to engineer new quantum phases in solids. We have previously shown that photons would coherently interact with Bloch electrons in the solid to generate hybrid dressed states known as Floquet-Bloch (FB) states. Building on this and using already available theoretical proposals, we will investigate realizing Floquet topological insulators and Floquet semimetals. Beyond topological materials, we will also use periodic driving to control competing ground states and modify the interactions parameters in the system. These experiments will make use of two important recent technical advances in the PI's group (i) In situ Molecular Beam Epitaxy (MBE) system and (ii) high harmonic generation (HHG) light source for ARPES that is capable of reaching 11 - 30 eV with high energy resolutions.

Recent Progress

Upon excitation with an intense ultrafast laser pulse, a symmetry-broken ground state can undergo a photo-induced phase transition. These non-equilibrium phase transitions are often characterized by the appearance of topological defects. Quasi-one dimensional charge density waves (CDWs), where electrons and phonons cooperatively condense to form a superlattice below a transition temperature, are known to host such topological defects. But these defects do not have a significant influence on the equilibrium metal-to-CDW phase transition. We performed time resolved measurements which demonstrate that photo induced topological defects dictate the restoration of long-range order (LRO) and can lead to creation of novel CDW configurations switchable by a single pulse.

We use ultrafast electron diffraction (UED) to selectively probe the lattice degree of freedom and employ transient reflectivity and time- and angle-resolved photoemission spectroscopy (tr-ARPES) to track the time evolution of the electronic system. We studied two different CDW materials. In $LaTe_3$ [1], despite a quick (~2ps) recovery of the CDW amplitude, a high density of topological defects remains, and LRO is only reestablished once the dislocations annihilate. In 1T-TaS_2 [2], a single femtosecond light pulse is shown to locally inject and remove mirror domain walls (DWs) in the condensate, with probabilities tunable by pulse energy and temperature. Using time-resolved electron diffraction, we are able to track anti- synchronized Higgs oscillations from both the lattice and the condensate, where photo-injected DWs can lead to a red-shifted frequency. Our results provide a framework for understanding various photo-induced phase transitions by identifying the generation of topological defects as a governing mechanism.

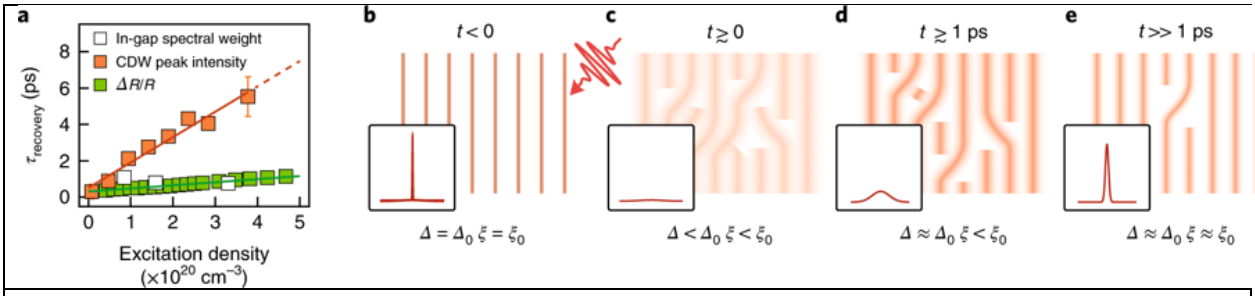

Figure a Characteristic recovery times of the amplitude and phase coherence as a function of excitation density. Transient reflectivity and tr-ARPES track the amplitude dynamics. The recovery timescale of the phase coherence is quantified by the diffraction intensity instead of the peak width owing to the better signal-to-noise ratio. Error bars, when larger than the symbol size, denote one standard deviation of fits. Lines are fits to the data; the dashed segment is extrapolated. **b**–**e**, Schematic illustration of the CDW evolution after photoexcitation. In each image, the unidirectional charge density modulation is depicted as stripes in real space. Stripe brightness indicates the strength of the CDW amplitude and smearing represents phase excitations. A cartoon of the CDW diffraction peak is presented in the lower left corner. Δ and ξ denote CDW amplitude and correlation length, respectively; Δ_0 and ξ_0 are values at equilibrium. **b**, Before photoexcitation, the CDW amplitude is large and the CDW is long-range ordered. The corresponding superlattice diffraction is represented by a narrow-width peak. **c**, Following photoexcitation, the CDW amplitude is suppressed and topological defects are formed. These effects lead to a reduction in the integrated intensity and a broadening of the peak width. **d**, After approximately 1 ps, the CDW amplitude is largely restored, while defects persist. The diffraction peak remains broad owing to the presence of these topological defects. **e**, Many defects annihilate at a further time delay though a non-zero defect concentration remains. The superlattice peak narrows substantially as the phase coherence sets in. Figure taken from [1].

Future Plans

There are several current and future directions that we are following:

- We are investigating how chemical disorder deliberately put in to the CDW samples affect the dynamics. Specifically, we will study the dynamics of melting as a function of chemical disorder.
- In some of these rare-earth tritellurides RTe_3 (R = rare earth) CDW compounds a second CDW appears below a certain temperature along an orthogonal direction to the first one. We intend to go to the part of the phase diagram where only one CDW phase exist. We will use light excitation to try to induce the second CDW using photoexcitation. Since the second CDW satellite spot appears at a distinct place in the diffraction pattern, the evolution of both order parameters can be independently tracked as a function of time.
- We are currently using our in situ MBE system to grow topological insulators and topological crystalline insulator. We are particularly interested in chemically doped systems that are near a topological to trivial phase transition. We will try to use photoexcitation to induce a topological to trivial phase transition and realize floquet topological insulators. We will probe the resulting dynamics using tr-ARPES.

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2. "*Ultrafast manipulation of mirror domain walls in a charge density wave*" Alfred Zong*, Xiaozhe Shen*, Anshul Kogar, Linda Ye, Carolyn Marks, Debanjan Chowdhury, Timm Rohwer, Byron Freelon, Stephen Weathersby, Renkai Li, Jie Yang, Joseph Checkelsky, Xijie Wang and Nuh Gedik, in print ***Science Advances*** , (2018)

Publications

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Elucidating Emergence in Multiscale Driven Systems

Naomi Ginsberg, PI, David Limmer, co-PI, Feng Wang, co-PI, University of California, Berkeley; Dmitri Talapin, co-PI, University of Chicago

Program Scope

The goal of this proposed project is to establish new pathways to control emergence of structure and function in optically driven material heterostructures. We focus on important emerging complex material heterostructures where symmetries and bonding interactions are important on multiple scales: *strongly coupled nanoparticle superlattices in ionic solutions.* We seek to relate the structure and symmetries of the individual components of the heterostructure to the structure and symmetries of the superlattice that emerges. To do so requires probing the structural and electronic properties over multiple scales in space and time, which will be afforded by leveraging the high brightness and high repetition capabilities of an XFEL. Well beyond probing the static configurations of these heterostructures, we seek to characterize and control their optically driven properties by coupling ultrafast optical excitation pulses with X-ray scattering characterizations. The ability to not only observe but to also develop new strategies to create and control emergent phenomena will open new possibilities for complex materials functionalities from renewable energy supply and storage to ultra-selective catalysts.

Recent Progress

Solvent restructuring and colloidal stability of nanomaterials in molten inorganic salts and ionic liquids. To investigate the local structure of ionic salts around colloidal nanocrystals (NCs), we used atomic pair distribution function (PDF) analysis of high-energy X-ray scattering patterns collected at the Advanced Photon Source, Argonne National Laboratory. PDFs were extracted by Fourier transform of the total scattering curves, which provided information about short-range (local arrangement of atoms) and intermediate-range order (intermolecular arrangements) in a sample. We obtained scattering data on the pure salt melt, NC powders without any solvent, and finally on NC/salt dispersions. To

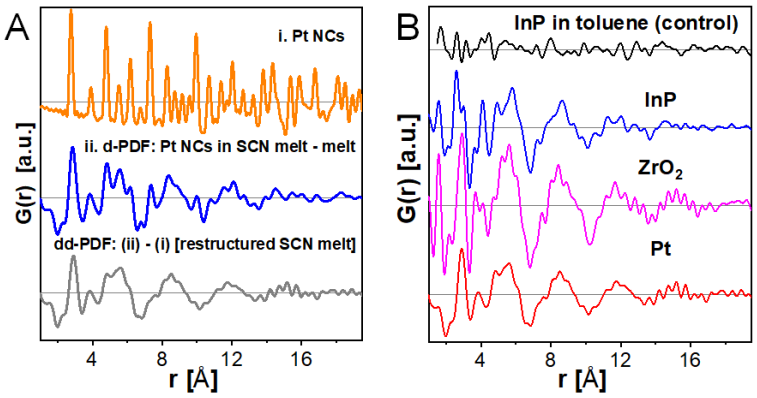

Figure 1. (A) Experimental pair distribution function (PDF) for Pt NCs in dry powder, d-PDF of Pt NCs in molten NaSCN/KSCN after the bulk liquid PDF subtraction, and dd-PDF after additional subtraction of the NC contribution. **(B)** Comparison of the dd-PDFs for various NCs in NaSCN/KSCN molten salts with the control experiment for InP NCs in toluene showing no solvent restructuring.

extract information about the solvent around the NC surface (restructured melt), we subtracted the total scattering of the pure melt from the NC/salt dispersions before the Fourier transform. The difference curve was further normalized by the atomic form factors of the elements in the melt, rendering the reduced structure factor, RSF=q[S(q)-1], which contains element-independent structural information. The Fourier transform of the RSF gives us the differential-PDF (d-PDF). Further subtraction of the contribution from the NC powders results in a double-differential PDF (dd-PDF). Figure 1a shows PDF, d-PDF, and dd-PDF results for Pt NCs in KSCN/NaSCN eutectic melt. Any features in the d-PDF, aside from the interatomic distances of the Pt NC, are due to solvent restructuring around the NCs. In a highly ionic environment, the wavelength of the intermediate-range order represents the physical size of the ion-pair. In bulk and restructured KSCN/NaSCN melts, the wavelength is fixed at 3.3 Å. This corresponds to the reported distance between K^+ and SCN^- ions in the KSCN melt. The dd-PDF of Pt NCs in the SCN melt shows oscillations with a distinct amplitude, decay length, and phase relative to the original NaSCN/KSCN melt. Further analysis showed that the ion–ion correlations near the Pt surface are more persistent than ion–ion correlations in the bulk melt. We observed similar enhancement of the amplitude and decay length for other NCs (ZrO_2 and InP NCs in KSCN/ NaSCN melt, Figure 1b), showing the generality for all studied NC materials. The amplitude of the oscillations varied for different NCs but no oscillatory solvent restructuring was observed in dd-PDF for NCs colloidally dispersed in traditional solvents (e.g., toluene) (Figure 1b). Solvent restructuring only happened for NCs that chemically bound ions in the melt.

Cathodoluminescence microscopy of strongly coupled superlattices. Preliminary results of cathodoluminescence (CL) microscopy of Au nanoparticle superlattices demonstrate that we are able to detect cathodoluminescence from the samples (Figure 2). We are currently able to see enhanced CL from the edges of the superlattice structures, potentially due to either a difference in efficiency of emitting light at corners or different plasmonic properties at the edges. While we do not resolve the individual 5 nm nanoparticles within the superlattices, we resolve the edges of layers of particles. The preliminary CL results are encouraging, and we anticipate being able to record the spectrum of the CL emission as well as to collect CL images in different color channels to determine any difference in the spatial profile of the emission at different energies. These measurements pave the way to performing *in situ* CL characterization of the superlattice self-assembly process within ionic solutions by virtue of their low vapor pressure.

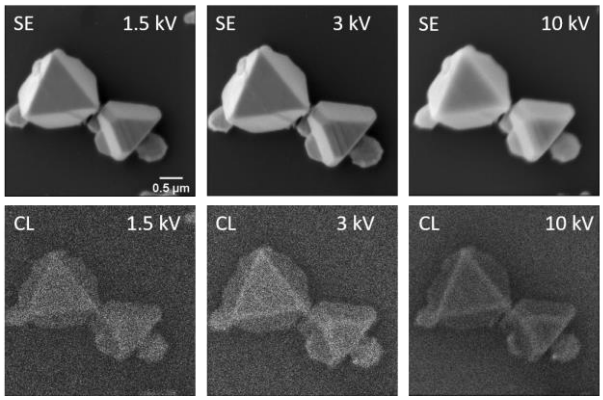

Figure 2. Cathodoluminescence (CL) compared to secondary electron (SE) imaging of Au nanoparticle superlattices shows enhancement at edges of the superlattice and also potentially at smaller terraced features.

Future Plans

We will systematically study colloidal nanoparticle superlattice self-assembly as a function of emergent particle-solvent interactions. Leveraging XFEL brightness and repetition rate, we will collect movies with high temporal resolution of the evolving scattering patterns reflective of nanoparticles forming superlattices under a variety of controlled trajectories. By working initially with different shapes of metal nanoparticles in molten salts we will leverage the coherent perturbation to the solvent charge field by plasmons induced in the particles to alter the dynamics. We will expand the scope of our inquiry by proceeding to target semiconductor nanocrystals. We will leverage what we learn on metal nanoparticle systems to accelerate progress on complementary semiconducting particle systems that are more delicate.

First, we will characterize the nature of the interaction between pairs of nanoparticles in ionic solvents with a tight feedback loop between experiment and theory. We will resolve the signatures of molecular interactions on the surface of the particles that mediate longer time scale self-assembly. We will characterize ultrafast solvation dynamics of the particles in ionic solutions via ultrafast transient absorption and transient scattering. We will compare the results of this process under various driving conditions, including ultrafast optical illumination to excite semiconducting nanocrystal constituents, modulating local surface charge distributions and thus the emergent macroscopic structure. The use of robust metal nanoparticles with inorganic ligands in inorganic molten salt solutions will enable us to initiate our studies and will shed light on the solvent density correlations surrounding the particles and mediating their interactions. Progressing to semiconducting particles in ionic liquids will further enrich the range of physical parameters that can be explored.

Second, we will theoretically determine the thermodynamics required to self-assemble particles into superlattices within ionic liquid-based solutions and will characterize the equilibrium states of the system both prior to and after mixing. We will perform synthesis and thermodynamic characterization in addition to equilibrium state characterization at Argonne's Advanced Photon Source (APS) using PDF analysis and SAXS. Structures will be characterized in direct space by electron and cathodoluminescence microscopy. We will computationally predict superlattice properties and compare results closely with the others to downselect from a large system parameter space for XFEL experiments.

Third, we will follow the kinetic processes by which final superlattice states are reached. Initial studies on thermally driven assembly will provide background knowledge and identify systems and structures of interest, which we will revisit under conditions where the self-assembly is driven, altered, or 'catalyzed' by the presence of impulsive optical fields. We will perform high-throughput transient optical scattering, terahertz spectroscopy, and in situ (dynamic) electron microscopy to obtain coarse estimates of kinetics. In situ SAXS and wide-angle X-ray scattering

(WAXS) at LBL's Advanced Light Source will also provide a coarse estimate of kinetics under thermally driven conditions and will aid in developing cells for controlled isothermal co-solvent evaporation to be employed at the XFEL.

At the XFEL, we will perform in situ WAXS and SAXS both with and without ultrafast optical excitation to establish the relationship between structure and symmetry within the nanoparticles (WAXS) and how those single particle properties affect ultimate superlattice formation (SAXS). The repetition rate and brightness will permit single shot scattering patterns, enabling us to follow self-assembly dynamics with sufficient time resolution. We are also eager to perform time-resolved coherent diffractive imaging to elucidate the full 3D dynamics of superlattice formation. These extensive datasets will enable us to elucidate the relationship between microscopic intermolecular interactions and macroscopic emergent structures and will identify the causal links between these multiscale relationships and the design rules for different types of superlattice formation. Molecular simulation will aid in determining which microscopic factors most substantially determine the emergent macroscopic structures and the different means by which these outcomes can be varied through subtle variations in the self-assembly parameter phase space.

The results of our combined hierarchical, multimodal efforts will open a new paradigm in the study and control of complex materials with designer functionalities. By following the dynamics of self-assembly as a function of particle type and morphology, solvent environment, and external driving conditions we will establish the design principles for creating new materials, with a careful eye toward the multiscale relationship between individual component interactions and symmetries and the many body effects that arise in order to assemble them on larger scales.

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Emergent Phenomena at Mott Interfaces – a Time- and Depth-Resolved Approach

Alexander Gray, Department of Physics, Temple University

Program Scope

Rational design and efficient ultrafast control of new electronic and magnetic phases of matter at oxide interfaces is considered to be one of the most promising avenues towards realizing new generations of energy-efficient devices. In this program (Start Date: 09/2018) we plan to utilize intense THz electric-field pulses generated by a femtosecond laser to directly modify the electronic structure and magnetic states at the atomically-abrupt interfaces between ultrathin Mott oxide layers ($CaMnO_3/LaNiO_3$), with the objectives of disentangling, understanding, and harnessing control over the intricate competing interactions responsible for tunable emergent two-dimensional magnetism at the interface [1]. As a key part of this project, we propose to marry the x-ray standing-wave (SW) methodology [2], which is presently being utilized only in equilibrium, with the ultrafast polarization-dependent x-ray scattering and imaging techniques enabled by the most recent technological advances at the DOE's free-electron laser (FEL) and synchrotron facilities. This will result in the development of a powerful new experimental platform that can be used to study electronic and magnetic systems driven out of equilibrium with time and depth resolution.

Recent Progress

In preparation for this research program, the PI and collaborators have carried out a set of feasibility measurements specifically on the $CaMnO_3/LaNiO_3$ system using depth-resolved SW photoemission spectroscopy in conjunction with scanning transmission electron microscopy and x-ray absorption spectroscopy. Our results, published in Ref. [3], (a) attest to the high quality of our samples, (b) show strong SW modulations for all the elements in the system, which demonstrates feasibility of the x-ray SW measurements in this system, and (c) reveal an increased concentration of Mn^{3+} and Ni^{2+} cations at the interface, which create an electronic environment favorable for the emergence of interfacial ferromagnetism mediated via the Mn^{4+}-Mn^{3+} ferromagnetic double exchange and Ni^{2+}-O-Mn^{4+} superexchange mechanisms. These findings demonstrate technical feasibility of the depth-resolved standing-wave measurements in equilibrium and pave the way for the future time-resolved x-ray scattering studies described in the Program Scope section.

As a precursor to this program, the PI and collaborators made significant contributions to the development and implementation of the THz-pump x-ray probe experiments at the LCLS [Ref. 4]. In these proof-of-principle experiments, ultrafast optical spectroscopy and x-ray scattering were utilized together to show that the electric-field-induced electronic and structural phase transitions in a prototypical strongly-correlated oxide VO_2 can be disentangled in the time domain. Specifically, following intense sub-picosecond THz electric-field excitation, a partial collapse of

the insulating gap was observed within the first picosecond. At temperatures sufficiently close to the transition temperature and for THz peak-fields above a threshold of approximately 1 MV/cm, this electronic reconfiguration initiated a change in lattice symmetry taking place on a slower timescale.

Future Plans

In this research program, we plan to build on these recent experiments and utilize the fs-level resolution of LCLS and LCSL II, along with the element-specificity of the soft x-rays tuned to the *L* and *K* absorption edges, to observe and control the emergence and evolution of the new electronic and magnetic phases in strongly-correlated Mott systems with lateral- and depth resolution. We plan to use a model Mott system $CaMnO_3/LaNiO_3$ as a materials platform for our time- and depth-dependent studies. In this system, emergent Mott physics and competing ferromagnetic exchange interactions are intertwined at the interface, giving rise to quasi-2D ferromagnetism, which can be tuned via a metal-insulator transition in $LaNiO_3$. Our approach will focus on triggering this transition dynamically with external stimuli, such as ultrafast THz electromagnetic pulses, and applying time- and depth-resolved x-ray scattering techniques to the element- and orbital-specific studies of the emergent electronic and magnetic phenomena at the interfaces.

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Publications

This program started 3 months ago (09/2018).

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

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Maxim Dzero, Department of Physics, Kent State University

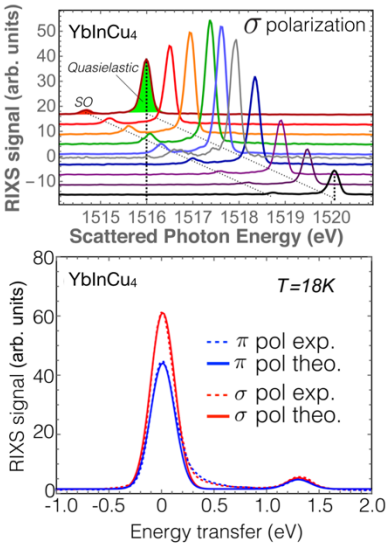
Program Scope: Rare-earth intermetallic materials host a fascinating landscape of correlated and topological phases resultant from the cooperation and competition of electronic degrees of freedom. Advanced spectroscopy of these correlated systems holds potential to assess the degree of localization and itineracy of specific excitations across phase transitions. Resonant inelastic X-ray scattering (RIXS) has brought new insight into competing instabilities in the *d*-filling series and responsive resolution and instrumentation developments have opened new areas of science in the *f* series. In this project, we have examined the strengths of the adaptable RIXS probe at multiple rare earth edges in a selective interrogation of the extended and localized electronic states in this materials class.

Recent Progress: The electronic origin of the low pressure-induced semiconductor-metal transition in $SmS_{1-x}Y_x$ as a function of temperature and composition to probe an extended boundary between these two phases. Using Sm *L* edge RIXS [P12], we find clear evidence of *f-d* excitations which broaden and reconstruct in the metallic phase as well as unusual valence behavior in response to doping and temperature, effectively mapping out the itinerant electronic states along the unusual phase boundary of this system.

Motivated by first-time benchmark measurements, we have investigated [P13] general aspects of the RIXS response at the rare-earth *L* edges of in hexaborides YbB_6 and EuB_6. These materials display very different physical behavior, but we find commonalities and agreement with density functional theory calculation that an effective *f-d* transition is observed at the divalent resonance of these systems. This identification permits us to determine effective *f* level positions in a bulk probe as well as resolve details of the *unoccupied* 5*d* electronic states. In addition, we find a manifold of transitions resonant at higher energy with distinct polarization dependence. This set of excitations reflects the spin state of the low-energy manifold but also appears consistent with scattering from free-electron states in these low work function materials.

A central feature of the class of Kondo lattice systems is the emergence of a hybridization gap and an associated many-body resonance which controls the magnetic response and other physical behavior. Using Yb *M* edge RIXS for the first time, we have shown unambiguously that quasiparticle excitations across the hybridization gap can be produced in a Kondo lattice, $YbInCu_4$. This advance [P1] portends exploration of the gap dispersion in the next generation of end station instrumentation and pursuit of this long-sought ambition is underway. In addition to revealing this general capability which will address a large body of problems in correlated systems, this study of $YbInCu_4$ follows on our itinerant *L* edge [R1,R2] and optical results [R3].

Early science commissioning work at the SIX instrument, NSLS-II has revealed the landscape of excitations in heavy-



M_5 edge RIXS reveals a Kondo lattice excitation upon crossing a valence transition [P1]

fermion superconductor family $CeCoIn_5$[P2]. We plan to exploit superlative planned improvements of energy resolution and implementation of the 3D momentum control on this system and others in its class.

Future Plans: Our near-term work aims to use next-generation instrumentation to (1) investigate the electronic structure, including crystal field information of heavy fermion and mixed valent systems (2) investigate charge-density wave excitations using high resolution RIXS and (3) observe the dispersion of the hybridization gap in rare-earth intermetallic systems in the Kondo limit. We continue 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.

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Synchrotron X-ray based study of Novel Quantum Materials

M. Zahid Hasan (Princeton University)

Program Scope

Our program is focused on discovery and understanding of topological materials using advanced spectroscopic techniques. We combine FP-DFT calculation techniques to discover novel topological materials harboring new protected quantum properties then probe and explore suitable materials primarily via ARPES, X-ray scattering and Ultrafast techniques. Currently we are also working on developing a novel ultrafast-ARPES technique suitable for the study of photo-induced changes in topological matter. The general focus of this proposal is to carry out novel and potentially high-impact experiments to advance the fundamental science frontier on quantum materials.

Recent Progress

Our recent progress [1-12] include identification and exploration of Weyl fermion semimetals, topological Fermi arc states including Lorentz-violating Weyl metals (2015-18), topological nodal-line states (2016-18), 3D topological magnets (2018), topological quantum properties of chiral crystals (2018) and demonstrated giant and anisotropic many-body spin–orbit tunability in a strongly correlated topological kagome magnet (Nature 2018). We have developed a novel artificial condensed matter lattice which will be able to explore tunable topological magnetic phases of matter (2017-18). We have also devised a novel platform for exploring chiral Majorana modes on the surface of superconducting topological materials (2018).

Future Plans

Starting 2019 we will be working on building an ultrafast laser pump-probe ARPES setup at Princeton University utilizing some of the latest advancements in laser (HHG) and detector technologies (multiplexing). Our goal is to utilize this instrument as an “ultrafast quantum microscope” to study the quantum dynamical formation of topologically invariant properties such as the nontrivial winding of wavefunctions and Berry potential or curvature field in solids which behave like a k-space pseudo-magnetic field and r-space Dirac string surface analogs that will answer a set of profound yet unanswered questions (such as why do they form?) through topological quantum phase transitions (how do they form?) in existing and upcoming materials as well as develop control (how to tame it?) of the wavefunction’s geometric properties that microscopically tunes topology thus the entangled nature of quantum matter while weakly or strongly (in both limits) interacting with light. The outcome of this project is targeted to not only answer some deeper questions about topology in matter, but also expected to spawn new frontiers in functional properties of optically tunable materials or light-induced novel topological

phenomena research taking us steps closer to some of the visions highlighted in recent articles in Nature News (homepage, July 2017), Scientific American (July, 2017), Nature Materials (Cover page article, October, 2016) and Discover magazine (October, 2018). These news articles cite recent works on topological matter supported by this DOE grant.

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Chiral Majorana Fermion Modes on the Surface of Superconducting Topological Insulators

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Magnetic Weyl fermion semimetals in the R-AlGe family of compounds

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

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Contributors: X. M. Chen, U. of Kentucky and LBNL, J. S. Woods, U. of Kentucky and ANL, B. Farmer, U. of Kentucky, S. Dhuey, LBNL, W. Hu, BNL, C. Mazzoli, BNL, S.B. Wilkins, BNL, I. K. Robinson, BNL, Andreas Scholl, LBNL, Rajesh Vilas Chopdekar, LBNL

Program Scope

The current program seeks to understand the spontaneous, thermally induced fluctuation of superdomain walls in artificial spin ices (ASIs) and to use this knowledge to understand phase transitions and emerging spin textures. Our second goal is to study generation and control of orbital angular momentum (OAM) of the scattered x-ray beams using ASI structure and texture. ASIs are periodic arrays of sub-micron-scale, elongated segments of ferromagnetic (FM) thin films as shown in Fig. 1. ASIs can exhibit well-ordered ground states, or can be topologically frustrated causing 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, ASIs can serve as models for understanding systems far from equilibrium. Control of these processes and engineering of their time scales through the introduction of defects may allow ASIs to be programmed into states with useful functions such as magnetic logic or phase control of an x-ray beam.

Recent Progress

Superdomain wall motion in ASIs studied with XPCS

Square ASIs have an antiferromagnetically ordered ground state as shown in Fig. 1(c). Regions of the ground state (superdomains) can be separated by boundaries (superdomain walls) in which thermal equilibrium dynamics can be observed. We used coherent resonant x-ray scattering to study the antiferromagnetic (AF) order parameter as a function of temperature though the antiferromagnetic to paramagnetic phase transition. As shown in Fig. 1(a,b) the AF order yields half-integer peaks that break into speckles upon the formation of superdomain walls and/or paramagentic regions. We used x-ray photon correlation spectroscopy (XPCS) to observe the characteristic motion of the superdomain walls in square ASI. We analyzed the speckle patterns using a continuous time, random walk model which showed that superdomain boundaries fluctuate via low-temperature ballistic and high-temperature diffusive motions. Our results bridge hard and soft condensed matter physics, showing that dynamical behaviors observed in soft matter are also present in hard condensed matter systems.

X-ray OAM Generation from dislocations in ASI

Introduction of a single dislocation in a square ASI introduces magnetic frustration.[1] Introduction of a double dislocation should remove frustration and restore an ordered ground state.

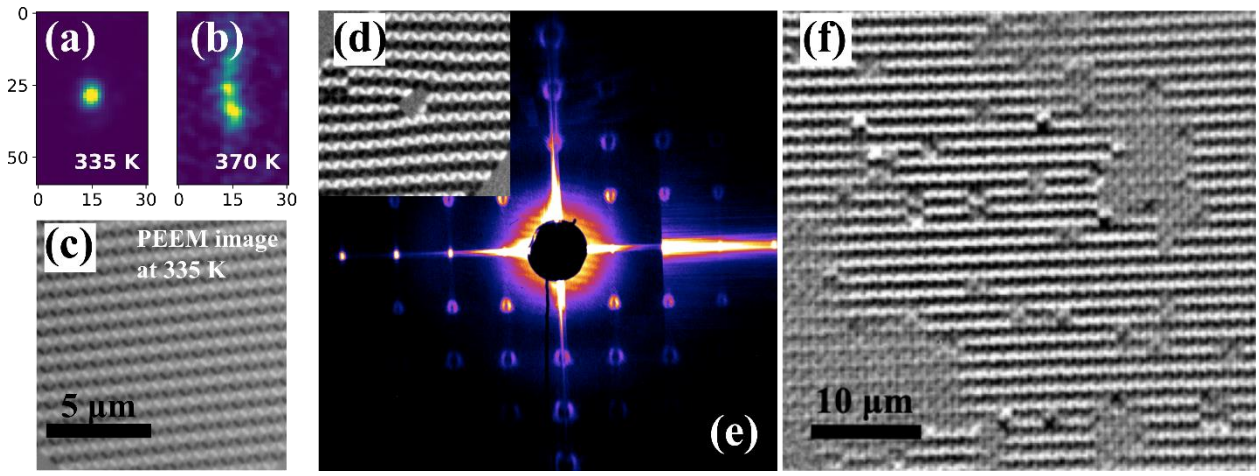

Figure 1. Coherent soft x-ray scattering from square ASI yields (a) a peak for a single AF superdomain and (b) a speckle pattern for a region with multiple superdomains. (c) X-ray PEEM image showing a single domain in the AF ground state. As temperature increases, multiple domains form and produce dynamic speckle patterns, as in (b), that can be studied with XPCS. (d) X-ray PEEM image of square ASI with a double dislocation showing an AF-ordered ground state and no pinning of superdomain walls. Charge scattering from the forked lattice should give rise to static x-ray orbital angular momentum in the integer Bragg peaks, shown in transmission in (e), while magnetic scattering should yield controllable OAM in the half-integer AF peaks. (f) PEEM image of square ASI with connected defects (4% concentration) that pin superdomain walls and alter the AF (striped) and paramagnetic (gray) phase separation.

Moreover, this ground state should exhibit the remarkable property of generating orbital angular momentum in x-ray photons resonantly and coherently scattered from the magnetic texture. As shown in Fig. 1(d), x-ray PEEM reveals that a permalloy, square ASI with a double dislocation relaxes to the AF ground state without pinning superdomain walls at the dislocation. Thus, a clear forked structure emerges in the AF texture. In addition, we expect the superlattice to exhibit diffraction peaks with $l = \pm 2m$ OAM at mth order peak, Fig. 2(e) shows diffraction consistent with OAM (vortex-like shapes). Experiments are underway to confirm that magnetic scattering from AF-ordered ground state yields $l = \pm 1$ OAM at first half-integer (AF) peaks. Moreover, the ground state is both thermally and magnetically active. This should allow the OAM beam to be extinguished or switched between states using field and temperature cycling protocols.

Effect of defects on ASI superdomains studied with PEEM and XPCS

Introduction of defects into magnetically frustrated materials can completely alter their ground state. To explore this phenomena, we systematically introduced lattice defects in square ASI at varying concentrations and studied their behavior with x-ray PEEM and XPCS. Defect types included segment vacancies, segment substitutions, and connected vertices. We found defect pinning of superdomain boundaries as shown in Fig. 1(f), as well as broadening of the phase separated region (antiferromagnetic and paramagnetic) in the temperature-doping phase diagram.

Superdomain imaging via BCDI

Real-time imaging of dynamics is a sought after pathway to understand properties of quantum materials. Bragg coherent diffraction imaging (BCDI) is a lensless technique that maps a crystal's strain or domain textures to real space. When this technique is extended to the soft x-ray regime, charge and magnetic domain dynamics in quantum materials will be revealed. Square ASIs are

ideal to commission this technique because of their known lattice structure and strong AF peaks. We have successfully used BCDI to reconstruct the artificial lattice as well as anti-ferromagnetic superdomains as shown in Fig. 2.

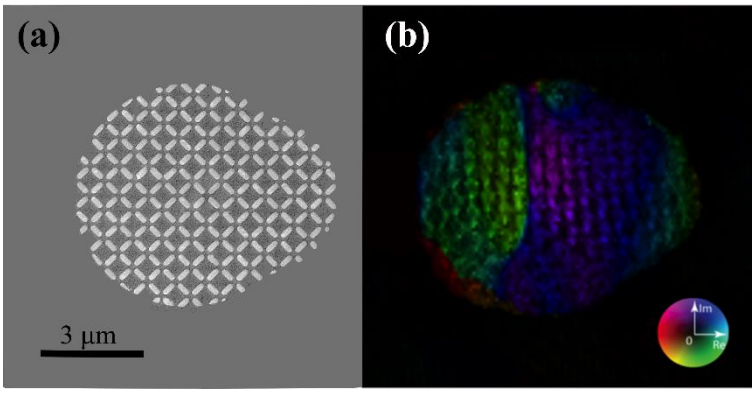

Figure 3. Magnetic superdomains can be imaged using Bragg coherent diffraction imaging (BCDI) with resonant soft x-rays. (a) A scanning electron micrograph of a square ASI establishes the region of support for the phase reconstruction in BCDI. (b) BCDI of superdomains in which the underlying superlattice is also resolved.

Future Plans

With regard to x-ray OAM, we plan to explore the control of OAM beams using field and temperature cycling of square ASIs with double dislocations. More deterministic control may be achievable using dislocations in magnetically programmable ASIs developed at Argonne National Laboratory.[2] In addition, it may be possible to switch between OAM states by moving superdomain walls through the dislocation region with a suitable field protocol. With regard to defects in ASI, we are currently extending this work to triangular and honeycomb lattices to understand how defects in *frustrated* magnetic lattices alter dynamics. With regard to BCDI of magnetic textures using resonant soft x-rays, we will continue developing this robust technique in collaboration with Dr. Ian Robinson and the CSX beamline at Brookhaven National Laboratory.

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2. *Thermally Induced Spontaneous AF Super-domain Wall Fluctuations in Artificial Spin Ice*, Coherence 2018, Port Jefferson, NY (2018)
3. *Spontaneous Domain Wall Fluctuation in Artificial Square Spin Ice Studied with Soft X-Ray Photon Correlation Spectroscopy*, March Metting (2018)
4. *Visualization of Spontaneous Domain Wall Fluctuation in Artificial Spin Ice using Bragg Coherent Diffraction Imaging (BCDI)*, March Meeting (2018)
5. *Superdomains in Artificial Magnetic Lattices: Fluctuations, Control, and Functionality*, ALS User Meeting (2018)

Coherent X-ray Studies of Surface Growth and Patterning Processes

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Program Scope

This project is to perform X-ray Photon Correlation Spectroscopy (XPCS) studies of thin film surface morphology and step-edge motion as the surface evolves during growth, and to participate in a parallel effort to study patterning of surfaces during energetic ion bombardment. Thin film growth systems include polycrystalline thin films of organic semiconductor materials (e.g. oriented polycrystalline C_{60} thin films) deposited by vapor deposition as well as single-crystalline thin films (e.g. III-Nitride thin films) deposited by Atomic Layer Epitaxy. The experiments are augmented by computational models of surface growth, ranging from one-dimensional models of step-edge motion to kinetic monte-carlo models of surface growth.

In the ion bombardment studies, energic ions (typically Ar^+) are used to bombard surfaces (e.g. Si, SiO_2, or sapphire) and produce organized patterns of ripples or mounds. The surface evolution and steady-state dynamics are monitored using XPCS. The motion of the surface and correlations is modelled through a non-linear Langevin equation, which predicts linear growth of surface features at the beginning of pattern formation, ranging to more complex dynamics that are dominated by non-linear terms at later times. Karl Ludwig (Department of Physics, Boston University) collaborates on both the growth and ion bombardment project, and he is the PI on a project that is funded separately from this project under NSF DMR-1709380 to participate in this effort.

Recent Progress

A key hypothesis of this project is that coherent X-rays can be used to study thin film growth without loss of information due to spatial averaging, even in the later stages when the growth surface is very rough, and the film may be composed of many separate crystalline grains. We have experimentally confirmed this conjecture for (111) oriented polycrystalline C_{60} growth on SiO_2 surfaces. Figure 1 shows XPCS results where step flow processes produce oscillations in the correlations during three-dimensional (mounded) growth. There is no change in the reflected X-ray intensity as the steps advance. However, each step advances by a distance equal to the local terrace length, leading to a self-similar configuration of the surface for time all intervals separated by the monolayer deposition time. These effects are analogous to oscillations in homodyne correlations under flow conditions or during elastic relaxation, which occur if there is a velocity gradient.[R1] The experimental correlation oscillations are in good agreement with a one-dimensional model for step propagation, where mounds are formed due to significant step-

edge barriers (Erlich-Schwoebel effect).[R2] A manuscript on these results is currently under review.[P1]

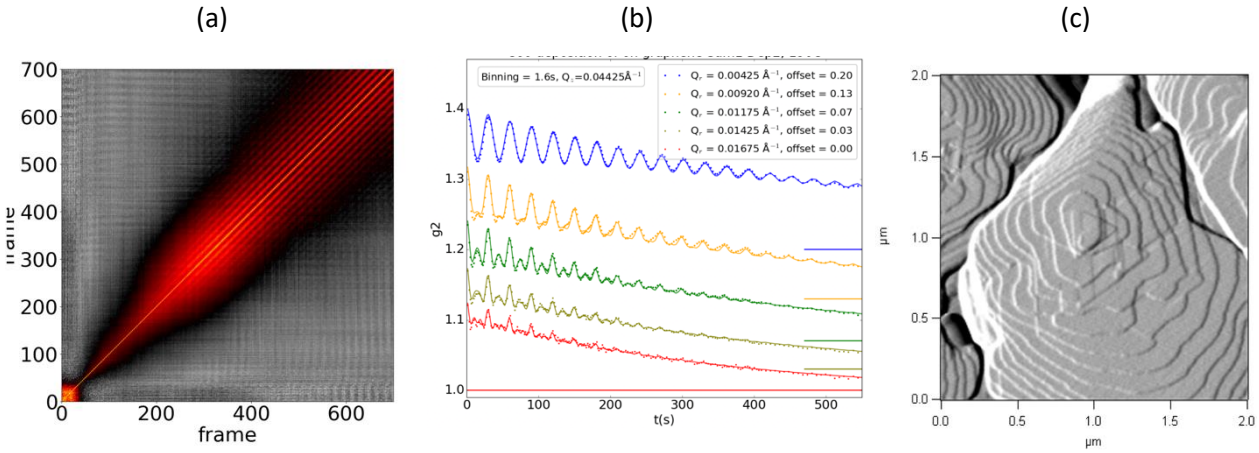

Figure 1. XPCS and AFM results for C_{60} thin films deposited on a SiO_2/graphene substrate. (a) Two-time correlations for deposition at 210°C at a rate of 1.6 nm/min. The growth was started at frame 25, and the transition to the steady-state behavior is complete near frame 500 (1.6 sec/frame). (b) One-time correlations in steady-state for growth at 190°C. (c) Atomic Force Microscope amplitude scan showing monolayer steps on a single mound that is bounded by deep grooves. The deposition was done in two steps (210°C, followed by 190°C) to a final thickness of 172 nm.

A manuscript on XPCS studies of ripple formation and dynamics during ion bombardment has also been submitted for publication. This study examines the classic case of ion beam rippling of SiO_2 surfaces. The early stages of patterning are shown to be consistent with linear stability theory. However, in the late stages of observed patterning, the surface reaches a steady state dynamical behavior whose length-scale dependence is shown to be consistent with simulations of the anisotropic Kuramoto-Sivashinsky equation. In addition, it is found that the surface ripple velocity, an important parameter of the ion-driven surface evolution, can be measured with XPCS using an inhomogeneous ion beam.

Future Plans

In the growth experiments, we plan to continue examining growth of organic small molecule thin films and we will extend this work to molecules in the perylene family. In particular, diindenoperylene (DIP) is a molecule that tends to grow in a layer-by-layer mode in the early stages. We expect to observe a transition from two-dimensional growth to three-dimensional growth at later times. It will be interesting to examine the dynamics of the surface as the surface morphology makes the transition from one regime to the other. This is in contrast to the case of C_{60}, which forms three-dimensional mounds almost immediately. In ion bombardment, we will study surface dynamics during Ar^+ ion bombardment of Si above and below the critical angle for pattern formation and including bombardment at high temperatures where the surface remains in a crystalline state. Most of our XPCS studies of ion bombardment

so far have been performed with the substrate at room temperature, where the ion bombardment produces a thin amorphous layer at the surface.

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

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

Program Scope

Exploring two-dimensional electron 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

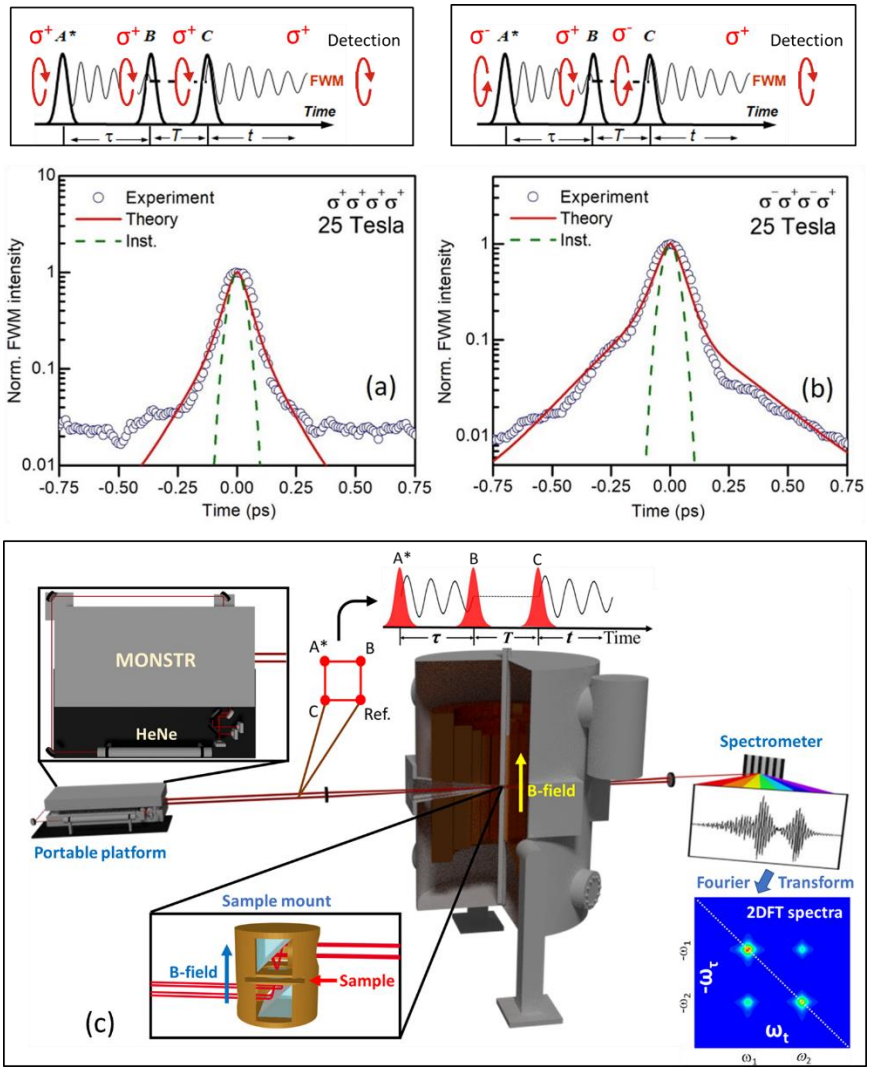


Figure 1: Time-integrated FWM intensity as a function of the time delay τ at 25 Tesla for two different polarization sequences (σ+ σ+ σ+ σ+) **(a)** and (σ- σ+ σ- σ+) **(b)**, where the individual polarizations correspond to the laser pulses A*, B, C and detection, respectively. The time delay T between pulses B and C is kept fixed at zero femtoseconds. Blue circles are the experimental data, whereas the red lines are the time integrated FWM calculated using time-dependent DFT [1]. **(c)** Schematic of the experimental setup. The three laser beams are provided by the multidimensional optical nonlinear spectrometer (MONSTR) to generate the two-dimensional spectra [2]. The magnetic fields up to 25 Tesla are applied perpendicular to the sample surface in Faraday geometry, facilitated by the sample mount.

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 hundreds of meV 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.

Recent Progress

We measured time-integrated FWM on monolayer $MoSe_2$ at the presence of magnetic fields up to 25 T shown in Fig. 1 (a-b). We observe an increase in the decay time with increasing magnetic fields due to the reduced scattering leading to less decoherence. At zero magnetic fields the time-integrated signal is symmetrical with the negative delay decay time equaling the positive decay. Significant changes are observed when excitons of opposite spins in different valleys are excited, leading to much longer dephasing times for intervalley biexcitons despite the large differences in crystal momenta. In external magnetic fields, we observe interesting ordering of the electrons and holes by means of strong Coulomb interactions into a four-particle correlated state. The optical dephasing takes place in a four-particle ordered state comprised of intervalley biexcitons, creating favorable conditions for interesting new states of matter, including the creation of multiple exciton complexes, exciton superfluidity, and biexciton condensates [1].

The results were published in Nature Communications **9**, 3720 (2018) and highlighted in Nature Nanotechnology **13**, 982 (2018).

We analyzed the optical transmission/absorption properties of exfoliated TMD samples for different numbers of layers, ranging all the way from monolayers to bulk-like configurations with more than a hundred layers [3]. We carefully characterize the respective sample thicknesses using atomic force microscopy; for thinner samples, photoluminescence and Raman spectroscopy were additionally used. The absorption was quantitatively measured for the A exciton resonance by carefully measuring transmission and reflection simultaneously, and by taking into account all the possible losses. The resulting optical density as a function of sample thickness deviates significantly from the Beer–Lambert law (Fig. 2). We model the observed effects employing the semiconductor Maxwell–Bloch equations for a classical optical field interacting with equidistantly spaced two dimensional layers, where the A excitons are assumed to be well localized within the individual layers.

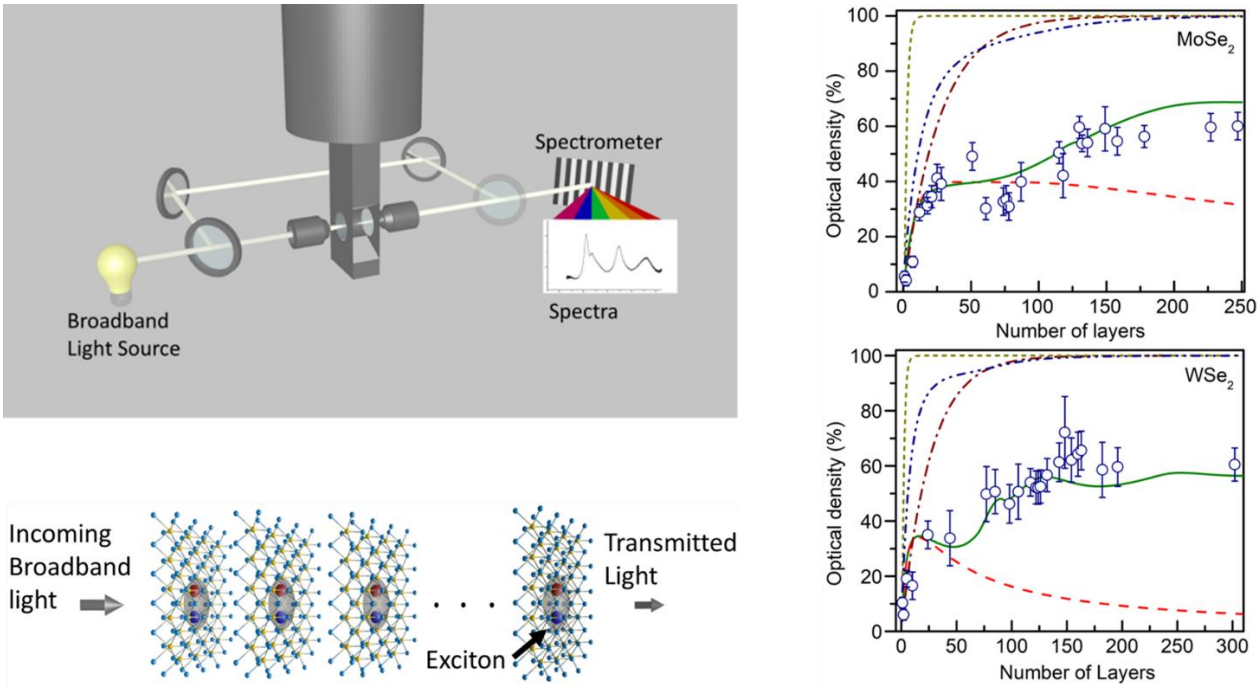


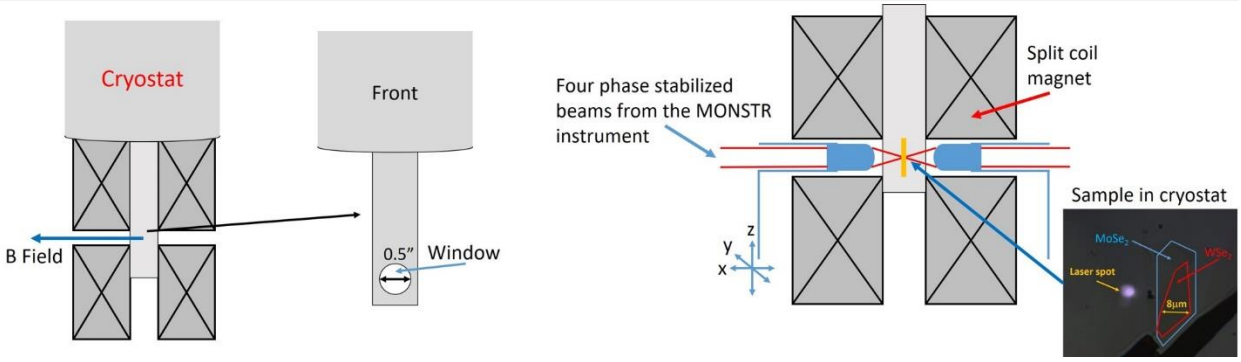
Figure 2: Experimental setup (Right top): The exfoliated samples are held at 5 K inside a cryostat designed for simultaneous measurement of the transmitted and reflected light. (Right bottom) Schematic of the light propagation through the samples. Quantitative optical density at the exciton absorption energy for (Left top) $MoSe_2$ and (Left bottom) WSe_2 as a function of the number of layers. The blue circles are the measured optical density values. The green solid lines show the theoretically computed peak absorptions for the full geometry, and the red dashed lines show the absorption in a superradiant (SR) geometry where the interlayer spacing has been artificially set to zero. The blue dashed-dotted lines show the extinction of the transmitted intensity (1-peak transmission). For comparison, we also show the expected extinction of the transmitted intensity assuming Beer's law, once based on monolayer extinction on a quartz substrate (short-dashed) and once based on the extinction of a monolayer embedded in a dielectric with the dielectric constant of the parent bulk material. Radiative coupling is needed in the theoretical calculations (green solid line) in order to reproduce the experimentally observed light propagation as a function of layer thickness, which deviates drastically from the curves calculated using Beer's law (dark yellow and brown dashed lines).

To validate the model assumptions, we carefully measure the excitonic Bohr radii in the two representative bulk TMDs using the diamagnetic energy shift of the excitonic resonance at magnetic fields up to 65 T. The exciton wave functions obtained from these measurements are well localized within the layers. The theoretical calculations reveal that the experimentally observed variation of the resonant optical absorption can be uniquely attributed to the superradiant coupling between the excitons in the different TMD layers. The results were published in Optica **5**, 749 (2018).

Instrumentation development:

Magnet development for high spatial resolution measurements: One very important challenge in working with TMD materials and devices is their small size. Typical TMD based devices are in the range of few to few tens of microns. This limitation makes it difficult to perform spectroscopy measurements. In particular, the 2DFT phase stabilized measurements using the MONSTR instrument are limited in terms of spatial resolution by the diffraction of the focusing lens, which is typically 30-100 microns. We have developed new instrumentation to address this limitation. We use a combination of pinholes and microscope objectives and have achieved a laser

Figure 3: Schematic of the magnet allowing high spatial resolution measurements. The specially designed magnet allows for the microscope objectives to be inserted and the sample can be located within their working distance.



spot size of few microns shown in Fig. 3. The figure also shows a bilayer sample comprised of $MoSe_2$ and WSe_2 atomic monolayers. The high spatial resolution will allow us to comfortably perform experiments on micron size samples. Furthermore, the optical magnets available at NHMFL do not allow for high spatial resolution measurements. The reason for this limitation is that the distance of the sample from the outer window is large and therefore makes the usage of microscope objectives impossible. As a result, the 2DFT measurements at high spatial resolution are limited to zero magnetic fields or very low fields. In order to perform 2DFT measurements at high fields, we have developed a new magnet that allows 2DFT and other optical spectroscopy measurements at high spatial resolution. The magnet is shown in Fig. 3. We will use the methods described to achieve high spatial resolution using the phase-stabilized MONSTR setup.

Broadband ultrafast terahertz spectroscopy in the 25 T Split Florida-Helix: We have developed a broadband (0.3–10 THz) optical pump-terahertz probe spectrometer with an unprecedented combination of temporal resolution (≤200 fs) operating in external magnetic fields as high as 25 T using the new Split Florida-Helix magnet system. Using this new instrument, we measure the transient dynamics in a gallium arsenide four-quantum well sample after photoexcitation at 800 nm. The results were published in Reviews of Scientific Instruments **89**, 073901 (2018).

Coherent two-dimensional Fourier transform spectroscopy using a 25 Tesla resistive magnet: We performed the first two-dimensional Fourier transform spectroscopy measurements using an optical resistive high-field magnet on GaAs quantum wells. Magnetic fields up to 25 Tesla can be achieved using the split helix resistive magnet. Two-dimensional spectroscopy measurements based on the coherent four-wave mixing signal require phase stability. Therefore, these measurements are difficult to perform in environments prone to mechanical vibrations. Large resistive magnets use extensive quantities of cooling water, which causes mechanical vibrations, making two-dimensional Fourier transform spectroscopy very challenging. A self-contained portable platform was used to setup the experiments within the time frame provided by a user facility. Furthermore, this platform was floated above the optical table in order to isolate it from vibrations originating from the magnet. Finally, we collected two-dimensional Fourier transform spectra at magnetic fields up to 25 Tesla and demonstrate the utility of this technique.

Future Plans

Although earlier studies have demonstrated the unique valley- and spin-polarized Landau level structure in monolayer WSe_2, the quantum Hall regime has not been achieved because the cyclotron frequency is comparable to the disorder broadening in the material. To access the quantum Hall regime, higher quality devices are required, which are now becoming available [4]. Another avenue is to perform magneto-optical spectroscopy under a higher magnetic field at the NHMFL (> 20 T). Under these conditions the Landau levels are expected to be spectrally resolved, and we would be able to probe the fully valley- and spin-polarized Quantum Hall State with FWM and 2DFT spectroscopy.

The TMD monolayer system becomes more interesting when two monolayer of the same kind or of different kind are brought together to form a bilayer or vertical heterostructure. Similar to independent monolayers, upon optical excitation excitons are formed in the individual layers, but because of the type-II band alignment indirect excitons are also formed, where the electron and hole reside in two different layers. Depending on the TMD materials chosen, excitons can experience a Moiré potential due to local variation in the atomic positions between the two layers. This can occur due to the lattice constant mismatch or a small twisting angle between the layers. Such energy modulations can be large and can be used to engineer exciton band structures. The Moiré potential can be combined with an external magnetic fields to achieve topological energy bands. Samples designed by our collaborators would be probed with 2DFT spectroscopy at high magnetic fields.

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Nanoscale Structure and Motion of Non-collinear Spin Phases

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*This program is part of the **Non-Equilibrium Magnetic Materials FWP** at LBNL*
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Sujoy Roy, Advanced Light Source, Lawrence Berkeley National Laboratory
Eric Fullerton and Sunil Sinha, University of California, San Diego
Josh Turner (DOE EC awardee 2018) and Matt Seaberg, LINAC Coherent Light Source, SLAC
Ben McMorran, Physics Department, University of Oregon
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Todd Hastings, Physics Department, University of Kentucky

Scientific scope

As part of the BES funded **Non-Equilibrium Magnetic Materials (NEMM)** FWP at LBNL, with its broad mission to understand the fundamental science of magnetic materials and phenomena enabled by interfaces and spin-orbit coupling (SOC), this program focuses on the application of emerging soft x-ray tools to probe phases of magnetic films that exhibit non-collinear and topologically distinct spin structures, e.g., skyrmions and helical domain walls, utilizing the unique capabilities at the Advanced Light source at LBNL and the LINAC Coherent Light Source at SLAC.

We couple the high spin contrast of near-edge soft x-ray spectroscopies to imaging and scattering modalities to probe nanoscale spatial and temporal correlations in these spin structures. We have also worked with primary collaborator McMorran to apply Lorentz transmission electron microscopy (LTEM) to these same systems. An important recent focus, as part of the NEMM program, has been materials in which several spin/magnetic interactions are at energy comparable to k_BT. Such interactions are thermally activated and make important contributions to the system entropy, and as a result, their collective interactions can conspire to support exotic spin phases. We are particularly interested in magnetic alloy films, since their properties can be easily tuned by varying the film thickness composition, and moreover they are readily deployed in functional thin film structures.

Example: Amorphous FeGd alloy films

The first such systems we have studied are amorphous FeGd films. Both Gd and Fe have weak magnetic anisotropy, and we operate at a composition and temperature about 100K below where the Fe and Gd spins compensate. In this situation, the saturation magnetization is small and the shape anisotropy the effective scalar exchange interaction occurs at modest energy scale as well. Finally, the Dzyaloshinskii-Moriya vector exchange interaction is also weak. Several of these interactions can be tuned with alloy composition and film thickness, and interesting phases are embedded in a high-dimensional space. In a single film, we have observed skyrmions, biskyrmions, “onion” domains, and stripes with varying degrees of structural order and spin canting (see Fig. 1). In some cases, we have developed field protocols to favor a particular structures. The location of these phases in (T,H) phase diagrams is remarkably sensitive to film thickness and alloy composition.

Skyrmions are topologically protected spin vortices and are predicted to exhibit unusually facile nanoscale motion. We have studied this motion in a-FeGd at vastly different time scales: slow average motion punctuated with intermittent cascades driven by varying the applied field, fast motion driven

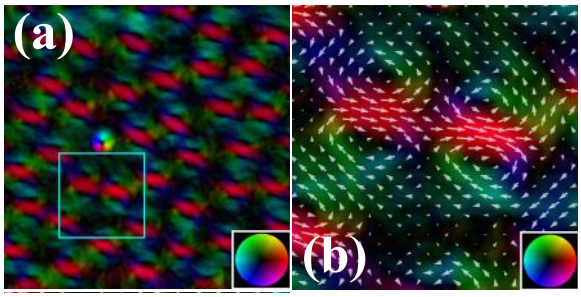

Fig. 1: Left: Lorentz TEM (LTEM) image of a weakly perpendicular a-FeGd showing a lattice of biskyrmions with a low concentration of single skyrmion "defects". This is produced with a particular field protocol that involve applying a small in-plane component as the magnetization is reduced from saturation. Right: Blow up of the boxed region on the left showing the induction near two skyrmion bound pairs, or biskyrmions. The red regions are where in-plane spins of the two skyrmions are shared, which reduces the anisotropy energy; this is the glue that binds skyrmions, which competes with the weak dipolar repulsion between skyrmions.[1]

with an rf field in ferromagnetic resonance (FMR), and fast equilibrium fluctuations measured with a new x-ray photon correlation spectroscopy (XPCS) technique using ultrafast pulses from the LCLS (Fig. 2).

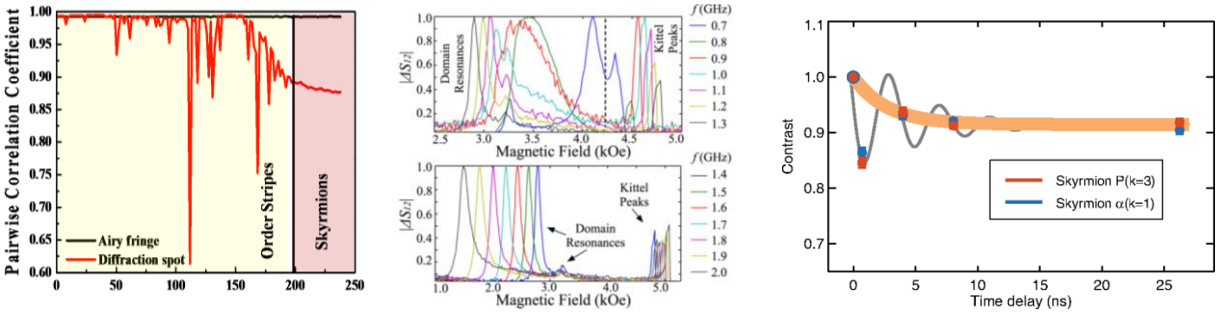

Fig. 2: Skyrmion nanoscale motion in a-FeGd films on a wide range of time scales. Left: Magnetization cascades in stripe and skyrmion phases during a quasi-static field scan (Singh, et. al., submitted). Middle: Driven motion of the skyrmion phase with FMR.[2] Right: Nanosecond fluctuations of the skyrmion phase measured with a new 2-pulse XPCS technique at the LCLS.[3]

Future directions

a) Instrumentation development harnessing the unique capabilities at LCLS-II and ALS-U

Our plans for the future developments in x-ray scattering techniques include

- In addition to helping develop the 2-pulse XPCS approach at LCLS and LCLS-II, Sujoy Roy is leading the commissioning a new XPCS beamline and end station at the ALS in Berkeley. Roy, Kevan, and others also have funding from the BES Scientific User Facilities Division Detector R&D program to develop a new class of fast soft x-ray XPCS detectors that will fill in the intermediate (ms – ns) time domain. This will be of major benefit to this task in the NEMM program.
- We have developed techniques to manipulate and measure the orbital angular momentum of coherent soft x-ray beams, and will use this capability in new scattering contrast mechanisms.

b) Scientific topics within the NEMM FWP at LBNL

- Continuing work on a-FeGd films. This will focus on current control of spin phase and domain motion, as well as continuing study of fluctuations using XPCS and related techniques.
- New work on a-FeGe films. In collaboration with the Hellman group, we have initiated study of a-FeGe films and have observed unusual but not yet fully understood spin structures at

compositions where the films are very weakly ferromagnetic. Crystalline FeGe is a known skyrmion system, and we are anxious to understand the relationship between the structures we have observed and the skyrmions in bulk FeGe, and to tune the film thickness and composition to probe the entire phase diagram in more detail.

- New work on a-TbCo films. The NEMM group has also initiated a study of a-TbCo near the spin compensation temperature and we are anxious to look for unusual spin structures in this system with high Tb magnetic anisotropy.

- With collaborator Hastings, we have an emerging interest in topological spin structures in systems with spin frustration. We have recently studied superparamagnetic fluctuations in artificial spin ices, and look forward to extending those studies to spin ice and quantum spin liquid materials.

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Structural Dynamics in Functional Materials

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Program Scope

This FWP is focused on understanding the role structure and dynamics play in the functionality of materials. Ultrafast, *in-situ* and *in-operando* approaches are carried out to probe these dynamical processes as they occur, across a broad range of applicable time-scales and length-scales extending down to atomic-scale motions and femtosecond time-scales and up to the mesoscale. We seek to engineer and manipulate these processes with the goal of inducing novel metastable and non-equilibrium states of matter with unique functional properties. The research scope is organized under two main themes: (1) probing dynamic microscopic interactions (e.g. electron-phonon coupling, phonon-phonon interactions, ion-lattice coupling) and (2) generation and visualization of metastable phases, which in turn builds directly on (1). These interconnected themes inherently involve studies of materials at phase boundaries, dynamic transition states, and the role of heterogeneity and span length-scales from atomic-to-mesoscale. Measurements of the first atomic/ionic steps associated with how these transformations occur are key to understanding these intrinsically dynamic processes.

Recent Progress.

Time-varying shear strain as an ultrafast symmetry switch in a Weyl semimetal

E. Sie et al., Nature (2018) (in press).

Topological materials provide a novel platform to pursue exotic physics from the seemingly distant field of particle physics in condensed matter systems, such as Weyl fermions. This has led to a worldwide effort focused on discovering new topological quantum materials. One prime example is WTe_2, which is a layered transition-metal dichalcogenide (TMD) that crystalizes in a distorted hexagonal net with an orthorhombic

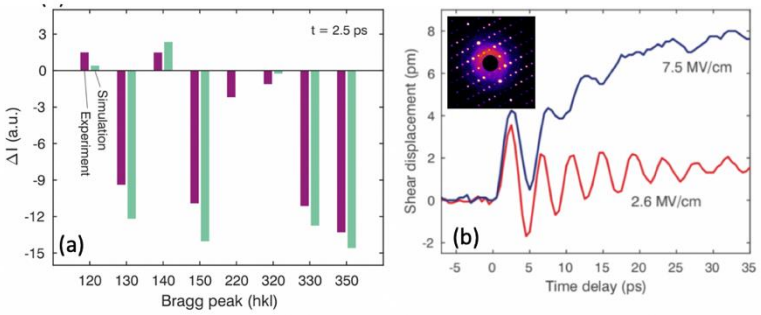

Fig. 1. (a) Measurement of many Bragg peaks enables observation of THz-driven interlayer shear mode occurring along the b-axis of WTe_2. (b) At high fields in a THz pump / UED probe experiment we switch the system from a non-centrosymmetric to a centrosymmetric phase, accordingly modulating the topological properties on picosecond time-scales.

unit cell. The lack of inversion symmetry in this material leads to a topological semimetal that was predicted and experimentally verified with type-II Weyl points (WPs), which can be manipulated through atomic-scale lattice distortions. In recent work, we demonstrate that terahertz (THz) light pulses can be used to induce THz frequency interlayer shear strain in the Weyl semimetal WTe_2 with large strain amplitudes, as crystallographically determined using relativistic electron diffraction, leading to a topologically distinct metastable phase. Separate nonlinear optical measurements indicate that this transition is associated with a symmetry change to a centrosymmetric, topologically trivial phase. We further show that such shear strain serves as an ultrafast, energy-efficient means to induce more robust, well-separated Weyl points or to annihilate all Weyl points of opposite chirality. This work defines new possibilities for ultrafast manipulation of the topological properties in solids and for a topological switch operating at THz frequencies.

Disorder and entropic effects of phase transitions viewed on ultrafast timescales

S. Wall et al., Science **362**, 572 (2018)

Ultrafast structural transitions are usually described in terms of a few long-wavelength phonon modes and it is assumed that the system evolves along a potential surface connecting the initial and final structures which also determines the speed of the photoexcited transition. However, this assumes a coordinated motion along a well-defined reaction coordinate and ignores the role of disorder and entropy, which are thought to develop on slower timescales, even though entropy may be the driving factor in the thermodynamic transition. A solid-solid phase transition where the symmetry of the crystal is raised (e.g. from M1 to R in VO_2) as the temperature increases can be dominated by either a displacive or an order-disorder process. To date, all attempts to measure the "molecular movie" of the dynamics of a phase transition at the atomic scale have exploited Bragg scattering, which can only measure the average motions of atoms and is insensitive to deviations from the average reaction coordinate. Using femtosecond pulses from an FEL, we measure the full x-ray scattering pattern, containing discrete Bragg peaks as well as the diffuse continuum between them. We use this approach to show that the lattice entropy of photoexcited VO_2, in the form of ultrafast vanadium disordering, can reach its equilibrium value on a timescale comparable to a single atomic oscillation.

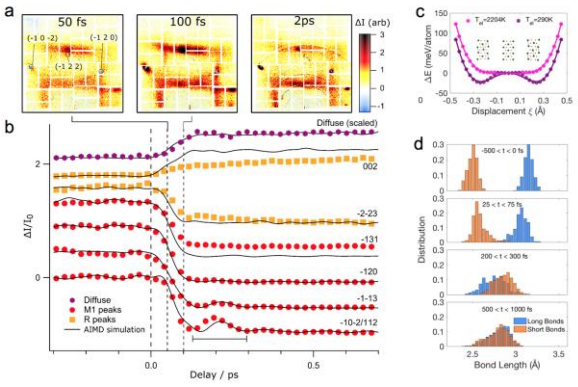

Figure 2. (A) Snapshots of the increase in the diffuse intensity ΔI(Q, t).(B) Temporal evolution of selected Bragg peaks and integrated diffuse scattering signal compared to AIMD simulations (solid lines). (C) Effect of photoexcitation on the potential for the V-V dimerization coordinate. (D) Distribution of dimer bond lengths from ab-initio molecular dynamics.

Our results show that the structural transformation in VO_2 occurs along many concurrent degrees of freedom spanning a large phase-space (See Fig 2), and thus a complete description must extend

beyond that of a single order parameter or discrete set of displacements. The rapid, large-amplitude disordering observed here is caused by the flatness of the photoexcited potential of the Vanadium dimers, and is intimately related with the high entropy of the rutile phase, but the implications of our findings extend well beyond the VO_2 system. In particular the role of disorder has been neglected in many ultrafast solid-solid phase transitions, even though the ultimate control of properties on demand relies on a reversible pathway between the two states. Our findings suggest that disorder may play an important role in some materials and that a description in terms of a single degree of freedom is incomplete. Understanding whether disorder plays a general role in vibrationally excited solids could ultimately provide a new perspective on how to control matter.

<u>Mesoscale mapping reveals new transport mechanisms</u>

Y. Li et al., Nat. Mater. **17**, 915 (2018)

Phase transformations driven by compositional change require mass flux across a phase boundary. In some anisotropic solids, however, the phase boundary moves along a non-conductive crystallographic direction. One such material is Li_XFePO_4, an electrode for lithium-ion batteries. With poor bulk ionic transport along the direction of phase separation, it is unclear how lithium migrates during phase transformations. Here, we show that lithium migrates along the solid/liquid interface without leaving the particle, whereby charge carriers do not cross the double layer. X-ray diffraction and microscopy experiments as well as ab-initio molecular dynamics simulations show that organic solvent and water molecules promote this surface ion diffusion, effectively rendering Li_XFePO_4 a three-dimensional lithium-ion conductor. Phase-field simulations capture the effects of surface diffusion on phase transformation. Lowering surface diffusivity is crucial towards supressing phase separation. This work establishes fluid-enhanced surface diffusion as a key dial for tuning phase transformation in anisotropic solids. It also provides new microscopic insights on how lithium migrates at the mesoscale can guide the engineering of safer, longer-lasting and higher-power batteries.

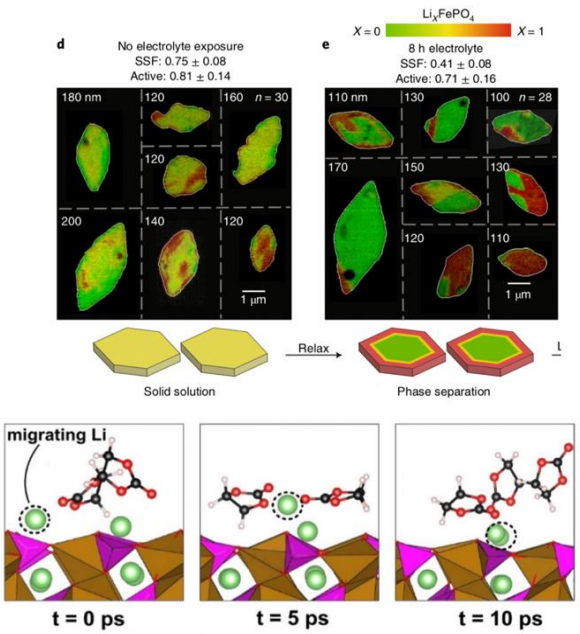

Fig. 3 (top) Real-time x-ray microscopy maps probing Li transport within Li_XFePO_4 nanoparticles, showing evidence for a new ion hopping pathway at the liquid-solid interface. (bottom) Ab-initio simulations identifying surface-mediated ion hopping mechanism occurring on ps time-scales.

Future Plans

Ongoing efforts are focused on a number of new directions developing from the above-mentioned work, all focused on ionic dynamics. We are investigating ion-intercalation-driven structural

phase transitions in the same 2D topological materials that we have studied via UED and have found new evidence for reversible structural transformations occurring on rapid time-scales, with current investigations focused on elucidating the corresponding symmetry changes and their mechanism. We are applying the suite of ultrafast structural characterization tools noted above to understand nonlinear phonon-phonon coupling processes and associated anharmonic interactions. These same probes are also being applied to studies of the hybrid perovskites, investigating the microscopic charge lattice coupling processes that underlie their unique functional properties. We are also extending the above-mentioned work on VO_2 to study switching dynamics in a range of phase-change and resistive switching materials, driven not only by light but by pulsed electric fields, coupling structural probes to *in-situ* monitors of the coupled electronic modifications that occur. Additionally, we are pushing above-mentioned work on ion hopping mechanisms in multiple new directions. THz pump, optical and x-ray probe studies are focused on measuring these processes directly in a range of ion-conducting materials. X-ray ptychographic approaches are being applied to enable nanoscale imaging of these same events. Combining ptychography with spectroscopy, we aim to map chemical changes during ion reaction and diffusion, and to develop time-domain synchrotron scattering approaches as a new kind of structurally-sensitive ion impedance spectroscopy.

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X-ray studies of functional materials under extreme environments

Wendy L. Mao, SLAC National Accelerator Laboratory & Stanford University
Yu Lin, SLAC National Accelerator Laboratory
Arianna Gleason, 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. To realize this goal, our research efforts are directed toward tuning functionality in complex hybrid systems through understanding their atomic and electronic structures under extreme environments. By utilizing existing static compression techniques and developing new X-ray probes, we have focused on studying complex structures with multi-functionality by investigating the connections between the material's individual constituents, and work towards establishing mechanistic models to predict new structures and emergent properties in complex hybrid systems.

Through studying complex hybrid systems like organohalide perovskites and analog materials, we seek to understand key questions like: What are the essential parameters for controlling structural and electronic transitions in complex hybrid systems? How do subunits in the system like sublattices, individually or cooperatively, contribute to the creation of novel structures and phases and what is the length scale of various types of interactions? Can we access exotic electronic states? How do interfacial stresses from different material deposition techniques, grain size, and chemistry influence the bulk response of functional materials?

The proposed scientific activities rely on the continued development of static high-pressure capabilities and instrumentation. The main characterization techniques include high-pressure X-ray total scattering for obtaining a pair distribution function, spectroscopic nanoscale transmission X-ray microscopy, phase contrast imaging, and a suite of tools to measure optical and transport properties including Brillouin scattering, optical absorption and reflectivity measurements, ultra-high pressure resistivity and magnetic susceptibility diagnostics.

Recent Progress

We have been working on a number of static compression experiments to elucidate the relationship between structure and material properties in halide perovskites. A few highlights are discussed below.

We discovered a potential superconducting state in certain $MAPbI_3$ ($MA = CH_3NH_3^+$) samples. A sharp resistance drop at ~4 K was observed in the material above 70 GPa, which can be further suppressed by applying a magnetic field. XRD measurements exclude the possibility of sample decomposition and suggest that the observed electronic behavior is intrinsic to $MAPbI_3$ itself. However, this electronic behavior can only be observed in certain $MAPbI_3$ samples. $MAPbI_3$ is a defect-benign host and found to be easily self-doped to be either n-type or p-type semiconductors. We are carefully tuning the growth conditions and plan to pin down the material's intrinsic properties in inducing superconductivity and understand how different carrier types affect the charge transport properties.

We achieved a potential indirect-to-direct optical transition in a lead-free bismuth-halide double perovskite. Upon mild compression, the material exhibits a significant PL intensity enhancement up to an order of magnitude along with a shortened PL lifetime. We are working towards understanding whether the modulated defect states and/or motions of the halide ions contribute to the optical transition.

To aid in understanding the evolvement of ion motions and local structures with compression, we have been developing high-pressure pair distribution function (PDF) measurements on halide perovskites, and very high-quality PDF patterns up to 10 GPa have been successfully acquired. We have been applying this technique to several $APbX_3$ ($A = Cs^+$, $CH_3NH_3^+$ and $CH(NH_2)_2^+$, $X = Br^-$, I^-) perovskites with different A-site cations and intend to answer the question of how the A-site cations, whose effects are usually neglected, contribute to the dramatic changes of the materials structural, optical, electronic, and opto-electronic properties at high pressure.

We have also made significant progress in continuing to develop static high-pressure imaging, including absorption-based 3D nanoscale transmission x-ray microscopy (nanoTXM) and spectroscopic nanoTXM at storage rings and FELs. Participation in LCLS beamtime for ultrafast X-ray imaging has revealed 2D and 3D feature reconstruction of features down to 30 nm resolution.

Future Plans

We will devote efforts to further optimize the DAC-sample geometry to enable PDF measurements up above 50 GPa. These measurements will allow us to improve our understanding of the observed pressure-induced metallization and partial amorphization in 3D halide perovskites.

We plan to survey a broader pressure-temperature space for creating new perovskites with enhanced performance. These improved perovskite materials are either not stable at ambient conditions or only theoretically predicted. We believe high pressure synthesis will open exciting opportunities for accessing these novel phases.

We will start efforts into examining low-dimensional halide perovskites at high pressure. This study will provide insight in understanding the length scale of specific types of interactions that contribute to the creation of novel structures and phases in hybrid perovskites. For instance, we will investigate atomically-thin and layer-controlled few-unit-cell-thick two-dimensional perovskites under static compression.

Further technical developments in ultrafast X-ray imaging are being pursued, including 2D and 3D reconstruction of features down to 30 nm resolution at 120 Hz rep rate on Si samples as a test case. These data are being used to develop a roadmap for fielding new ultrafast X-ray characterization tools at LCLS to image halide migration in hybrid perovskites.

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

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(i) Program Scope

Ultralow-power, high-performance nonvolatile memory and logic devices based on magnetic spin ("spintronics") are starting to make inroads into conventional computing, and represent a prime candidate for practical quantum technologies. However, fully exploiting the capabilities of new materials and technologies will require a detailed understanding of the underlying physics, as manifested by nanoscale dynamic magnetization properties. At present, our understanding of spin system interactions is crude and predominantly phenomenological: a comprehensive, self-consistent, microscopic model that rigorously includes the spin, electronic, photonic and phonon-degrees of freedom and their interactions 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. While the fundamental length- and time-scales for magnetic phenomena are nanometers (exchange length) and femtoseconds (exchange splitting), tools that enable the exploration of dynamics at these scales have only recently become available.

Ultrafast X-ray pulses make it possible to probe element-specific spin dynamics in multi-component magnetic systems, providing rich new information not accessible using visible light. However, until very recently, only large-scale synchrotron and X-ray free-electron laser facilities could view element-specific dynamics in magnetic materials — and could do this only with limited time resolution. In a complementary approach, we showed that tabletop, laser-based, high harmonic (HHG) beams can capture the fastest spin dynamics in magnetic materials and are unique as a probe of magnetic dynamics. In the past year, we made exciting progress. We also helped other groups in academe and national laboratories to duplicate our HHG capabilities.

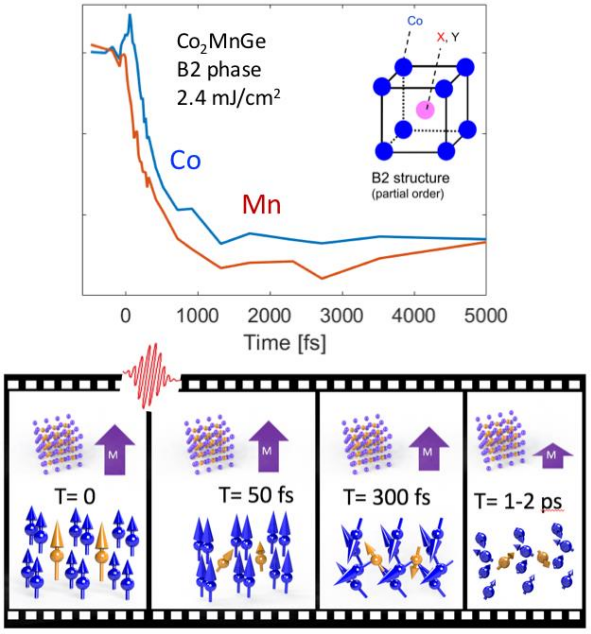

Fig. 1. (top) Ultrafast spin transfer from one magnetic sublattice to another in a Heusler alloy Co_2MnGe, that occurs during the femtosecond excitation pulse. The data shows that the magnetization of Co is enhanced, while that of Mn is reduced. This suggests optical excitation from one magnetic sub-lattice to another.

(ii) Recent Progress

Ultrafast optical-induced spin transfer in Heusler and ferromagnetic alloys [14, 16]: We made an unexpected discovery that light can excite spins in many materials on timescales much faster than previously thought, within <20fs to 50fs. In particular, in new work, we studied Heusler alloys[14] - that are exciting materials for future applications because they display a wide range of tunable electronic and magnetic interactions such as metallicity, ferromagnetism, superconductivity, and giant magneto-resistance. The coupled charge and spin dynamics in magnetic materials are among the fastest processes relevant to function, determining how fast one can manipulate the magnetic state. Our previous work had shown that light-induced spin dynamics in simple ferromagnets can occur on timescales 10x faster than previously suspected,

within 20fs.[1] However, the fundamental dynamics in Heusler alloys were expected to be slower than those of conventional ferromagnets, due to the presence of a blocked spin channel. In contrast to this prediction, we directly observe ultrafast spin transfer from one magnetic sublattice to another in half-metallic heusler alloy Co_2MnGe, that occurs during the timescale of the femtosecond excitation pulse. Ultrafast high harmonic pulses make it possible to simultaneously track the element-specific magnetic dynamics of Co and Mn as the half-metal Co_2MnGe undergoes ultrafast demagnetization. Our data shows that the magnetization of Co is enhanced, while that of Mn is reduced. This suggests optical excitation from one magnetic sub-lattice to another, which is also supported by density functional theory. The observed enhancement of ferromagnetic ordering demonstrates a response to laser manipulation within the time duration of the excitation pulse and provides a path towards logic applications such as switches that can operate on femtosecond or even attosecond timescales. We have also observed such ultrafast spin transfer in other ferromagnetic alloys.[16]

Critical Behavior within 20fs Drives the Out-of-Equilibrium Laser-induced Magnetic Phase Transition in Nickel [1,2]: It has long been known that ferromagnets undergo a phase transition from ferromagnetic to paramagnetic at the Curie temperature, associated with critical phenomena such as a divergence in the heat capacity. A ferromagnet can also be transiently demagnetized by heating it with an ultrafast laser pulse. However, to date the connection between out-of-equilibrium and equilibrium phase transitions was not known, nor how fast the out-of-equilibrium phase transitions can proceed.

By careful fluence- and temperature-dependent studies using two ultrafast spectroscopy techniques (time-resolved HHG photoemission and time-resolved HHG magneto-optical Kerr spectroscopy), we for the first time definitively connect the physics of equilibrium phase transitions (usually probed using static probes), to ultrafast-laser-induced out-of-equilibrium phase transitions. The beautiful and unexpected discovery shown in Fig. 1 is that the same critical phenomena associated with equilibrium phase transitions (e.g. the divergence of magnetic heat capacity near the Curie temperature), also govern the out-of-equilibrium laser-induced phase transition. Based on our observations, we demonstrate that the transient electron temperature within the first 20 fs alone dictates the magnetic response and re-magnetization timescales. Most interestingly, the timescale we find for energy transfer from the laser to

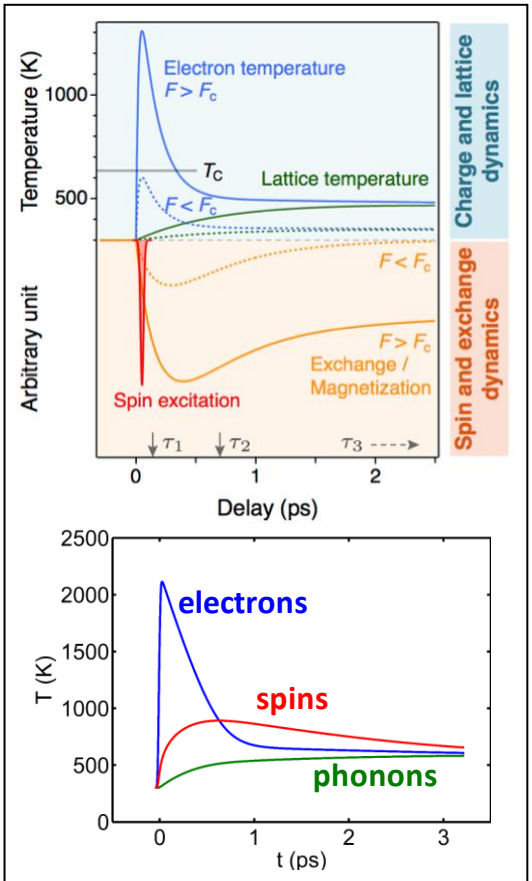

Fig. 2. New out-of-equilibrium spin state excited within 20 fs in Ni. (top) Schematic of the experimentally observed timescales of the charge, spin, exchange and lattice systems, using correlated EUV ARPES and MOKE data. The spin system absorbs sufficient energy within 20fs to subsequently proceed through the magnetic phase transition. (bottom) Previous understanding of the response of Ni to ultrafast laser excitation: it was presumed that the laser energy was first absorbed by the electrons, and later coupled to

the spin system is unexpectedly fast – within 20fs, which represents the first experimental evidence for a new timescale for spin excitation by a femtosecond laser.

Distinguishing Attosecond Electron-Electron Scattering and Screening in Transition Metals [5]: Electron-electron interactions are the fastest processes in materials, occurring on femtosecond to attosecond timescales, depending on the electronic band structure of the material and the excitation energy. However, to date it has not been possible to experimentally distinguish fundamental electron interactions such as scattering and screening. Here, we use sequences of attosecond pulses to directly measure electron-electron interactions in different bands of different materials with both simple and complex Fermi surfaces. By extracting the time delays associated with photoemission, we show that the lifetime of photoelectrons from the d band of Cu are longer by ~100 attoseconds compared with those from the same band of Ni. We attribute this to the enhanced electron-electron scattering in the unfilled d band of Ni. Using theoretical modelling, we can extract the contributions of electron-electron scattering and screening in different bands of different materials with both simple and complex Fermi surfaces. Our results also show that screening influences high-energy photoelectrons (≈20 eV) significantly less than low-energy photoelectrons. As a result, high-energy photoelectrons can serve as a direct probe of spin-dependent electron-electron scattering by neglecting screening. This can then be applied to quantifying the contribution of electron interactions and screening to low-energy excitations near the Fermi level. This information provides unique information for a host of quantum materials.

Participation in experiments at LCLS and other DOE-related collaborations [17, 18]: Our group was part of a large team working with Tom Silva (NIST) and Erik Fullerton (UCSD) that used the LCLS XFEL to show: 1) that spin transport leads to non-uniform magnetization dynamics of domains, while domain walls are unaffected by spin currents; and 2) we also discovered a sub-ps excitation mechanism for surface acoustic waves in thin films. Publications are in preparation.

(iii) Future Plans

Speed Limits and Mechanisms underlying Fast Spin Dynamics: We will build upon our ability to generate linear and circular HHG beams to address fundamental questions of magnetism, and also to probe more complex materials e.g. Heusler-alloy-based half-metals, multiferroics, molecular magnets, films of Ni, Fe and Co, and in-plane and perpendicular-magnetized thin films and multilayers. To best inform theory and extensively test our conclusions regarding the materials outlined above, data from as many different experimental configurations, using polarization ranging from linear to circular, is necessary. Collaborators (both experiment and theory) include Peter Oppeneer. Tom Silva, Justin Shaw, Hans Nembach, Eric Fullerton, Martin Aeschlimann, Stefan Mathias, Olle Erikkson, Paul Canfield, Jak Chakhalian and others.

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Novel Terahertz-Induced Quantum States Probed with Ultrafast Coherent X-Rays

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James Freericks, Georgetown University
Rohit Prasankumar, Los Alamos National Laboratories
David Reis and Dr. Mariano Trigo, SLAC National Accelerator Laboratory

Program Scope

This new project is aimed at exploring control over quantum phases of matter using light in the terahertz and long-wavelength infrared spectral regions (roughly 0.2-20 THz frequency range) and using ultrafast x-ray diffraction, spectroscopy, and imaging techniques enabled by X-ray free-electron lasers (XFELs), as well as tabletop probes, to monitor the dynamic material responses to THz/LWIR (hereafter sometimes simply "THz") excitation. The electric and magnetic fields of THz pulses will drive lattice vibrational, spin, and electronic degrees of freedom in controlled ways that guide crystals from their structural, magnetic, and electronic states in one phase toward and in some cases into their corresponding states in a new phase. The results will be incorporated into first-principles theoretical descriptions of the driven phase transitions, with predictive power that may guide the discovery of new phases through proper design of the driving fields. Improved experimental capabilities and fundamental understanding may yield practical applications in ultrafast switching of electrical, magnetic, and optical properties, as well as applications in novel material fabrication.

A wide range of quantum materials will be studied including soft mode systems (quantum paraelectrics) in which lattice vibrations will be driven by THz fields; multiferroics, in which THz fields will drive both vibrational and spin degrees of freedom; correlated electron systems including nickelates, cuprates, and transition metal chalcogenides, in which phonons, magnons, and electronic modes will be driven; and topological insulators and topological crystal insulators whose time-reversal or mirror symmetries can be modulated by THz magnetic or electric fields respectively. Single-cycle THz fields may drive far-from-equilbrium excursions that lead to new transient phases whose formation and return to the initial phase will be monitored, or that lead to long-lived new phases. For the latter case, methods will be developed that permit x-ray measurements of the dynamical transformations in real time, on a single-shot basis. Nonresonant (Floquet) excitation with multicycle THz fields may drive systems back and forth between substantially different states to reveal collective responses that only occur under rapid modulation.

The work will address the research opportunity "Discovering novel quantum phases through coherent light-matter coupling," identified in the DOE BES Roundtable report on Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science. The report invites exploration of how light can be used to create novel states of matter with unique properties that do not exist in equilibrium. The report specifically describes the promise of THz fields for manipulating

quantum phases in many material classes, the use of both resonant and nonresonant excitation to induce novel quantum states, and the value of cross-cutting measurements such as simultaneous x-ray diffraction and x-ray absorption spectroscopy or simultaneous x-ray and optical probes.

Recent Progress

Given the recent start of the project, here we describe prior experimental and theoretical results that put us in position to conduct the research. The project has been enabled experimentally by two parallel developments. First, the availability of femtosecond hard and soft coherent x-ray pulses at XFEL sources, initially at the LCLS and more recently at several other locations around the world, has enabled incisive probing of dynamical changes in lattice structure and charge/spin/orbital orders associated with quantum material structural, electronic, and magnetic phase transitions [Buzzi 2018]. Second, intense tabletop pump pulses in the ~0.1-10 THz spectral range have become available [Yeh 2007, Vicario 2015] and these, along with LWIR fields generated by established difference-frequency mixing methods, have been used to drive far-from-equilibrium excursions including electronic and structural phase transitions in several quantum materials [Liu 2012, Rini 2007, Mitrano 2016, Fausti 2011, Dienst 2013]. The two capabilities have recently been combined for x-ray probing of THz/LWIR-driven quantum phase transitions [Gray 2018, Esposito 2017]. The capabilities for driving of quantum phase transitions are illustrated in Fig. 1 which shows recent unpublished Nelson group results. THz fields drive the soft phonon mode in strontium titanate (STO) to sufficient amplitude to induce a

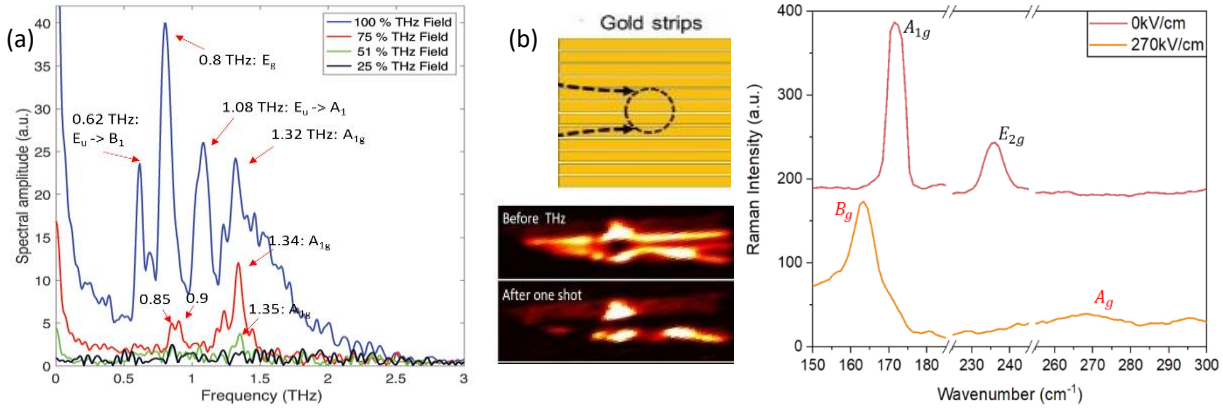

Figure 1. (a) Fourier transforms of THz-induced optical birefringence (THz Kerr effect) signals in STO at 10 K reveal new phonon peaks at high THz E field levels. The new peaks are known to appear in the low-symmetry ferroelectric Raman spectrum [Fleury, 1968]. Similar results were observed using optical SHG as a probe, indicating both Raman and IR activity as expected for a non-centrosymmetric FE phase. Note the highly nonlinear THz-induced response, with the new peaks growing in sharply when the THz field level is increased from 75% to 100% of its peak value of 500 kV/cm. MD simulation results (Rappe group, U Penn) are consistent with the experiments. (b) THz-induced permanent 2H → 1T′ phase transition in single-layer $MoTe_2$. (Left, top) Schematic illustration of parallel gold lines with 1.5-μm gaps between them, providing ~10x THz field enhancement in the gaps. (Left, bottom) SHG images of a $MoTe_2$ flake that was placed over a gap, before and after irradiation just once by a single-cycle THz field with enhanced amplitude of ~5 MV/cm. SHG signal and the 2H Raman spectral peaks (Right, top) disappeared from the region of the strongest THz field after just one shot. The 1T′ phase Raman peaks (Right, bottom) grew in upon irradiation with additional THz pulses. DFT calculations (Kaxiras group, Harvard) indicate an intermediate H* phase.

transition from the low-temperature quantum paraelectric phase to a transient ferroelectric phase, as shown by the appearance of new modes in optical measurements that are associated with the ferroelectric Raman spectrum [Fleury, 1968]. In single-layer $MoTe_2$, metamaterial-enhanced THz fields generate carriers that result in an irreversible transition from the initial 2H phase to the topological insulator 1T′ phase [Peng 2017, Tang 2017, Wang 2017a], likely through an intermediate H* phase structure. These recent results illustrate that quantum phase transitions may be driven effectively through excitation of electronic or lattice vibrational responses with THz as well as LWIR fields. Nonlinear magnon responses also have been driven recently by THz fields, and two-dimensional THz spectroscopy of magnons has been demonstrated by Nelson [Lu 2017]. The results suggest that magnon modes may be driven by THz magnetic fields to induce or assist quantum phase transitions.

Development of novel x-ray methods and the use of x-ray probes of quantum materials have been key components leading to the present project. Fourier-Transform Inelastic X-ray Scattering (FT-IXS) was developed and refined by Reis and Trigo [Trigo 2013, Zhu 2015] to enable direct time-resolved measurement of dynamical lattice deviations from perfect crystalline order. This information is not available in the diffraction peaks, which reflect the average long-range order of the crystal structure, or the Debye-Waller factor, which provides limited information about disorder. XFEL sources are sufficiently intense to permit measurement of the diffuse scattered intensity between Bragg peaks with femtosecond resolution following a pump laser pulse, revealing distinct time-dependent oscillations due to inelastic scattering from phonons at well resolved wavevectors q throughout the Brillouin zone. As with any time-domain approach, the frequency resolution of this measurement is in principle only limited to the inverse of the measured time-window, yielding extreme frequency resolution, particularly for low-frequency modes [Zhu 2015]. More importantly for our purposes, the dispersion obtained this way is that of the transient photoexcited state, and thus can be used to extract information on how electrons are coupled to the lattice [Jiang 2015] and on momentum-resolved phonon-phonon coupling matrix elements [Teitelbaum 2018]. Reis and Trigo have conducted FT-IXS measurements to date using optical pumping of electronic resonances and, in very recent work in collaboration with Nelson, using x-ray pumping of core transitions. In this project, we will integrate THz-LWIR pumping with FT-IXS measurement to drive optical phonon and magnon modes and directly observe their coupling to other lattice degrees of freedom.

The Prasankumar group has performed optical-pump, THz-probe (OPTP) experiments on the multiferroic material $TbMnO_3$ to track the temporal evolution of electromagnons, magnetic excitations driven by the electric field of light that are signatures of entangled electric and magnetic order. Electromagnon properties can shed light on the magnetoelectric (ME) coupling in multiferroics, which could enable control of the ferroelectric (FE) polarization with a magnetic field or magnetism with an electric field [Eerenstein 2006]. Following electronic photoexcitation (Fig. 2), the measurements revealed that the resulting dynamics are governed by spin-lattice

relaxation [Bowlan 2016]. The results motivate exploration of light-driven states in multiferroics by coupling intense THz pulses with ultrafast x-ray measurement techniques, as described below.

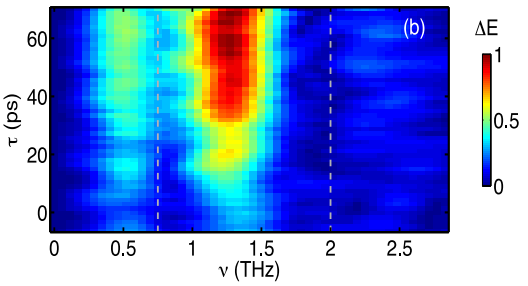

Figure 2. Optically induced changes in the time-and-frequency-dependent THz electric field of $TbMnO_3$.

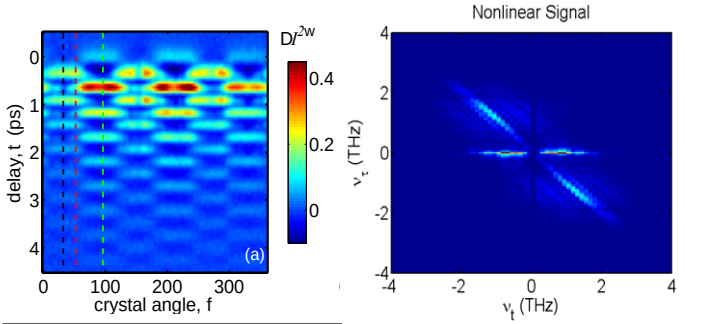

Figure 3. (a) THz-driven structural dynamics in Bi_2Se_3, probed via the time (τ) and polarization (ϕ)-dependent SHG response. (b) 2D THz-SHG measurements on Bi_2Se_3 at 300 K.

Topological insulators (TIs) exhibit a host of unique properties, most notably topologically protected gapless surface states in which carriers can propagate with reduced scattering within an insulating gapped bulk [Hasan 2010, Ando 2015]. One can potentially manipulate topological order by breaking the respective symmetries that protect it with intense THz pulses, as the tabletop THz magnetic field can reach values of ~0.3 T (with corresponding electric fields of ~1 MV/cm). The Prasankumar group has performed THz-pump, SHG-probe and 2D THz-SHG experiments on Bi_2Se_3 (Fig. 3), revealing THz-induced structural dynamics [Bowlan 2017] as well as THz-induced frequency-dependent changes that we are currently analyzing. The Nelson group has conducted similar measurements on the topological crystal insulator $Pb_{0.5}Sn_{0.5}Te$ [Xu 2012], observing time-resolved SHG and reflectivity (believed to be dominated by surface conduction electrons [Wang 2017b]) that both show soft mode oscillations, suggesting phonon-driven modulation of the topological surface conductivity.

Rare earth nickelates are an intriguing family of strongly-correlated electron systems characterized by multiple ordering tendencies involving the lattice, charge, and spin degrees of freedom. The electronic (metal-to-insulator) transition is accompanied by a structural transition whereby two sublattices are formed, one with compressed, the other with expanded NiO_6 octahedra, leading to a bond-disproportionated phase. This transition is accompanied by magnetic order (period-4 antiferromagnetic texture) at the Neel temperature [Torrance 1992]. The nature and class of these instabilities and the coupling between these degrees of freedom is a matter of ongoing debate [Green 2016]. The Comin group has recently studied the spatial reorganization of antiferromagnetic domains in rare earth nickelates, across the Neel transition. Measurements were performed at beamline CSX of the National Synchtrotron Light Source II using resonant soft X-ray magnetic scattering at the Ni-L_3 resonance (850 eV), on a special setup with high spatial resolution (< 100 nm) and scanning capabilities. We observed a large return point memory effect even after complete erasure of the Neel order well above the Neel temperature (Figure 4). This finding suggests the presence of domain pinning mechanisms which could be due to the charge or lattice degrees of freedom, but our present measurements could not

provide more insights on this matter. Therefore, we aim to explore the nature of the charge-spin interplay in the time domain, inspecting the dynamics of the coupled electronic orders using optical and THz pump and X-ray probe (magnetic scattering) experiments.

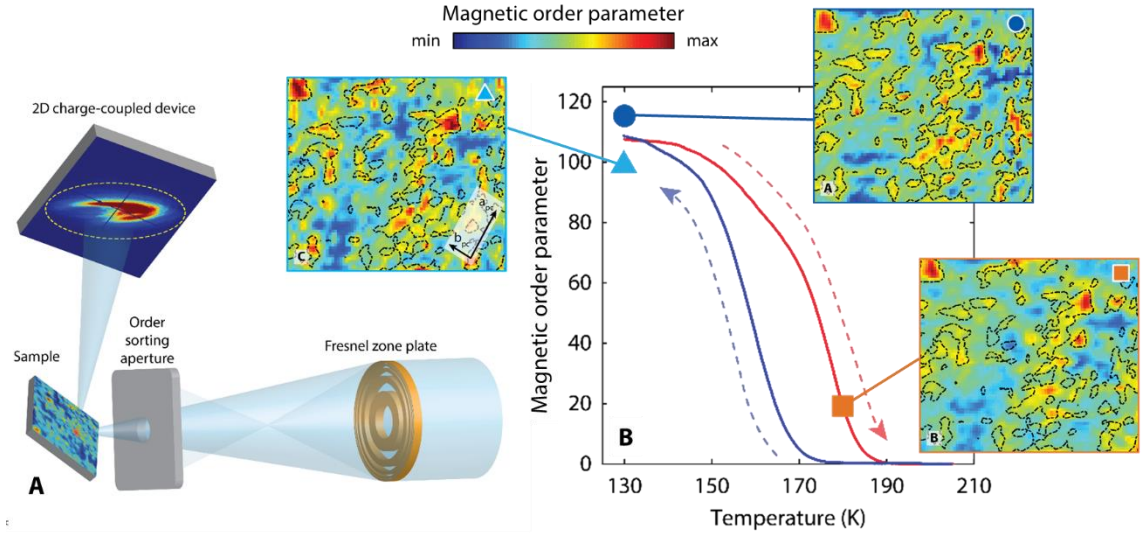

Figure 4. (a) Resonant soft X-ray scattering geometry. (b) Temperature evolution of the antiferromagnetic order parameter across the (hysteretic) Neel transition. Spatial maps of the order parameter are shown at 130 K (circle; warming cycle), 180 K (square; warming cycle), and 130 K again (triangle; cooling cycle).

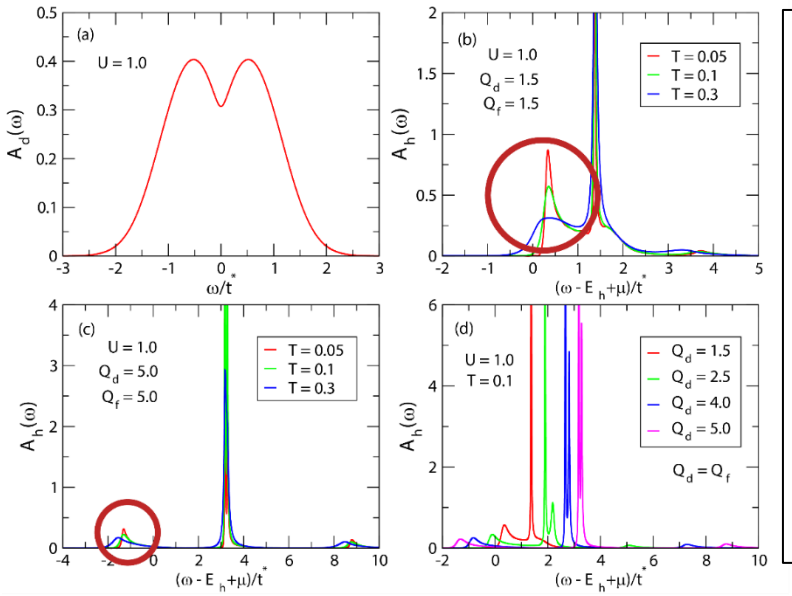

Figure 5. Core-hole spectra for a strongly correlated metal. (a) The local DOS of the metal, showing the presence of a "pseudo-gap-like" feature. (b) Core-hole XPS spectra for weak core-hole correlation at different temperatures. Note the strong T dependence of the low-energy feature. (c) Core-hole XPS spectra for strong core-hole correlation at different temperatures. Note the strong T dependence of the low-energy satellite. (d) High-T core-hole spectra for different core-hole correlations. From [Pakhira 2018].

The effort led by the Freericks group will focus on developing new theory for pump/probe x-ray scattering and applying the theory collaboratively to experiments led by the experimental PIs. The initial focus will look at strong-correlation effects and nonequilibrium effects on both x-ray core photoemission and x-ray absorption spectroscopy (only the latter is expected to be measured by this group, but the theory for the two probes is quite similar). In recent work [Pakhira 2018], we calculated the x-ray core-hole photoelectron spectra for strongly correlated materials as a function of temperature. As the temperature is raised, we find the

satellite peaks have strong temperature dependent features, especially in strongly correlated metals below the Mott transition. Figure 5 shows two examples of this, one for a relatively weak core-hole correlation (b) and one for a strong correlation (c). We believe that these results point toward the possibility of using such spectral features as local many-body electronic thermometers to track the thermal energy in the electrons on ultrafast time scales (whether or not the hot-electron model holds). This needs to be verified in a fully nonequilibrium pump/probe theory which we will engage in during the grant period. Because the core-hole response function is closely related to the x-ray absorption response function, we anticipate similar effects in x-ray absorption spectroscopy.

Future Plans

All the x-ray measurements and analysis will be collaborative among multiple PIs. Our recent results from quantum paraelectric STO indicate this as a prototype THz-driven soft mode system, in which excursions of sufficient amplitude along the soft mode coordinate lead to coupled responses in other modes and through them to collective ferroelectric ordering. XRD probing of the responses will enable direct and detailed elaboration of the driven and coupled displacements and comparison to MD simulations of the dynamics. FT-IXS will reveal additional lattice degrees of freedom that are excited through coherent coupling or incoherent relaxation. Small-angle x-ray scattering may provide insight into the dipole correlation length scale and its time-dependence, which may be influenced by the initial presence of polar nanoregions in the macroscopically paraelectric phase. When LCLS-II is operational at high repetition rate, it will be possible to conduct 2D THz/x-ray measurements (with the delay between two THz excitation pulses and the delay of an x-ray probe pulse both scanned) on a practical data acquisition time scale. A collaborative MIT-SLAC effort (Nelson-M. Hoffmann) is being launched to develop high-field THz generation using the SLAC 100-kHz repetition rate amplified laser system so that the THz field strength is sufficient for such measurements which will be enabling for many of the systems of interest in this project.

By coupling our advanced tabletop THz methods with ultrashort x-ray techniques, we can break new ground in the study of light-driven states in multiferroics. The first direction we will pursue focuses on using electromagnons to control ME coupling, which will also address the question of their origin. We will drive specific phonon modes while monitoring the electromagnon response with THz pulses, shedding light on the contribution of these modes to the electromagnon response. Temperature-dependent 2D THz measurements on $TbMnO_3$ will then enable us to understand the evolution of correlations between electromagnons and other low energy modes as the system undergoes phase transitions between different magnetically ordered states. We can also reveal the link between the electromagnon response and ordered magnetic and FE states using time-resolved Kerr rotation (TRKR) [Prasankumar 2011] and SHG measurements after resonantly driving electromagnons. Resonant THz driving of specific low energy modes followed by x-ray probing we provide even more insight into the interplay between magnetic, structural, and ferroelectric order in multiferroics. XRD and XAS will

measure THz-induced changes in structural and magnetic order, respectively, and RSXS will complement the 2D THz experiments described above to track the temporal evolution of specific low energy modes. FT-IXS can also be used to examine the coupling among low-energy excitations, particularly electromagnons and phonons, complementing the 2D THz experiments described above. These these experiments will provide unprecedented insight into the intrinsic properties of multiferroics.

Driving topological materials with intense THz pulses also offers new opportunities for controlling their properties. This will break time-reversal symmetry in Bi_2Se_3, just as it has broken mirror symmetry in $Pb_{0.5}Sn_{0.5}Te$, in both cases inducing a topological phase transition to a gapped state in which the Dirac fermions acquire mass. This would ideally be observed using TR-ARPES to track the induced changes in electronic structure, particularly at an XFEL, because the greater penetration depth of soft x-rays (vs. commonly used 6 eV sources) as well as the ability to tune the incidence angle will enable us to directly measure photoinduced changes in both the bulk and surface states. We will prepare for these XFEL experiments by first doing nonlinear 2D THz studies of conventional TIs, as the intense THz magnetic field should modify the Drude conductivity of the surface states by inducing a gap that can be detected in the 2D THz spectrum. This will go beyond the studies of Fig. 4 [Bowlan 2017], since the THz field resonantly drove an IR-active phonon mode in those experiments; here, we will use non-resonant, stronger THz fields at lower frequencies to enhance the effect of the THz magnetic field. (Note that we can use multicycle THz fields to avoid phonon resonances and magnetic field enhancement structures so that magnetic field effects dominate the response.) In addition, TR-RXS and TR-XRD can be performed to track low-energy excitations and correlate the temporal evolution of the lattice and electronic structure.

In order to elucidate the microscopic link in the rare earth nickelates between the ordering of the Ni spins and the lattice or charge instabilities, we will study how different pathways to photoquench the structural and charge orders (using an optical pump to close the Mott gap or a THz photoexcitation to resonantly drive the lattice) will affect the dynamics of magnetic order. Our goal is to elucidate the mutual hierarchy of the electronic and spin order parameters – which one drives the transition and what is the nature of their coupling. We will focus on two members of the nickelate family, $SmNiO_3$ and $NdNiO_3$ [Catalano 2015, 2016]. We will start by examining the dynamics of the coupled electronic and magnetic phases following optical excitation across the Mott gap (> 0.5 eV), to determine the influence of spectral weight redistribution on the electronic instabilities (XAS proposal has been submitted to PAL-XFEL). Subsequently, we will use resonant THz photoexcitation tuned at the zone-center IR-active breathing mode (~550 cm^{-1}, or ~16 THz, in NdNiO3) to selectively drive the lattice in its symmetry-broken, bond-disproportionated phase (XRD proposal has been submitted to SACLA). We will first use ultrafast (nonresonant) diffraction to assess the melting of the structural and charge order at the superlattice reflection (1/2,1/2,1/2). We will later repeat the same experiment using resonant magnetic X-ray scattering at the Ni-L_3 edge to track the response of the magnetic order parameter.

The initial theoretical task will be to develop the capability to calculate x-ray absorption spectra for strongly correlated materials in pump/probe experiments. We also will examine other situations relevant to experiments, such as how fast CDW order is formed or destroyed and how this can be imaged with x-ray diffraction. This work will entail developing new formalism, developing new computational algorithms, and implementing them on parallel computers at NERSC. Close dialog between theory and experiment is planned to be able to explain the behavior seen in experiments.

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Publications

One publication is far along in preparation. We expect to submit it in early December.

J. Shi, Y.-Q. Bie, W. Chen, S. Fang, J. Han, T Taniguchi, K. Watanabe, V. Bulović, E. Kaxiras, P. Jarillo-Herrero, and K. A. Nelson, "Terahertz-driven irreversible quantum phase transition dynamics in $MoTe_2$."

A publication on the STO results is in the early stages of preparation. We hope to submit it in January.

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

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Program 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 studied catalysts.

Recent Progress

We synthesized and characterized catalytically several families of binary Pd-Pd, Pt-Cu, Au-Co, Pt-Au, Pt-Ir, Pt-Rh, Pt-Fe, Pd-Sn and ternary Pt-Ni-Co, Pt-Ni-Cu, Pt-Au-Ni and Pt-Pd-Cu nanocatalysts. The catalysts were found to exhibit greatly enhanced activities for the so-called Oxygen Reduction Reaction (ORR), taking place at the cathode of virtually all fuel cells, oxidation of CO to harmless CO_2, and dehydrogenation of ethanol. The catalysts were characterized by *ex situ* synchrotron HE-XRD and atomic PDF analysis (see our papers 3, 4, 7, 8, 9, 10, 11, 12, and 15 listed below).

We also conducted *in situ* studies on Au nanowires grown in solution. The nanowires exhibited an unusual Frank-Kasper type structure (see Figure 1) and are promising catalysts for the electroreduction of CO_2 to

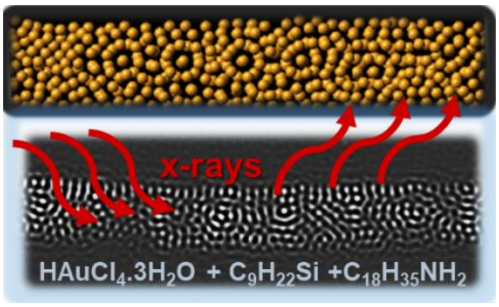

Figure 1. *(lower part)* Frank-Kasper type Au nanowires, as growing in solution and studied by *in situ* HE-XRD. (*upper panel*) 3D model of the wires, as refined against the experimental HE-XRD/PDF data.

hydrocarbons, alcohols and CO-rich feeds of interest to energy related applications. Results are published in our paper (1).

We conducted two resonant HE-XRD experiments. One of the experiments was conducted at the K edge of Pt (E=78.395 keV). The other was conducted at the K edge of Ir (E=76,111 keV). Results are published in our papers (2, 9, 13). The experiments demonstrated the great potential of resonant HE-XRD in structure studies of interfaces in nanosized materials. Another resonant HE-XRD experiment is scheduled for the last week of November 2018. Currently we are considering the possibility to increase the data collection rate of resonant HE-XRD experiments by introducing a 5-element Ge detector. The success of this endevour hangs on securing $200K for the detector.

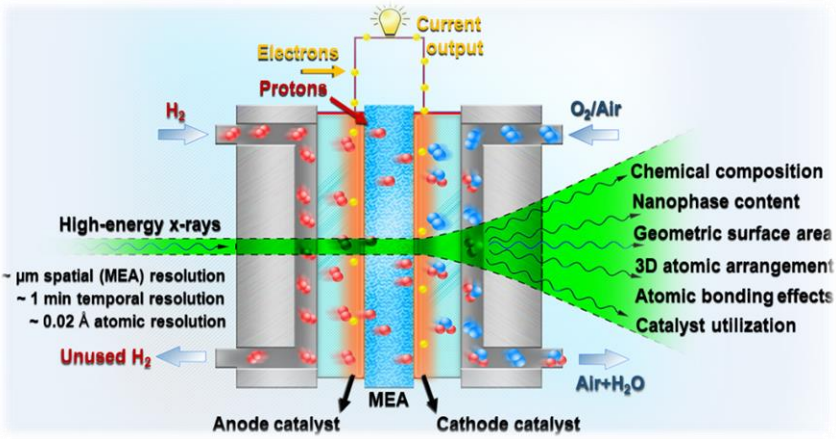

Figure 2. Sketch illustrating the wealth of structure knowledge for ORR catalysts delivered by in operando HE-XRD/PDF and EDS experiments. The sketch features a PEMFC developed by us (see our papers 5, 14).

We conducted combined *in situ* HE-XRD/PDF and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments on ternary noble-transition metal catalysts under CO and oxidative atmosphere. The experiments indicated the importance of surface structural disorder in enhancing the activity and stability of nanocatalysts for low-temperature oxidation of CO. The experiments also showed the great potential of *in situ* HE-XRD/PDFs and DRIFTS in characterizing the surface atomic structure of nanosized materials under reactive atmosphere. Results are published in our paper (6).

We conducted two combined *in operando* HE-XRD/PDF and energy-dispersive spectroscopy (EDS) experiments on catalysts functioning at the cathode of an actual proton exchange membrane fuel cell (PEMFC). Results showed that catalysts for fuel cells undergo specific structural changes under operating conditions that may inflict significant losses on their performance. Possible strategies for reducing the losses by taking control over the changes were suggested, and one of it was demonstrated. Results are published in our papers (5, 14). Another *in operando* experiment is scheduled for the third week of November 2018. The potential of HE-XRD/PDF and EDS in structure studies on materials inside operating devices is illustrated in Figure 2.

We continued developing improved procedures for PDF-guided modeling the 3D structure of nanosized materials of any size, shape and chemical composition under non-periodic boundary conditions. Also, we are developing a streamlined approach to computing the electronic structure of studied nanocatalysts using their coordinates in the 3D structure models and electronic-structure parameters trained against DFT. Results of electronic structure calculations are shown in our papers (1, 3, 13).

Future Plans

It is increasingly recognized that i) materials for energy related applications, in particular nanocatalysts, are inherently dynamic systems whose local and extended structure changes

continuously from the pristine state to the active form and further along their utilization and ii) advances in nanoscience and technology for energy related applications, including nanocatalysis, will indeed be achieved by understanding the roles of compositional and structural heterogeneities, interfaces, and disorder in determining the performance of explored nanomaterials. Also, it is recognized that these advances will require both more powerful experimental techniques for atomic-level characterization of multicomponent nanomaterials in both pristine and active state and integration of the experimental data with sophisticated methods for modeling and prediction of complex 3D nanostructures, including computation of their electronic properties.

We would like to continue studying nanosized catalysts for energy related applications using a combination of advanced x-ray scattering techniques, including pushing the techniques beyond their current capabilities. In particular, we intend to use combined *in situ* HE-XRD/PDF and SAXS to study the mechanism of growth of nanocatalysts in solution, combined *in situ* HE-XRD and DRIFTS to study nanocatalysts under reactive atmosphere, combined *in operando* HE-XRD/PDF and EDS to study the evolution of nanocatalysts inside fuel cells, and resonant HE-XRD to study heterogeneous interfaces in nanocatalysts. We also intend to continue optimizing resonant HE-XRD in terms of data collection time(detectors) and processing procedures, develop methods for analysis of series of experimental PDFs from high-throughput experiments and streamline further approaches for computing the electronic structure of metallic nanocatalysts from their 3D models based on data from scattering experiments.

Publications in last two years:

1. J. A. Vargas, V. Petkov, El Said A. Nouh, R. Kumar Ramamoorthy, Lise-Marie Lacroix, R. Poteau, G.Viau, P. Lecante and R. Arenal " *Ultrathin Gold Nanowires with the Polytetrahedral Structure of Bulk Manganese"* ***ACS Nano*** (2018), 12, 9521. Experiment type: *In situ* in solution (E=58.62 eV).
2. H. N. Nong, T. Reier, H.-Suk Oh, M.l Gliech, P. Paciok, T. Ha Thi Vu, D. Teschner, M. Heggen, V. Petkov, R. Schlögl, T. Jones, P. Strasser "*A unique oxygen ligand environment facilitates water oxidation in hole-doped $IrNiO_x$ core-shell electrocatalysts*" ***Nature Catalysis*** (2018), 1, 841; Experiment type: *Resonant* XRD at the K edge of Ir (E=76,111 keV).
3. V. Petkov, S. Shastri, J. Woo Kim, S. Shan, J. Luo, J. Wu and Ch.-J. Zhong "*Application of differential resonant high-energy X-ray diffraction to three-dimensional structure studies of nanosized materials: A case study of Pt–Pd nanoalloy catalysts*" ***Acta Cryst. A*** (2018), 74**,** 553; Experiment type: *Resonant* XRD at the K edge of both Pt (E=78.395 keV) and Pd (E=24.341 keV).
4. A. Demortiere, D. N. Leonard, V. Petkov, K. Chapman, S. Chattopadhyay, Ch. She, D. A. Cullen, T. Shibata, M. Pelton, and E. V. Shevchenko "*Strain-Driven Stacking Faults in CdSe/CdS Core/Shell Nanorods*" ***J. Phys. Chem. Lett.*** 9 (2018) 1900; Experiment type: *In situ* in solution (E=58.62 keV).
5. V. Petkov, Y. Maswadeh, Y. Zhao, A. Lu, H. Cronk, F. Chang, S. Shan, H. Kareem, J. Luo, Ch.-J. Zhong, S. Shastri and .P Kenesei "*Nanoalloy catalysts inside fuel cells: An atomic-level perspective on the functionality by combined in operando x-ray spectroscopy and total scattering*" ***Nano Energy*** 49 (2018) 209; Experiment type: *In operando* fuel cell (E=100.2 keV).
6. V. Petkov, Y. Maswadeh, A. Lu, S. Shan, H. Kareem, Y. Zhao, J. Luo, Ch.-J. Zhong, K. Beyer and K. Chapman "*Evolution of Active Sites in Pt-Based Nanoalloy Catalysts for the Oxidation of Carbonaceous Species by Combined in Situ Infrared Spectroscopy and Total X-ray Scattering*" ***ACS Applied Materials & Interfaces*** 10 (2018) 10870**;** Experiment type: *In situ* gas phase (E=86.70 keV) combined with DRIFTS spectroscopy
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Dynamics and Control of Magnetic and Charge Order in Complex Oxides

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The complex phase diagram of quantum materials presents tantalizing opportunities for using ultra-fast excitation both to control and to understand properties. This complexity is intrinsic to doped Mott insulators, which tend to feature strong charge-spin-lattice coupling and multi-length-scale interactions as well as inherent inhomogeneity. This program will develop new ways to probe charge, orbital, spin, and lattice on both short and long length scales with ultra-fast x-rays. Our goal is to deliver detailed pictures of ultra-fast spin and charge behavior in layered copper and iridium based complex oxides and how this organizes into domains once it couples to the lattice. This multi-degree of freedom, multi-length-scale understanding of canonical strongly correlated oxides is a vital step towards "properties on demand" via strategic ultra-fast excitation of quantum materials.

Our main goal is to use laser pump, X-ray probe methods to understand how charge, spin and orbital degrees of freedom interact to form charge and magnetic order in four prototypical layered Mott insulating materials: the optimally doped cuprates $La_{2-x}Ba_xCuO_4$ (LBCO) and $La_{2-x}Sr_xCuO_4$ (LSCO) with x~1/8 and the iridates Sr_2IrO_4 and $Sr_3Ir_2O_7$. We will apply the two techniques in which we have expertise and a demonstrated track record at LCLS to these materials: time-resolved Resonant Inelastic X-ray Scattering (trRIXS) [1] and time-resolved Bragg Coherent Diffractive Imaging (trBCDI) [2]. The structures of all four materials contain the same square-planar Oxygen-Transition Metal layers, which are involved in high-temperature superconductivity (HTSC). The connection between the physics of the 5d iridates and the 3d cuprates has been noted many times in the literature [3-5], even though the former do not actually show full HTSC behavior.

These four materials have been chosen because we know a lot about the cuprates already and, more recently, the iridates as 5d analogs [6-10]. They are also highly accessible with the trRIXS and trBCDI methods we will be applying. The discovery of HTSC ranks among the major scientific events of the twentieth century [11], a field to which BNL has contributed substantially. Of particular relevance to this proposal is the discovery by BNL physicists of intertwined CDW and spin-density wave order back in 1995 [12]. Since the cuprates and iridates have relatively simple electronic structures, they represent the best chance to understand the problem of strong correlations in quantum materials more generally. The Iridium L_3 edge is in the prime range of accessible X-ray wavelengths at LCLS and is a requirement for both trRIXS and trBCDI methods to access the magnetic excitations.

The new development of RIXS and BCDI techniques at 3rd generation synchrotron facilities is having impact already in mapping out the excitation spectrum and domain properties of these materials, but their ultrafast response times are largely unknown. For the cuprates, the CDW in

LBCO was found to melt in 500 fs upon mid-IR excitation [13], but no information was gained about the domain structure or the lattice response time, as discussed below. For photo-doped Sr_2IrO_4 iridate, the magnetic excitations were found to decay faster than 300 fs and recover with two fluence-dependent rates, shown in our previous work [1]. Both these previous experiments at LCLS used different wavelength laser pumping and, given the richness of the excitation spectrum, there is much to be learned in future work from targeting specific excitations with both short and long wavelength pumps.

Recent Progress

1. FIB Preparation of samples for trBCDI (Ian Robinson)

The antiferromagnetic order in Sr_2IrO_4 (214) is strong enough that by enhancing the magnetic cross section by resonance at the Ir L_3 edge at 11.2keV we expect there will be sufficient signal for BCDI imaging. We tested this with the coherent X-ray beam at sector 34 of APS using a large crystal of 214 below its magnetic ordering temperature of T_N = 225K, conveniently accessed with the Linkam stage of sector 34, which has low vibrations. Indeed there was a signal around 10^3 counts/sec/pixel. The domain sizes, known from the correlation lengths of the magnetic Bragg peaks, were found to be very large as there were hardly any speckles generated by the 600nm incident beam.

This is consistent with our original estimate, based on the previously reported intensity of 10^6 counts/second for magnetic peaks for an open monochromatic beam on a large sample at resonance (11.2 keV). We next looked at FIB-sculpted small crystals of 214 to attempt the BCDI experiment for imaging the internal domains. Since the absorption length is only 5 microns on resonance at 11.2 keV, the penetration depth is even smaller, but not a big loss for a small crystal of 2x2x2 microns^3, as needed for BCDI, so long as the beam is focused onto it. Given that the number of domains contributing to the coherent diffraction pattern is quite small, we would expect a signal around 10-100 counts/second/pixel, which is practical for BCDI. However when we tried this, there was no magnetic peak from the small crystal. It is possible that the FIB cutting damages the material sufficiently to quench the AFM order. We plan to repeat these experiments with FIB-cut crystals large enough that the AFM peak is preserved to try to understand the damage issue.

2. Time-resolved magnetism in $Sr_3Ir_2O_7$ (Mark Dean)

We recently performed a tr-RIXS study of the magnetic correlations in bilayer iridate $Sr_3Ir_2O_7$ using the XPP beamline of Linac Coherent Light Source. Upon photo-doping the system with 600 meV pump photons, we observed a strong momentum-dependent modification of the short-range magnetic correlations. These data are currently being analyzed and interpreted alongside measurements of the magnetic Bragg peak evolution taken at the SPring-8 Angstrom Compact free electron Laser. Our working hypothesis is that coupling to phonons may be the dominant factor in determining the out-of-equilibrium magnetic dynamics, but this needs to be verified via supporting matrix product state theoretical calculations and home-lab optical reflectivity characterization. Supporting structural information from tr x-ray and electron diffraction will be important regarding these efforts

3. Ultrafast Electron Diffraction (Jing Tao and Yimei Zhu)

Taking advantage of large scattering cross-section with sufficient momentum transfer, ultrafast electron diffraction (UED) techniques will provide detailed structural characterization that complements the information obtained by time-resolved (tr) BCDI and RIXS. Recently, we have demonstrated unique capabilities of MeV UED on revealing the structural dynamics in a number of correlated materials and quantum materials, including a 2D charge-density-wave (CDW) material [14], a doped manganite with colossal magnetoresistance [15], a high-Tc superconductor [16] and a superionic conductor [17]. Those works illustrated the crystal dynamics that is associated with distinct phonon modes and identified the structural transition pathway by monitoring the transient states. In addition, our recent UED work on a 2D CDW material, 1T-TaSeTe, distinguishes the atomic displacements of Ta and Se/Te ions, respectively, precisely ascertaining atomic trajectory of Ta and Se/Te in this crystal during pump-probe processes using momentum-sensitive ultrafast electron probes.

4. Theory (Robert Konik)

To tackle the problem of computing the non-equilibrium temporal dynamics in a strongly correlated 2D system, we are employing an approach that weds the exact solvability of 1D systems with matrix product state algorithms. In essence we think of the 2D system as a set of coupled (perhaps strongly) chains. Using exact methods we obtain an exact characterization of the component 1D chains. We then use matrix product states to "glue" the chains together. This approach allows one to import information coming from 1D exact solvability into the problem thus making subsequent numerics on the 2D system easier. We have already demonstrated this approach on 2D quantum Ising systems and have preliminary results that show our approach works well on 2D Heisenberg spin systems. We expect then to be able to simulate, using TEBD and iTEBD, the time evolution of spin-spin correlation functions after a pump in various iridate systems.

Future Plans

Under the new FWP funding, our first goal will be to recruit a team of postdocs. These have been identified in the subject areas of trBCDI, trRIXS, UED, theory and algorithm development. All positions will be held at BNL and have been advertised on the BNL jobs website.

The magnetic domain arrangements in 214 Iridate will be visualized in 3D by inversion of the BCDI coherent diffraction pattern measured around the Bragg peaks using standard algorithms. The only modification expected in the standard phasing procedure will be the use of a fixed support and well-formed crystal shapes, prepared by FIB. Domain imaging will commence at base temperatures below T_N = 225K, where the peaks are reported to be perfectly sharp, suggesting there may be just one or a few domains. Then the temperature will be raised above T_N = 225K to look at the pattern of domain formation associated with the correlation lengths of the diffuse scattering, which are reported to be as large as 300 unit cells in-plane (150 nm) and 20 unit cells along the c-axis (50nm) [18]. If time allows, we will study domain fluctuations and return-point memory effects [19-21] associated with the magnetic phase transition at 225K. Then we will be ready for the ultrafast trBCDI experiment to look at lattice coupling effects in the response of 214 Iridate to light pulses.

The long-range magnetic domain evolution will be interpreted alongside RIXS studies of the short-range dynamics and measurements of how the crystal structure is modified under the same photo-excited conditions. The strong spin-orbit interaction may be crucial here as effective J moments have a large orbital angular momentum component coupling the magnetism to the lattice and generating a potentially crucial role for magneto-elastic effects.

We plan to prepare MeV UED specimens from bulk cuprates and iridates using mechanical polishing, FIB and ion milling methods as the first step. MeV UED experiments will be performed and UED data will be analyzed to reveal the dynamic interplay between charge and the lattice in each material system after correlating with the trBCDI and trRIXS results.

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Advancing High Pressure Materials Science Using X-rays

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Pressure drastically changes interatomic interactions and provides an effective means, both theoretically and experimentally, to discover functional materials with exceptional properties and to study materials' performance at extreme environments. High energy x-rays provide powerful micro-sampling probes to reach the minute samples through the walls of the pressure vessels and to distinguish the weak sample signals from the often overwhelming background signals produced/excited by the massive surrounding vessel materials. Through this collaborative project, we have developed an array of x-ray diffraction, x-ray spectroscopy and scattering, and x-ray imaging techniques optimized for high pressure devices and for studying materials at extended extreme conditions. The 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

- *Crystal structure of H_2 above 200 GPa*: Solid hydrogen, under extreme compression, is predicted to become metallic with exotic properties, *e.g.*, superconductivity at room temperature and superfluidity. Before the metallization is achieved, at least seven high pressure phases have been reported in hydrogen. Direct measurements of their crystal structures by x-ray diffraction (XRD) provide the very basis for understanding solid hydrogen under high compression in general, however, remaining a formidable technical challenge. We have developed a new soller slit system optimized for tight collimation in synchrotron XRD using a diamond anvil cell, and successfully retrieved the weak hydrogen XRD signals above 230 GPa at room temperature [1]. Our data suggest that the hydrogen phase-IV stays in a hexagonal-close-packed-like lattice. Our studies pave the way for directly measuring the crystal structures of the new phases of hydrogen at higher densities, the phases IV', V, VI, and ultimately the metallic hydrogen.
- *Electronic band gap enclosure*: Metallization of solid hydrogen, the process of electronic band gap closure under extreme pressures, has been regarded as an apex challenge in modern physics. A fundamental challenge is that the electronic band structure of hydrogen is inaccessible experimentally and has never been observed under pressure. We have developed a high-pressure inelastic x-ray (IXS) probe that can access compressed solid hydrogen in a diamond-anvil cell, and monitor the pressure-induced changes in the electronic band gap and the density of states of the conduction band over an energy range of 45 eV [2]. We have directly observed the electronic structure of solid hydrogen and its evolution up to 90 GPa which corresponds to an 8.6 times (ρ/ρ_0) densification of hydrogen. The extrapolation of our data provides a lower bound for the metallization pressure of solid hydrogen at ~550 GPa corresponding to ρ/ρ_0 of ~20.
- *Hydrogen rich compound*: H_2 in its elemental form and $Ar(H_2)_2$ compound were studied experimentally by synchrotron XRD to 265 GPa, and by Raman and optical absorption spectroscopy to 358 GPa. Our measurements of the optical bandgap and the vibron frequency show that $Ar(H_2)_2$ retains 2-eV bandgap and H-H molecular bonding units up to 358 GPa [3]. This is a record high pressure reached for hydrogen studies, indicating that higher pressures are required for metallization. We conducted a

systematic investigation of the diamond anvil deformations for understanding the geometrical constraints for optimization of diamond anvils up to 400 GPa [4].

- *Exotic chemistry of hydrogen*: Drastic changes have been observed in high-pressure reactivity [5] and chemistry of hydrogen. Above 75 GPa, H_2 can be released from H_2O by reacting with iron or iron oxides to form FeO_2Hx [6,7] where x is found to be approximately 0.5 [8]. The FeO_2Hx is a new type of compound that the oxygen form dimers with anion valence state less than 2, and with hydrogen forming symmetrical hydrogen bonding at low temperatures, and superionic bonding at high temperatures (arXiv:1810.08766).

Magnetic and superconducting materials

- *Discovery of room temperature superconductor*: Recent predictions and experimental observations of high T_c superconductivity in hydrogen-rich materials at very high pressures are driving the search for superconductivity in the vicinity of room temperature. We have developed a novel preparation technique that is optimally suited for megabar pressure syntheses of superhydrides using pulsed laser heating while maintaining the integrity of sample-probe contacts for electrical transport measurements to 200 GPa. Lanthanum superhydride samples display a significant drop in resistivity on cooling beginning around 280 K and pressures of 190 GPa. The loss of resistance is explained as a signature of the predicted room-temperature superconductivity in LaH_{10}, in good agreement with density functional structure search and BCS theory calculations. (Somayazulu et al, arXiv 808.07695v2)
- *New iron-based superconductor with a honeycomb iron sublattice*: So far, all iron-based superconductors structurally adopt FeSe-type layers with a square iron sublattice. We have discovered a new type that has a honeycomb sublattice of iron atoms [9]. The newly reported layered honeycomb-type $FePX_3$ (X=S, Se) compounds undergo abrupt spin collapse of Fe(II) and concomitant insulator-metal transition under pressure. Superconductivity emerges in $FePSe_3$ with a maximum Tc ~5.5 K around 30 GPa. The discovery of honeycomb-type iron based superconductors opens up a whole new class of materials for optimization of superconducting properties and exploring superconductivity mechanisms in iron-based compounds.
- *New pressure-induced phase in $SnSe_2$ with periodic lattice distortion*: Various periodic lattice distortion related to the charge density wave have been observed in transition metal dichalcogenides (TMDs). We have found an unusual pressure induced lattice distortion in $SnSe_2$ [10]. The Fermi surface nesting and the strong electron-phonon coupling are found to occur at the same momentum wave vector. This observation is in contrast to findings in metallic TMDs, where Fermi surface nesting was found to play a less significant role. Our findings provide new insights for understanding the intricate mechanisms governing the emergence of lattice distortion in TMD-related materials.

Enabling high-pressure synchrotron techniques

- *Studying materials metastability and phase transformation kinetics using time-resolved x-ray probes and rapid pressurization:* Fast x-ray diffraction and x-ray imaging techniques have been integrated with dynamic diamond anvil cells capable of controlling rapid compression/decompression for studying materials metastability and phase transformation kinetics. Information on metastability, nucleation mechanism, grain growth, transition time, and activation energy has been obtained [11,12].
- *Generating pressures beyond 500 GPa using double-stage configuration in the diamond anvil cell*: We have established small focused x-ray beam and developed scanning x-ray diffraction imaging techniques, which enables exploring different double stage configurations to generate ultra-high pressures beyond 500 GPa.
- *Weak scattering materials at megabars:* In megabar experiments, the sample size is typically in a few microns in dimensions. For weak scattering materials such as hydrogen, it remains challenging to

obtain detectable signals out from overwhelming background arising from large surrounding materials (anvils, gasket). We have designed a soller slit for post-sample collimation that effectively improves the S/N ratios, thus enabling structural probes for hydrogen above 200 GPa [1].

- *Double stage large volume press for studying amorphous materials to >130 GPa*: We have developed a double-stage large volume cell for compressing large volume samples to over 130 GPa and for in situ structural measurements. This development is well suited for studying structures of low scattering materials at megabars, such as amorphous and low-Z materials [13].
- *Enabling inelastic x-ray scattering measurements at megabars*: For high pressure samples surrounded by anvil and gasket materials, collecting the weak IXS signal out from the overwhelming background is experimentally challenging. This is in particularly difficult for IXS experiments over 100 GPa. We have developed a new post-collimation design using poly-capillary optics, which enables IXS studies on electronic excitations, bonding related to elements such as H, Li, Be, B, C, N, O, etc over Mbar [2,14].
- *Microstructure analysis reveals epitaxial and topotaxial growth:* The newly developed modulated laser heating technique together with the fast x-ray detectors allow us to record x-ray diffraction images for samples at various controlled temperature pathways. The recorded diffraction images display materials microstructures, revealing information of microstructural transition, epitaxial growth, and topotaxial transformation [15](arXiv:1804.05109).
- *High-pressure studies using x-rays*: High-pressure synchrotron technology [16], and high-pressure physics in general [17] have been reviewed thoroughly.

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Electronic and Magnetic Structure of Quantum Materials

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Quantum materials research represents an exciting opportunity to advance our understanding of grand scientific challenges, to address BES priority research needs, and to impact energy technologies. The interplay and coupling of multiple degrees of freedom from spin, charge, orbital and lattice often conspire to give rise to remarkable emergent properties – as exemplified by high temperature superconductivity and topological phases of matters. We develop a comprehensive program to tackle this important but complex problem, through a "complete set" of ARPES experiments that includes energy, momentum, spin and time resolution, further complemented by in-situ materials synthesis and tuning, as well as theory/simulation. ARPES has grown to be a leading technique in the modern study of quantum materials and is now recognized as an essential ingredient in the path towards a fundamental understanding of materials properties. This FWP has been an active player in that development and has had a set of important progresses – which we will present both orally and through four posters that focus on synchrotron based experiments on single crystals, in-situ MBE films, time-resolved photoemission and the development of spin-resolved photoemission experiments. The scientific topics include cuprates and Fe based superconductor, transitional dichalchoginides, Bi2Se3, and oxide surfaces.

Leveraging on past success and focusing on a few model systems (novel superconductors, quantum spin hall insulators, etc.) the program aims at fundamental questions with broad implications on quantum materials. The program will bring many new capabilities to our ARPES experiments and theory of spectroscopy for bigger impact. The recently developed new experimental capabilities include: a) new experimental station at a recently commissioned beamline with improved flux, resolution, polarization control and spectral range; b) sample environment control capability through in-situ MBE synthesis, strain, current, gate and light field control capability; c) femtosecond laser-based tr-ARPES system with record of combined time and energy resolution; d) new spin-resolved sr-ARPES system. At the same time, improvements in computational methods and architectures have enabled highly accurate simulations of photon-based spectroscopies often able to connect quantitatively with measured spectra. We intend to further drive this development through refined commissioning. We select two major scientific areas on which to focus, including strongly coupled quantum systems with novel properties and material property under external control. We will also continue the tradition of advanced tool development that matches the experiment. This synergetic mixture of science drivers and experimental and theoretical/numerical tools promises the best opportunity to attack the "problems of scale" presented by the complexity of quantum materials.

Synchrotron Radiation Studies

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Program Scope

The long-term goal of this program is to advance the frontier for *in situ,* real time studies of materials through creative use of the Nation's x-ray facilities. Our approach is to identify critical challenges in materials science that can be addressed using advanced synchrotron x-ray capabilities, to develop novel x-ray methods exploiting the unique features of synchrotron sources to address these challenges, and to demonstrate the broad impact of these methods on materials research. The current focus of our effort is to take advantage of emerging methods using coherent x-rays to provide new windows into fundamental mechanisms in materials. These coherent x-ray methods include Bragg coherent diffraction imaging (BCDI), in which phase-retrieval algorithms allow real-space images of both electron density and atomic-scale displacement fields to be directly obtained from scattering patterns, and x-ray photon correlation spectroscopy (XPCS), which reveals atomic-scale fluctuation dynamics. We employ BCDI for *in situ* imaging of strain and composition in electrochemical systems, as well as charge, orbital, and magnetic order in quantum materials. We develop new BCDI algorithms for 3D ptychography, high x-ray energy, and dynamic studies. We extend XPCS to study dynamics of weakly scattering surfaces and high-speed fluctuations in liquids.

Recent Progress

Imaging and Reactivity of Electrode Materials: We used BCDI to study dissolution of Ag nanoparticles and dealloying of Ag-Au alloys. While Ag is a prototypical system for dissolution studies [L1], the microscopic mechanisms of dissolution have been difficult to observe. Our BCDI study of Ag nanoparticles [42] revealed a new dissolution mechanism that has not previously been described. We observed a long incubation time before the start of dissolution. At the end of the incubation period, electrochemical-potential-induced pressure nucleated a dislocation loop terminated at the particle surface. Only then, rapid dissolution was activated at the loop termination sites. This result points to an important connection between defects, strain, and stability in an electrochemical environment and demonstrates the potential of BCDI to elucidate this relationship. The dissolution process is also important in cases of dealloying, i.e. leaching of one component of a binary alloy [L2]. Information on lattice strain is needed to understand and control properties for applications such as catalysis [L3]. In our BCDI studies, 3D strain distributions within individual nanoparticles and thin film grains of silver-gold alloys were investigated during dealloying in nitric acid [39]. Dealloying produced dramatic shape

changes (Fig. 1) as well as various amounts of local strain. Isolated nanoparticles became significantly more strained than grains embedded in a polycrystalline film. We also carried out a study of alkali fluoride and chloride electrolyte structure above a Pt(111) electrode [9], using a crystal truncation rod analysis to observe the long-proposed but never-before-seen electrochemical Stern layer. Surprisingly, the Stern layer persisted over wide potential ranges where the Gouy-Chapman model was generally thought to apply.

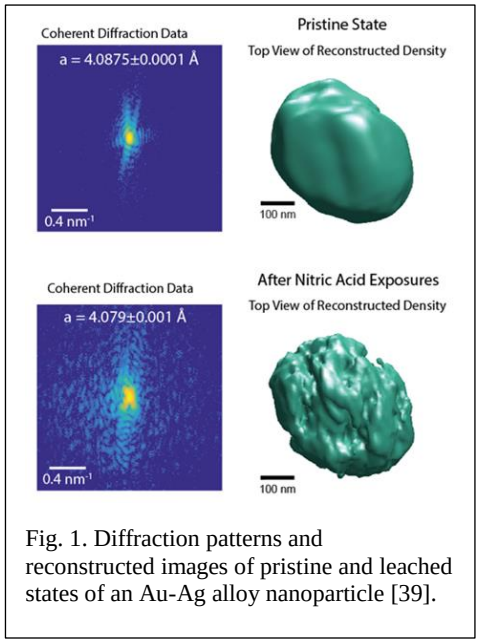

Fig. 1. Diffraction patterns and reconstructed images of pristine and leached states of an Au-Ag alloy nanoparticle [39].

BCDI Studies of Local Electrochemical Behavior: Recent advancements in BCDI have allowed for its application in complex systems and environments. We have contributed to this area by demonstrating the imaging of individual grains in polycrystalline films [37] as well as the imaging of nanoparticles during chemically driven phase transformations [24, 25]. Despite these achievements, a number of long-standing challenges remain in the application of BCDI to electrochemical studies. Two such challenges are the co-location of x-ray and electrochemical information and the efficient and reliable exchange of gas in x-ray-measurement-compatible electrochemical cells. We have made recent process in overcoming these challenges by integrating scanning electrochemical cell microscopy (SECCM) with BCDI. SECCM is a state-of-the-art electrochemical technique in which a micro-tipped pipette fitted with electrodes is used to create a sub-micron sized droplet that, when in contact with a conductive substrate, forms a fully functional electrochemical cell [L4]. Since the size of this cell is well matched to the x-ray spot sizes typically used for BCDI, we can largely eliminate the problem of co-location and ensure that the electrochemical signals measured originate from the same nanoparticle(s) or grain(s) being imaged. Figure 2 shows preliminary results for cyclic voltammetry measured from grains in a polycrystalline Au film using SECCM, as well as simultaneously measured coherent x-ray diffraction patterns from a single grain. The evolution of the diffraction pattern shows reversible structural changes occurring during the electrochemical cycling. Additionally, since the working region of the electrochemical cell in these experiments is a sub-micron droplet, gas exchange

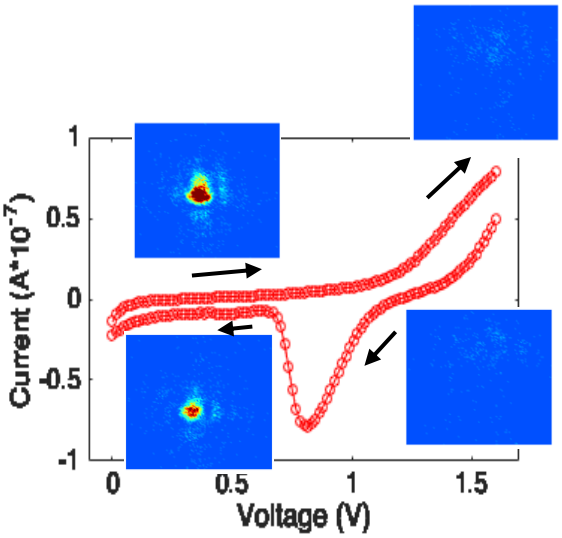

Fig. 2. Cyclic voltammetry and select coherent diffraction patterns from polycrystalline Au film measured simultaneously using BCDI/SECCM instrument.

with the electrolyte can occur very close to the electrode being studied by streaming gas to the SECCM. This methodology allows for the quick exchange of gas while maintaining the localized nature of the electrochemistry studied. We have utilized this new tool for initial studies of the oxidation and reduction of Au grains within a film. These studies reveal structural evolution and defect migration associated with exposure to different electrochemical potentials.

Coherent X-ray Studies of Lattice and Electronic Order: In preparation for an expanded experimental program in this area, we performed simulations of Bragg ptychography from realistic lattice order domain patterns in a pseudocubic ferroelectric thin film, and we determined a roadmap for feasible coherent x-ray diffraction measurements that resolve heterogeneous local ordering in these materials at few-nanometer length scales [53]. In addition, we have utilized *in situ* BCDI to investigate changes at elevated temperatures of the strain state of diamond and SiC nanoparticles [13, 43]. Observing and modifying these strain states are critical to the performance of these materials for quantum sensing applications. Using the full transverse coherence of the ultrafast x-ray pulses from free electron laser (FEL) source, we have observed the dynamics of acoustic phonon modes excited in a ZnO nanoparticle by obtaining BCDI snapshots of the displacement field at various time delays within the first nanosecond after an optical pump (Fig. 3) [34].

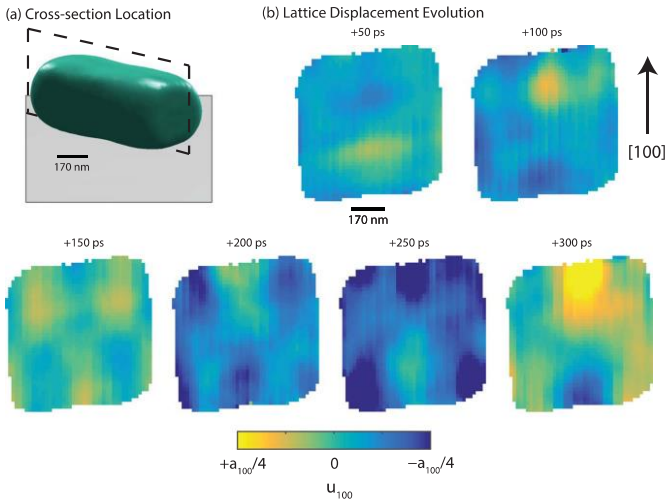

Fig. 3. Displacement fields in a ZnO nanoparticle imaged by BCDI at various times after an optical pump, showing picosecond dynamics of acoustic phonon modes [34].

Improved BCDI Methods for In Situ Materials Studies: We have developed robust reconstruction algorithms that enable Bragg coherent diffraction imaging studies of a wider spectrum of defects and nanostructures in crystalline materials than has been possible to date under real-world environments. This includes developing a methodology for BCDI at highly penetrating x-ray energies above 50 keV [10] (illustrated in Fig. 4), strategies for improved imaging of defects through genetic algorithms [35], and a flexible 3D Bragg ptychography approach suitable for highly focused x-ray nanobeams [5]. In particular, demonstration of our new 3D Bragg ptychography approach enabled both strain and stacking disorder to be imaged from an InGaAs nanowire relevant to optoelectronics at spatial resolutions as high as 3nm.

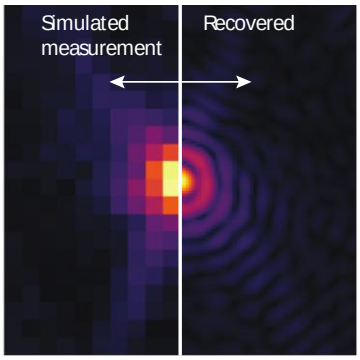

Fig. 4. A split image of a coherent x-ray Bragg coherent diffraction intensity pattern simulation from a nanocrystal showing (left) the coarse pixilation expected due to the compression of reciprocal space at 54 keV, and (right) the finely pixelated pattern recovered with our approach [10].

XPCS Studies of Surface and Liquid Dynamics: We have made significant progress in developing new experimental and computational infrastructure and strategies for XPCS studies of atomic-scale dynamics at surfaces and in liquids. We used surface x-ray diffraction to investigate monolayer-height island dynamics on the (100) m-plane surface of GaN as a function of temperature and vapor conditions [23]. Elongated monolayer-height island morphologies were observed, in agreement with our kinetic Monte Carlo simulations [40], which indicated that the morphologies result from a significant anisotropy in step edge energy. We completed the construction and commissioning of a new instrument that can accommodate a variety of environmental chambers and provides high-resolution positioning of the sample and detector including full rotations, an x-ray transparent chamber wall for incident and diffracted beam access over a wide angular range, and minimal thermal sample motion, giving the sub-micron positional stability and reproducibility needed for coherent x-ray studies [41]. The instrument enables XPCS studies of surfaces, as well as BCDI and Bragg ptychography studies of thin films. These have previously been difficult due to the limited coherent x-ray flux available at existing synchrotron sources. While the APS upgrade will deliver orders-of-magnitude larger fluxes of monochromatic coherent x-rays compared with what is available today, there are already opportunities to employ XPCS methods in characterizing dynamical behavior of surfaces and thin films. For example, to increase the transversely coherent flux available from the present APS source, we demonstrated that removing the monochromator and accepting the full pink beam bandwidth of the third harmonic of the undulator spectrum leads to sufficient coherent flux to perform XPCS studies of surface dynamics [7]. While this relatively large bandwidth decreases the Q resolution in the radial direction, it can be adequate for near-specular XPCS measurements from surface features, since the speckle are extended in the surface normal direction. We used this pink beam XPCS method to study surface island behavior on m-plane GaN [2] (Fig. 5). We demonstrated that the arrangements of the islands forming during layer-by-layer growth are correlated from layer to layer, consistent with Monte Carlo simulation results and a mechanism in which island nucleation on successive atomic layers occurs preferentially in regions of high adatom density. We have also pioneered a split-pulse FEL method that allows nanosecond and faster equilibrium dynamics in liquids and colloids to be observed using speckle visibility XPCS [11].

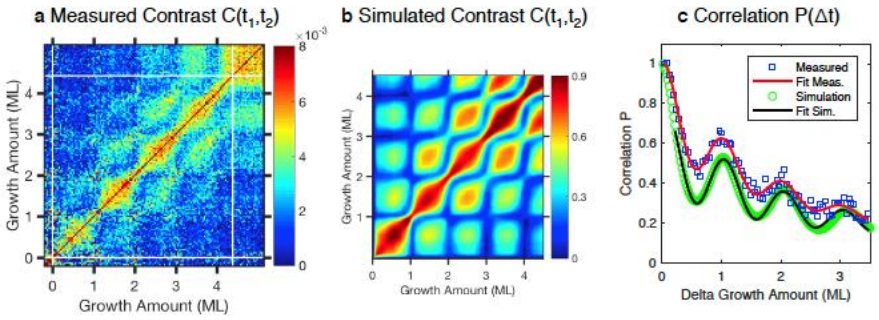

Fig. 5. a, Two-time correlations in the measured speckle from 2D islands before, during, and after growth at 796 K. The time axes have been converted to growth amount using the observed growth rate. White lines indicate the start and end of growth. The "checkerboard" pattern indicates that the arrangement of islands formed in successive layers is correlated with that in previous layers. b, Two-time correlations in the simulated speckle from 2D islands during growth, which also show correlations between island arrangements in successive layers. c, Points: measured and simulated correlations averaged over equal time differences, showing oscillatory behavior with a period of 1 ML. [2]

Future Plans

Imaging and Reactivity of Electrode Materials: Alloys are extensively studied for efficiency and selectivity of catalysts [L5, L6] and widely used for practical and industrial applications. However, it is not well understood why some alloy nanoparticles, often chemically or thermally treated, have a significantly better reactivity and selectivity. We will use BCDI to investigate *in situ* the behavior of alloy nanoparticles undergoing phenomena such as shape change, strain evolution, or compositional redistribution during chemical and thermal treatments and under reaction conditions. As in the case of single-component particles, the amplitude of the reconstructed images will give particle shapes. However, the phase distribution in the images, which provides a map of elastic strain for single-component nanoparticles, will also contain information on composition inhomogeneity in binary alloy nanoparticles, since the dependence of lattice constant on composition produces a stress-free strain distribution related to the composition distribution that contributes to the total strain. To separate the contributions from elastic strain and composition, we will develop resonant BCDI to obtain independent information on composition by tuning the x-ray energy through an absorption edge.

BCDI Studies of Local Electrochemical Behavior: The ability to perform localized SECCM/BCDI measurements from nanoparticles or grains in a polycrystalline film with efficient gas exchange significantly widens the set of problems that can be addressed by with BCDI. Among the many problems we plan to study, keen interest lies in understanding the relationship between structure and activity during the reduction of CO and CO_2 in metal nanoparticles and polycrystalline films with high numbers of grain boundaries. Catalytic reduction of CO and CO_2 is a key step in the production of fuels from these materials. Recent studies indicate that defects and grain boundaries are important to this process [L4, L7], but a detailed mechanism remains elusive. Combined BCDI/SECCM studies will help in formulating

this detailed understanding and the ultimate goal of engineering defects and grain boundaries for enhanced CO and CO_2 reduction.

Coherent X-ray Studies of Lattice and Electronic Order: We will continue to extend coherent diffraction imaging to the study of quantum materials with emergent charge/orbital/magnetic orders [3]. The key goal is to directly visualize the competition and/or collaboration between the lattice, charge, spin and orbital degrees of freedom. Direct information concerning the interplay of different order parameters in real space and in heterogeneous quantum materials will allow precision control of desired orders using strain, electric/magnetic field or ultrafast lasers. This requires progress on several fronts. On the instrumentation side, we will develop the low temperature, high pressure and strong magnetic field capabilities needed to access the phase transitions in quantum materials. We will also develop procedures to prepare nanoscale samples from bulk crystals or thin films for BCDI, where nanocrystals do not exist in most cases. These procedures will allow broader application of coherent x-ray imaging in the condensed matter physics community. With the help of nanofabrication technologies, we will study quantum materials as electronic devices, and understand the key factors that enhance the performance of materials. From the algorithmic perspective, we will develop reconstruction methods required by study of lattice/electronic orders. This includes 3D Bragg CDI and Bragg projection ptychography data taken across the elemental resonances, datasets taken at cryogenic temperatures (where sample vibration leads to reduced fringe visibility), and data with reduced numbers of photons (for weaker electronic orders).

Improved BCDI Methods for In Situ Materials Studies: We plan to develop new BCDI algorithms that enable studies of dynamic nanocrystals in unstable environments, and to utilize these algorithms for BCDI experiments at elevated temperatures and under catalytic conditions where sample dynamics occur at time scales that are faster than a typical BCDI scan. We will also continue to develop algorithms for high energy BCDI [1], anticipating the capabilities of the APS Upgrade, and we will perform experiments that demonstrate the feasibility of integrating high energy BCDI with high-energy diffraction microscopy in order to enable multi-length-scale structural imaging of large populations of grains in bulk structural materials under real-world stresses and thermal loading.

XPCS Studies of Surface and Liquid Dynamics: The steadily increasing coherent x-ray flux from new and upgraded light sources will enable XPCS studies of equilibrium fluctuations with ever higher time and spatial resolution. Advances in detectors [L8] are allowing sequential-mode XPCS studies of nanoscale dynamics with microsecond time resolution. We will develop this new capability to address key issues in the characterization of nanostructured liquids used in chemical separations and battery electrolyte applications. Anticipated further improvements in detectors and in synchrotron sources (such as the APS Upgrade) will extend our ability to observe fluctuations in liquids down to atomic length scales and nanosecond time scales. To reach picosecond time scales in atomic liquids, we will also further develop split-pulse FEL

methods designed to avoid x-ray beam interaction with the material dynamics. The single-Q, delta-time and two-time correlations that we have employed so far are but two of many correlation functions that can be explored by coherent x-ray methods. Our future use of higher-order correlation functions will provide a richer view of the atomic-scale processes that give rise to ordered nanostructures. The penetrating nature of high energy x-rays will allow us to pursue studies of the dynamics of a wide range of surfaces and interfaces under *operando* conditions.

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

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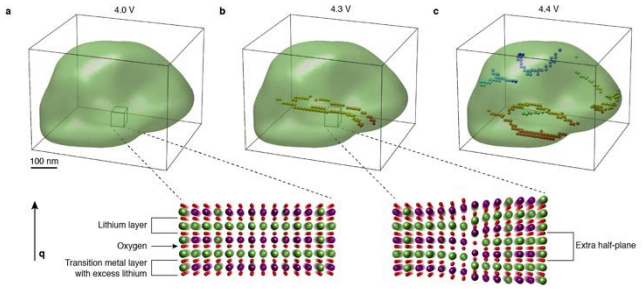
Program Scope

Understanding the relationship between structure and function is one of the crucial cornerstones of the modern materials physics. Recent advances in synchrotron radiation allow imaging of nanoscale order parameters and spatial inhomogeneities, as well their temporal evolution with unprecedented resolution. The central theme of this proposal is the development and application of these methods in *operando* materials and devices.



Formation of a dislocation network during charge. Isosurface rendering of a Lithium-Rich particle measured in operando during charge. [1]

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

Recent Progress

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

Our recent work has focused on imaging nanoscale heterogeneities, such as crystalline topological defects (dislocations), strain, as well as electronic defects (orbital ordering), with an emphasis on understanding the formation mechanisms of these defects and their dynamics – studied by either coherent diffractive imaging methods or by XPCS.

We also expanded our group's activities to ultrafast x-ray scattering performed at XFELs. [2]

Future Plans

We propose a number of research activities that built on the results, expertise and techniques developed in our group, with continued strong focus on studies of in-situ studies of energy storage materials and devices, new exploits in area of photovoltaic perovskite solar cell, as well as slow fluctuating domain walls and order parameters in correlated electron systems. These proposed directions will involve continued use and development of coherent x-ray scattering tools, a major expertise of our group, including Coherent X-ray Diffractive Imaging, X-ray Photon Correlation Spectroscopy as well as Scanning X-ray Nanodiffraction.

We will focus on three major research themes:

1. Operando Imaging of energy-relevant materials and devices: this project focuses on studies of emerging energy storage materials (primarily Li-based transition metal oxides).
2. Defect formation in photovoltaic hybrid perovskite solar cell materials.
3. Studies of domain walls and texture defect fluctuations in correlated electron systems, such as orbitally-ordered and/or charge-ordered transition metal oxides as well as helical antiferromagnetic metals.

Understanding of fundamental nanoscale physics of electronic materials is a crucial cornerstone for developing ways in which electronic and magnetic order parameters can be designed, controlled and manipulated, producing a new generation of electronic computing, communication, media and energy storage devices with desired functionality at nanometer length scales.

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Creating New Quantum States of Matter in Time and Space Through Engineering Artificial Interfaces and Structures

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John Harter (UCSB)

Program scope

The objectives of this research are to tailor chemistry, deformations, and interfaces for controlling quantum states and their lifetimes following ultrafast photoexcitation. The research focuses on magnetic properties, metal-to-insulator transitions, and possible photoinduced superconductivity. The project will integrate theory and computational methods of non-equilibrium dynamics, synthesis of structures with the desired blueprint, and multi-modal characterization using optical lasers and high-repetition x-ray free-electron lasers. The unique characteristics of x-ray lasers will be crucial in establishing a synthesis-characterization feedback loop for engineering artificial quantum materials out-of-equilibrium.

Recent progress

One specific possibility to realize the transition to a non-thermally accessible quantum phase of matter occurs in the epitaxially strained rare earth titanate $GdTiO_3$. A recent theoretical study by the theory member of our team (Benedek) hypothesizes a dynamical access to a previously experimentally inaccessible magnetic phase[2]. The study shows that a delicate balance between tuning strain, atomic composition, and the strength of the induced vibrational excitation allows for inducing a magnetic phase transition from the ferromagnetic ground state to a hidden A-type antiferromagnetic phase (A-AFM). Recent developments by the synthesis member of our group (Schlom) show unprecedented control of strain in titanates[3-7] (**Fig. 1**), making the experimental realization of the advanced control of quantum phases within reach. A key enabler for the controlled strain engineering of perovskite systems is the multitude of commercial single-crystal substrates of perovskites with different lattice constants and octahedral rotation patterns, half of which were developed by Schlom and his collaborators over the last 15 years [1].

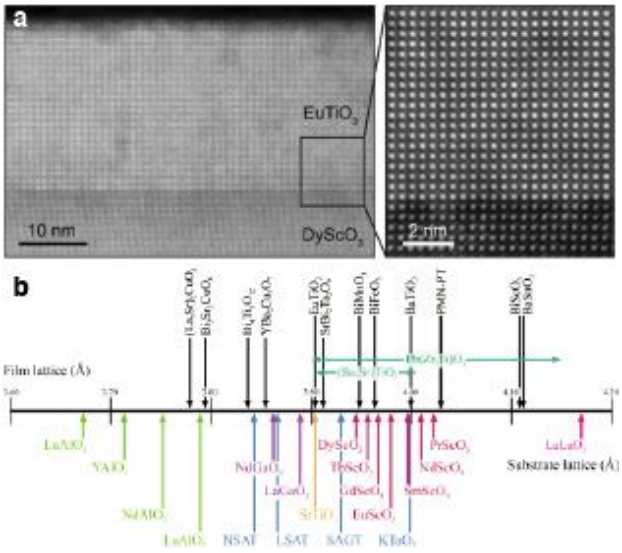

Figure 1: (a) Using the strain of a commensurate interface to statically tune the ground state of a titanate ($EuTiO_3$) from a ground state that is simultaneously antiferromagnetic and paraelectric into a ground state that is simultaneously ferromagnetic and ferroelectric (the strongest multiferroic known), **(b)** the multitude of perovskites substrates now available for tuning strain in perovskite systems. (Figure adapted from[1]).

Future plans

The objectives of our proposed program include: (A) Access and control of non-thermal phases, (B) Controlling pathways in systems with multiple quantum states, and (C) Controlling the lifetime by dimensional confinement and interface engineering.

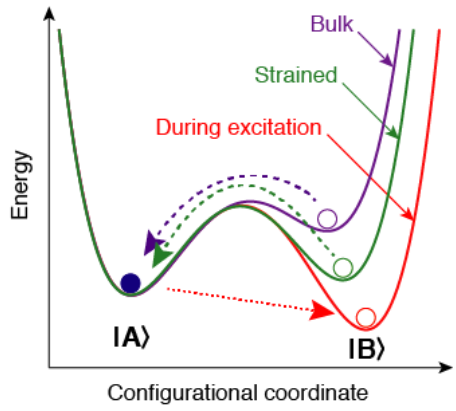

Figure 2: Landau free-energy phenomenology for two quantum states |**A**> and |**B**>. The red dashed arrow shows the non-thermal phase transition from state |**A**> to the excited state |**B**>. Subsequently the system thermalizes, and the static strain determines the lifetime of the state |**B**>. In the strained system the |**B**>→|**A**> transition is slower than in bulk

(A) We will control the static energy landscape of quantum materials through epitaxial strain or interfacial engineering in concert with pump-probe techniques to realize new quantum states of matter, which only exist under transient conditions. This objective will also establish design principles for lengthening or shortening the lifetime of non-thermal states and will enable the design of artificial quantum phases of matter with a specific lifetime (**Fig. 2**).

(B) We will deliberately engineer artificial quantum materials (using control parameters that include composition, strain, and heterostructuring) to position them on the brink between three or more different states. We will then identify and optimize non-thermal excitations for inducing specific transitions between each of the three or more states. This objective will establish design principles for controlling transition pathways in the energy landscape of quantum materials.

(C) We will use interfacial engineering in thin film heterostructures to control the transport of heat flow in quantum materials with the goal of controlling (either extending or reducing) the lifetime of the photoexcited states. This objective is relevant to studying the properties of excited phases, e.g., the purported room-temperature superconductivity of photoexcited cuprates, or to enable high speed switching between states, as is desired for optical limiting applications in which a metal-insulator transition can be optically switched on or off at high speed.

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Probing Fundamental Mechanisms of Plastic Deformation with High Energy X-rays
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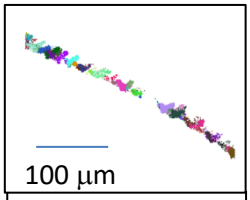
Program Scope

The incomplete understanding of plasticity in metals is due in part to a lack of multiscale experimental observations connecting nano-scale defects and their interactions with emergent meso- and macro-scale materials responses. Here, we will aid in the development and combining of multiple synchrotron based high energy x-ray probes of bulk materials that span relevant length scales and will work towards the incorporation of resultant new knowledge into models ranging from dislocation dynamics to spectral based continuum plasticity. Experimental probes include far-field and near-field High Energy Diffraction Microscopy (HEDM) which we will extend to new length scales and new sensitivity, Bragg Coherent Diffractive Imaging (BCDI) of nano-scale defects and their interactions which will be coupled with global knowledge gained from HEDM[1,2]; Dark-field x-ray microscopy[3] will also be developed at the APS 1-ID beamline with future implementation planned for the long HEXM beamline associated with the APS Upgrade.

Recent Progress

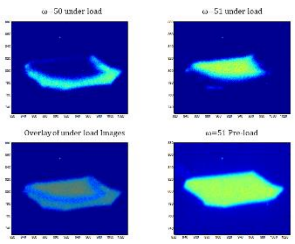
Near-field HEDM maps the crystal unit cell orientation field in three dimensions, inside of bulk polycrystalline samples. Grain orientations and boundary positions are determined to < 0.1 degree and ~ 1 μm, respectively. BCDI measurements map Angstrom scale atomic displacement fields in ~ 1 μm nanoparticles with ~ 30 nm spatial resolution, allowing observation of individual dislocations and their motions. A limitation of current BCDI measurements is the incomplete knowledge of particle orientations (only a single Bragg peak is detected) and of surrounding neighborhoods in polycrystalline samples. We have performed a proof-of-principle measurement showing that nf-HEDM can determine complete orientations of micron sized grains. The figure at right shows reconstructed grains along the intersection of a line-focused beam with a free standing film of copper nanoparticles (supplied by R. Sandberg of LANL). Extended data collection protocols and analysis methods should allow the mapping of an area of such a sample or a volume of a nanocrystalline sample; particles in the known orientation field can then be measured with BCDI at either 34-ID-C or at 1-ID-E.[4] Such measurements will allow the study of dislocation motions and interactions in known microstructural environments yielding valuable input to computational models.



Near-field HEDM reconstruction of micron sized Cu grains in a free standing film. Colors are mapped from unit cell orientations.

Recent work has shown that appropriately collected nf-HEDM data are sensitive to intra-granular elastic lattice strain variations at least at a level somewhat below 10^{-3}. In the presence of such

inhomogeneous strains, spatially resolved images of grains, as collected in standard nf-HEDM measurements, become divided between successive rotation intervals; observation of over 100 Bragg peaks is sufficient to yield local strain tensors for each reconstructed volume element. An example of peak splitting is shown at right. The complete projected image observed in the unloaded state (LR) is split between rotation intervals under load (UL, UR); superposition of the split peaks (LL) yields the unsplit peak shape. Current work is underway to develop and validate analysis procedures.



Future Plans

At APS 1-ID we will perform more extensive measurements on LANL provided copper foils with micron sized grains. A form of "super-resolution" scanning will be used to more accurately determine center of mass positions. Longer counting times will pull out signal from additional Bragg peaks and from a larger fraction of the grains. We will develop methods to move samples from the 1-ID beamline to the BCDI station at 34-ID-C and to locate the mapped region (work with LANL collaborators). We will collaborate with the Hruszkewycz group at ANL (including Suter's former graduate student, Maddali) in performing high energy BCDI[4] at 1-ID so that samples do not have to be transferred between beamlines and more bulk-like samples can be probed. This work will yield one of (if not the) first BCDI measurement that analyzes multiple non-co-linear Bragg peaks from the same grain and that probes multiple neighboring grains.

The first supported student under this grant will make an extended visit to LANL starting in December 2018 to learn BCDI measurement procedures, reconstruction software, and develop sample handling procedures for transfers between beamlines.

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J. P. Hanson, et al., "Crystallographic character of grain boundaries resistant to hydrogen-assisted fracture in Ni-base alloy 725," Nature Communications, **9**, 3386 (2018).

L. Wang, et al., "Direct measurement of critical resolved shear stress of prismatic and basal slip in polycrystalline Ti using HEDM", Acta Materialia, **132**, 598610 (2017).

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Fluctuations in Quantum Materials

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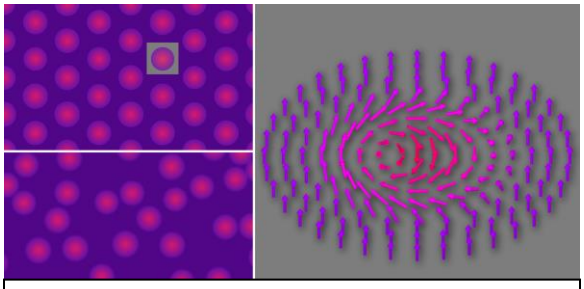
Program Scope

This program is to advance the frontier in quantum materials through the measurement of fluctuations of novel types of order. This is at the heart of the fundamental physics in these solids, but has remained challenging to directly measure. One key component for this research is in the application of newly developed coherent scattering methods using x-ray free electron lasers (XFELs), which can access these fluctuations on relevant energy scales. This will allow one to make direct, element-specific and momentum-resolved measurements of the fluctuations of a complex material and connect them to requisite response functions calculated from first principles. Extracting spontaneous fluctuation information from the system under study provides opportunities to answer many fundamental questions in this field, such as: do density wave fluctuations in unconventional superconductors induce high-temperature superconductivity?

Recent Progress

We have recently used the spatial coherence of the short x-ray pulses generated at an XFEL to perform x-ray quanta fluctuation spectroscopy (XQFS), a method to measure fluctuations in equilibrium through the use of photon counting and speckle statistics. This allows for an extraction of the contrast function, C(q,t), which can be directly related back to the dynamic structure factor, and hence the dynamic susceptibility. This method enables measurement of stochastic fluctuations in the ground state.



Pictures depict both the static and fluctuating skyrmion lattice (left) and a schematic of a unit magnetic skyrmion vortex (right), which is the quasiparticle that makes up the skyrmion lattice in GdFe (MRS Bulletin, Materials News, 9/2017).

We demonstrated this technique by studying the topological skyrmion system, GdFe, to measure fluctuations three orders of magnitude faster than what had previously been achieved [1].

Preliminary investigations showed the fluctuations depended on the magnetic field applied to the skyrmion lattice, but differed from classical critical phenomena. We have recently designed a new instrument for further investigations, which can deliver tens of thousands of times more data. This was constructed and used to measure additional information at LCLS to provide understanding of the skyrmion lattice phase ground state fluctuations.

Future Plans

We propose to study unconventional superconductors, such as the cuprates, and specifically the dynamic properties of the CDW and SDW states. A momentum-resolved measurement of thermal fluctuations that underlie the ground state of the CDW ($T \neq 0$) is necessary for understanding how superconductivity emerges from the CDW ordered and pseudogap states. Though the effect of an external excitation mechanism on the CDW state is important, ultrafast measurements of CDW fluctuations in equilibrium are fundamental if one wishes to study how the ordered system breaks symmetry spontaneously.

We will shed new light on this problem by studying the dynamic, quantum-disordered stripes and their collective fluctuations [2] that could be relevant for understanding the superconducting mechanism, and which may even be responsible for pairing in the formation of the superconducting state. This notion that has been investigated theoretically [3], but to date has remained experimentally elusive. To contribute to this debate, we will obtain new information on this physics problem by answering the following questions:

- Does the CDW state fluctuate in time and if so, on what time scales?
- How do the fluctuations scale, in time and momentum, near T_c?
- How does the doping dependence affect the relationship between superconductivity and dynamic fluctuations?
- Will dynamic fluctuation studies allow us to understand how unconventional superconductivity forms out of the high-temperature state?

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Publications

This award has not yet generated any publications.

Understanding Mesoscale Nonequilibrium Heterogeneity by Multimodal X-ray Imaging

Haidan Wen, Advanced Photon Source, Argonne National Laboratory

Program Scope

This program is targeted at probing and understanding mesoscale heterogeneities to help bridge the knowledge gap from atomistic to macroscopic length scales as materials evolve. The approach to achieve this goal is to apply multimodal spatiotemporally resolved probes using suitable ultrafast terahertz, optical and x-ray radiation. 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 or enhanced functionalities. The developed methodology and instrumentation will be generalizable for use at large-scale synchrotron x-ray facilities and free electron lasers.

Recent Progress

We have made significant progress on both instrumentation development of new x-ray imaging capabilities and scientific discoveries of new mesoscale dynamics. Part of the results is reported in 11 publications and highlights are categorized into two themes below.

1. ***Mesoscale phenomena studied by ultrafast probes.*** We utilize multimodal ensemble-averaged optical and x-ray probes to understand electronic [1], lattice [4, 9], and spin [2] dynamics. These studies reveal unique mesoscale dynamics and help identify material systems that can be further studied by time-resolved nanoscale x-ray imaging.

- *Unconventional slowing down of electronic recovery*. Electronic dynamics is usually fast, on the order of sub-ps to hundreds of ps time scales. But we found that electronic dynamics can become ultraslow in systems with energy-degenerate mesoscale heterogeneities. An unusually slow recovery of charge ordering is observed close to the phase transition temperature in $La_{1/3}Sr_{2/3}FeO_3$ [1]. Multimodal ultrafast probes using optical and x-ray radiation unambiguously show that this recovery extends to microseconds, much slower than the cooling of the lattice, highlighting a unique mesoscale electronic behavior that strongly decouples from the lattice close to the first-order phase transition. The controlled slow electronic recovery may provide a route to stabilizing exotic transient electronic phases. DFT+U calculations suggest that two charge-ordered domains with distinct local ordering can coexist close to the transition temperature, motivating future experiments to directly image the dynamical exchanges between two charge-ordered domains.

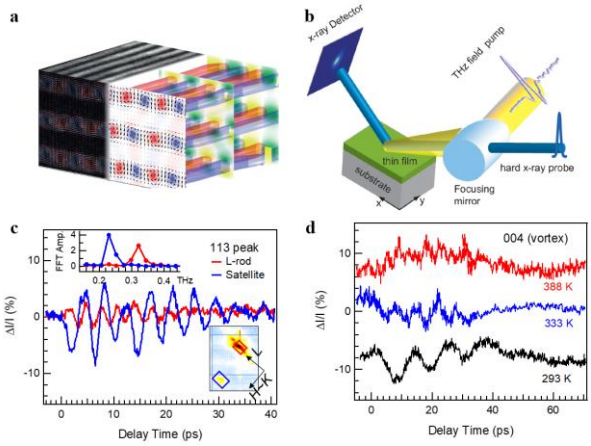

Fig. 1 a) Schematic of the THz ferroelectric vortices. b) The THz-pump, XRD probe experiment at LCLS. c) Diffraction intensity modulation of 113 peaks from vortex (re) and a1/a2 phase (blue), respectively. d) Diffraction intensity modulation of 004 Bragg peak of vortex phase at various temperatures.

- *Ultrafast dynamics of polar vortices driven by terahertz fields*. We performed the THz-pump, x-ray diffraction probe experiment at the LCLS to investigate the dynamics of a new mesoscale object, in which rotating polarization forms ferroelectric vortices (Fig. 1a from Ref.1). The intense THz field is employed to directly excite the ferroelectric polarization (Fig. 1b). The intensity modulation of Bragg peaks from conventional *a1/a2* phase and vortex phase fingerprint their distinct frequencies at 0.24 and 0.33 THz respectively (Fig. 1c). In addition, we identified a unique mode at lower frequency, 0.08 THz, manifesting as the intensity modulation of vortex 004 peaks. Remarkably, the frequency of this mode can be tuned significantly with only a moderate temperature increase (Fig. 1d), in contrast to the temperature-

independent high-frequency modes. It suggests this low-frequency mode is a collective mode uniquely associated with the order parameter of the ferroelectric vortex. These modes are not predicted by conventional acoustic phonon propagation, indicating a new coupling of ferroelectric polarization upon THz excitation. Dynamical phase-field simulation and second-principle calculations are on-going to help understand these observations.

2. ***Mesoscale phenomena studied by nanoscale imaging.*** Moving beyond ensemble-averaged probes, unique multimodal static and time-resolved x-ray diffraction imaging capabilities are developed to provide insights into nanoscale structure-property relationship [8] and local structural dynamics [3, 6, 7, 10].

- *Development of in-situ scanning near-field optical microscopy (SNOM) and x-ray diffraction microscopy (XDM).* We have achieved an instrumentation milestone to enable simultaneous data collection of near-field optical signal and x-ray diffraction intensity. Various technique challenges were overcome to allow stable SNOM performance on a tilted goniometer at 7ID-C beamline of the Advanced Photon Source (Fig. 2a). This new system is the first of its kind and is capable of probing electronic and structural properties using SNOM and XMD with 20 nm and 200 nm spatial resolutions, respectively.

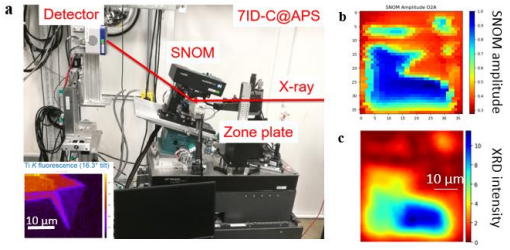

Fig. 2 a) The newly developed *in-situ* SNOM and XDM instrument. b) The amplitude of the SNOM signal that shows heterogeneous near-field optical reflectivity of a tip-pressure written regime in SmS, probed at 10 μm wavelength. c) The corresponding diffraction intensity map measured at the Bragg angle of the metallic phase.

- *Structural characterization of tip-pressure or tip-field induced phase transition.* Using the newly developed imaging platform, we studied various local structural dynamics driven by tip-applied local pressure or electric fields. For example, in a prototypical ferroelectric $PbZrTiO_3$ thin film, we reveal that defects play an important role in pressure-induced ferroelectric domain switching. In SmS crystals, we can simultaneously measure and correlate the local electronic (Fig. 2b) and structural (Fig. 2c) properties after tip-pressure-induced metal-to-insulator phase transition. In VO_2, the nanoscale substrate processing [8] and tip-bias are able to modify the MIT. This in-situ imaging technique is particularly suitable to study the local structural properties of short-lived metastable states. Several manuscripts are in preparation.
- *Time-resolved x-ray diffraction microscopy.* Combining nanoscale x-ray imaging with pump-probe technique, we developed and applied time-resolved x-ray diffraction microscopy to study various mesoscale phenomena including characterizing domain-dependent acoustic wave dynamics [3] and imaging ballistic phonon transport as a result of selective THz excitation [7]. Utilizing coherence of the x-ray radiation, we have mapped the strain field evolution in core-shell [6] and ferroelectric ZnO [10] nanoparticles by time-resolved coherent diffraction imaging. The recent advance of time-resolved x-ray imaging is summarized in an invited review article by the PI [11].

Future Plans

Capitalizing the recent discoveries of mesoscale dynamics presented above, we will further investigate the local dynamics of mesoscale electronic domains in charge ordered systems, and local vortex dynamics using time-resolved microscopic tools. In addition, we will apply in-situ SNOM and XDM instrument to study nanoscale structure-property relationship in phase-change materials. The capabilities of the newly developed multimodal imaging platform will be further improved and extended by coherent x-ray imaging techniques and ultrafast SNOM measurements. A customized cryostat will be designed and installed to enable time-resolved x-ray diffraction microscopy at cryogenic temperature. New strategies for analyzing data collected with multimodal spatiotemporally resolved methods will be developed, leveraging the high-performance computing facility at ANL.

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Quantum Engineering Exciton Dynamics in 2D-Heterostructures

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Program Scope

The objective of this proposal is to investigate exciton dynamics with unique spin/pseudospin properties by the combination of ultrafast optical spectroscopy and quantum engineering 2D heterostructures. The recent emergence of two-dimensional (2D) quantum materials, such as 2D semiconductors and magnets, have provided new platforms for study light matter interactions with external controls.[1,2] The accessibility to high quality heterostructures formed by different 2D materials further enabled the exploitation of emerging phenomena which otherwise not possible. We aim to investigate and understand these emerging phenomena associated with excitons via advanced heterostructure engineering. We will study exciton wave function engineering, transport, and many body interactions with Berry phase effect, and explore exchange field control of exciton dynamics in magnetic heterostructures.

Recent Progress

The creation of moiré patterns in crystalline solids is a powerful approach to manipulate their electronic properties, which are fundamentally influenced by periodic potential landscapes[3-5]. In two-dimensional (2D) materials, a moiré pattern with a superlattice potential can form by vertically stacking two layered materials with a twist and/or finite lattice constant difference. So far, this approach has led to several scientific breakthroughs using graphene-based moiré superlattice structures with electronic excitation. However, moiré superlattice effects on optical excitations (e.g. excitons) based on 2D semiconductors have not been realized. In this project, we observed moiré excitons for the first time using $MoSe_2/WSe_2$ heterobilayers with twist angle control (Fig. 1). At low temperatures, we observe photoluminescence near the *free* interlayer exciton energy but with over 100 times narrower linewidths (~100 μeV). The emitter *g*-factors are homogeneous across the same sample and only take two values, -15.9 and 6.7, in samples with twisting angles near 60° and 0°, respectively. The *g*-factors match those of the free interlayer exciton, which is determined by one of two possible valley pairing configurations. At a

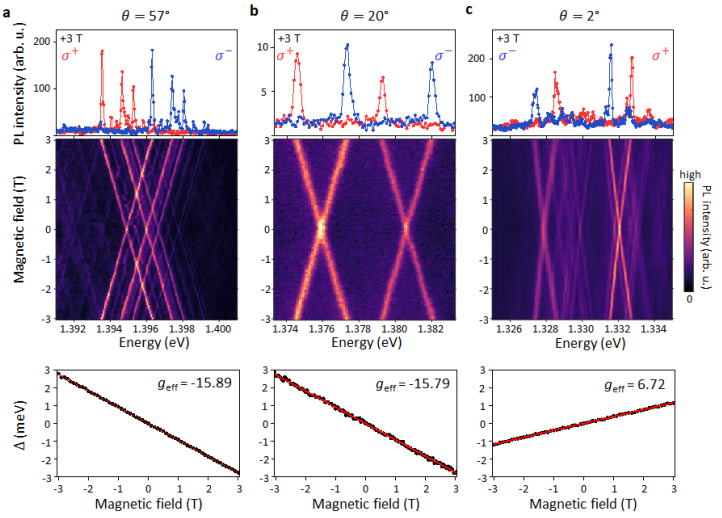

Fig. 1. Observation of moiré excitons. Magnetic-field-dependent photoluminescence from interlayer excitons in the $MoSe_2/WSe_2$ heterobilayer with twist angle of a, 57°, b, 20°, c and 2°. Top row: Helicity-resolved PL spectra at 3T. Middle row: Total PL intensity plot as a function of magnetic field. Bottom row: Zeeman splitting of the polarization-resolved PL as a function of the applied magnetic field.

twist angle near 20°, the emitters become two orders of magnitude dimmer, but remarkably, they possess the same *g*-factor as the heterobilayer near 60°. This is consistent with the Umklapp recombination of interlayer excitons near the commensurate 21.8° twist angle. The emitters exhibit strong circular polarization, which implies the preservation of three-fold rotation symmetry by the trapping potential. Since the moiré potential can function as a smooth quantum-dot-like confinement potential but with the preservation of three-fold rotational symmetry, our observation of quantum-dot-like photoluminescence features with the unique inheritance of valley-contrasting properties from the heterobilayer demonstrates the observation of moiré excitons. This result provides a promising starting point to explore several intriguing theoretical proposals related to quantum photonics, such as entangled photon sources, topological exciton, and more[6].

Future Plans

We will continue to investigate the exciton dynamics due to quantum confinement effect in moiré superlattice structures with external control, including twist angle, electrical field, doping, and exchange field effect.

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Ultrafast Control of Emerging Electronic Phenomena in 2D Quantum Materials

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

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 phenomena resulted from the interactions between spin, charge, and lattice degrees of freedom in novel two-dimensional (2D) quantum materials and their heterostructures. We employ a wide range of state-of-the-art ultrafast technologies involving terahertz, (magneto) 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), the Linac Coherent Light Source (LCLS), and ultrafast electron diffraction (UED) play crucial roles of advancing this research program.

Recent Progress

1. Spin Dynamics and its coupling to charge and lattice degrees of freedom

Electrical control magnetic order in 2D magnets (Xu, Xiao): Controlling magnetism using an electric field is of great fundamental importance and has a wide range of technological applications such as low-energy dissipation magnetic memories. With the recent discovery of magnetic 2D materials, the field has now emerged as an unprecedented platform to explore controllable magnetism in the atomically thin limit[1]. In this work, using layered antiferromagnetic bilayer CrI_3 as a model system, we demonstrate two forms of electrical control of 2D magnetism in van der Waals magnetic insulators. (1) Electrical control of metamagnetic transition. We showed that the critical field for the metamagnetic transition can be tuned by around 30% by an electrostatic doping effect (Fig. 1a&b). By setting the magnetic field near the critical field of the metamagnetic transition, we realized an electrically driven magnetic phase transition from a layered AFM phase to a fully spin-polarized FM phase (Fig. 1c). (2) Demonstration of gate-controlled magneto-optical Kerr effect (MOKE) from layered AFM states at zero field. We unambiguously

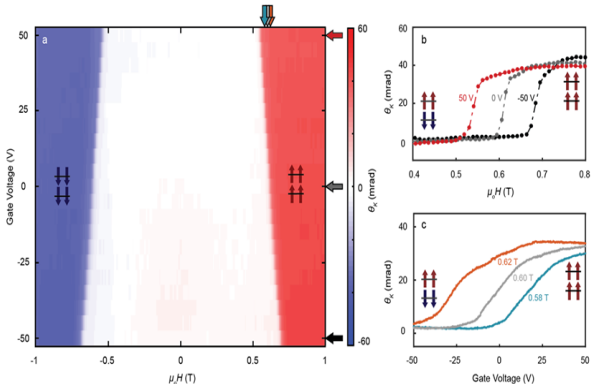

Fig. 1. (a) Intensity of the polar MOKE signal of a non-encapsulated bilayer CrI_3 device as a function of both gate voltage and applied magnetic field. **(b)** Selected horizontal line cuts of (a) demonstrating the gated induced change in critical field of the metamagnetic transition at V_{bg} = -50 V (black), 0 V (gray), and 50 V (red). **(c)** Gate induced transition from layered antiferromagnetic to ferromagnetic states at selected $\mu_0 H$ = 0.58 T (blue), 0.60 T (gray), and 0.62 T (orange).

established that CrI_3 bilayers have a time-reversal pair of layered AFM states which exhibit a spin-layer locking effect with a remarkable linear dependence of their MOKE signals on gate voltage. Our work provides an important conceptual foundation and experimental toolset for future explorations of magnetoelectric phenomena and gate-tunable ultrafast magnetic dynamics, and gate tunable spin lattice coupling effects.

Control of terahertz emission by ultrafast spin-charge current conversion at 2D Rashba interfaces (Wen): The direct measurement of ultrafast electron dynamics at the interfaces of 2D heterostructures are challenging because the signal is rather weak due to the reduction of the volume of electron at the interface. In order to probe the electronic processes at interfaces, we recently developed a new THz emission spectroscopy using ultrafast spin-charge current conversion processes at Rashba interface. In particular, we show that a femtosecond spin current pulse can generate terahertz (THz) transients at Rashba interfaces between two non-magnetic materials (Fig. 2a). Our results unambiguously demonstrate the importance of the interface in this conversion process that we interpret in terms of the inverse Rashba Edelstein effect, in contrast to the THz emission in the bulk conversion process via inverse spin-Hall effect. Furthermore, we show that at Rashba interfaces the THz-field amplitude can be controlled by the helicity of the light (Fig. 2b) and gating. Optical generation of electric photocurrents by these interfacial effects in the femtosecond regime will open up new opportunities in ultrafast spintronics Similar THz emission experiments are planned to study spin transport in 2D magnets that envision to shed light on the emergent ultrafast charge-spin coupling processes across 2D magnet heterostructure.

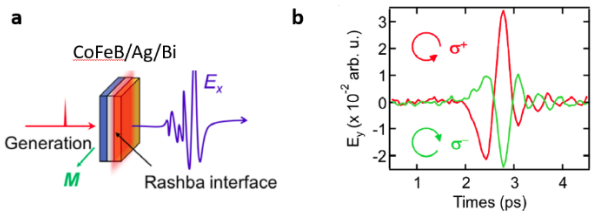

Fig. 2. (**a**) THz emission from non-magnetic heterostructures via spin-to-charge current conversion at the Rashba interface between Ag and Bi. (**b**). Control THz emission via helicity of the excitation laser pulses.

Observation of strong spin lattice coupling in 2D magnets (Xu, Wen, Xiao): The layered antiferromagnetism[2] in CrI_3 provides unique interlayer spin superlattice structures defined by the ferro- and antiferromagnetic interlayer domains. This provides a highly tunable platform, where acoustic and magneto-optic properties can be tuned and even programed. Xu and Wen's groups collaborated on ultrafast optical spectroscopy measurements, which indicate possible strong spin-lattice couplings in CrI_3. As shown in Fig. 3a, transient reflectivity shows coherent acoustic phonon type of oscillation at 17.6 GHz. The same oscillatory behavior was also observed in the TR- MOKE, indicates the lattice vibration is coupled with magnetic ordering. In addition, drastic changes of coherent acoustic phonon frequency were observed (Fig. 3b). Under the ultrafast laser pulse excitation, the interlayer domain configuration changes over time,

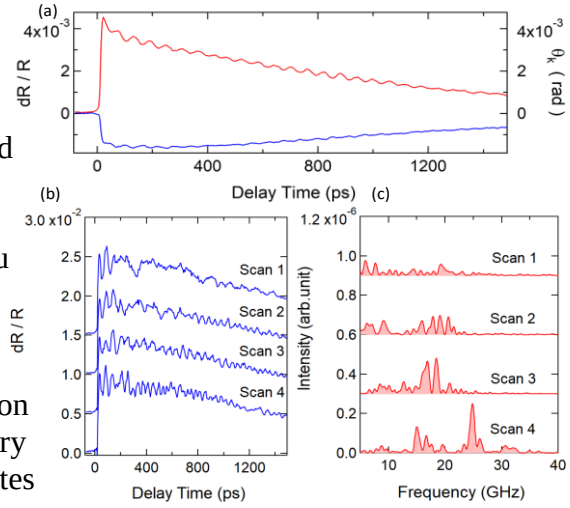

Fig. 3. (**a**) Pump-probe and TR-MOKE signal for bulk CrI_3 flake at 6K. (**b**) Photo-induced dynamics in thin flake CrI_3 at 6 K and zero field, taken at 5 minutes interval at the same location. (**c**) The frequency domain spectrum of each scans shows oscillations cover a wide range of frequency, likely due to the rearrangement of magnetic domains inside the thin bulk CrI_3.

which lead to the change of the coherent acoustic phonon modes over a wide range (Fig. 3c, 1 GHz to a few tens of GHz). This is highly unusual, suggesting the interlayer AF coupling and the spin superlattice played a critical role.

2. *Exciton dynamics and coupling to lattice degrees of freedom in monolayer semiconductor*

Ultrafast spectroscopy of 2D excitons (Gedik, Xu, Xiao): Excitons dominate optical properties of exfoliated semiconductor transition metal dichalcogenides (TMD), such as WSe_2 and $MoSe_2$. Combined with high quality hBN sandwiched samples and the reduced screening effect at 2D limit, the excitons possesses large binding energies with optical accessibility of higher order excitonic states[3,4]. Furthermore, the valley degree of freedom (K and K') is also reflected into these exciton states, increasing their degeneracy. To study these valley excitons, Gedik group built a transient reflection microscope with magnetic field control to 0.6T. Currently, the setup is fully functional, and we reproduced the previously measured valley selective Stark shift observation in hBN capped WSe_2 samples (Fig. 4). This confirmation will pave the way for observation of novel quantum optical phenomena other than valley selective Stark shift[5].

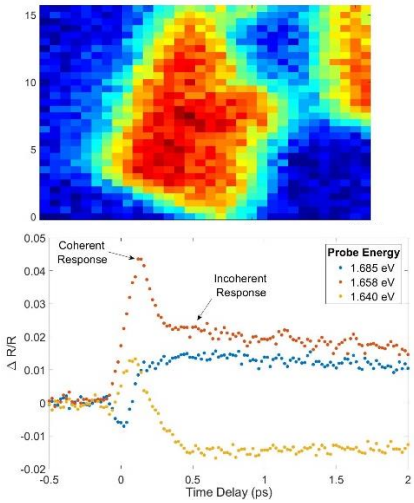

Fig. 4. **(a)** Pump-probe microscopy image from hBN capped single layer WSe_2 (center of the image) and tri-layer WSe_2 (partially visible on the upper right corner) flakes. **(b)** Traces from the single layer flake in (b) at three different probe photon energies. In all traces the sample is pumped with 1.590 eV photons. The coherent part of the trace is due to optical stark shift of the 1s excitonic resonance.

Formulating optical selection rule of excitons in gapped chiral 2D fermion systems (Xiao): Our understanding of optical absorption in semiconductors relies on two essential approximations: effective mass approximation and electric dipole approximation. Together, these two approximations yield the optical selection rule for excitons, as derived in a classic paper by Elliott. However, the validity of the above theory has been recently challenged in a new class of materials called gapped chiral fermion (CF) systems. Examples include gapped topological surface states, biased bilayer graphene, and monolayers of group-VI transition metal dichalcogenides. It has been shown that in these systems the effective mass approximation must be modified to include the Berry phase carried by the CFs to give a proper account of the exciton energy spectrum. In this work, Xiao showed that the exciton optical selection rule in gapped CF systems is governed by their winding number w, a topological quantity of the Bloch bands.[6] Specifically, in a C_N-invariant chiral fermion system, the angular momentum of bright exciton states is given by $w \pm 1 \pm nN$ with n being an integer. We demonstrate our theory by proposing two chiral fermion systems capable of hosting dark s-like excitons: gapped surface states of a topological crystalline insulator with C_4 rotational symmetry and biased 3R-stacked MoS_2 bilayers. In the latter case, we show that gating can be used to tune the s-like excitons from bright to dark by changing the winding number. Our theory thus provides a pathway to electrical control of optical transitions in two-dimensional material.

Anisotropic structural dynamics of monolayer crystals (Wen, Xu): X-ray scattering is one of the primary tools to determine crystallographic configuration with atomic accuracy. However, the measurement of ultrafast structural dynamics in monolayer crystals remains a long-standing

challenge due to a significant reduction of diffraction volume and complexity of data analysis. Led by the collaboration between Wen and Xu, we have demonstrated the first femtosecond x-ray diffraction measurement and applied it to reveal unique anisotropic structural dynamics in a prototypical 2D system, monolayer WSe_2, at the LCLS (Fig.5). We found the absorbed optical photon energy is preferably coupled to the in-plane lattice vibrations within 2 picoseconds while the out-of-plane lattice vibration amplitude remains unchanged during the first 10 picoseconds. The model-assisted fitting suggests an asymmetric intralayer spacing change upon excitation. The demonstrated methods unlock the benefit of surface sensitive x-ray scattering to quantitatively measure ultrafast structural dynamics in atomically thin materials and across interfaces.

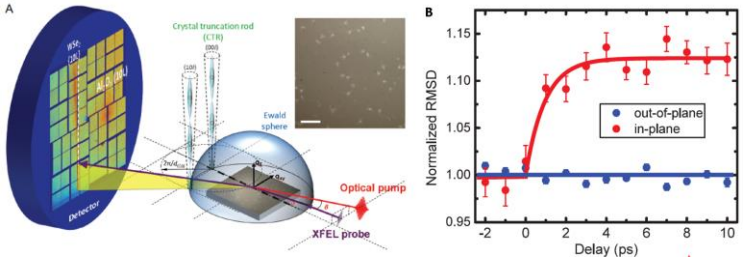

Fig. 5. a) The optical-pump and x-ray-probe setup. b) The extracted atomic vibration amplitude along the in-plane and out-of-plane direction as a function of delay following optical excitation.

3. Dynamics of charge density waves in 2D quantum materials

Clocking the melting of the charge-density-wave order in van der Waals materials (Nuh and Wen): Many previous studies on photo-induced phase transitions focused on the reestablishment of the low-temperature broken-symmetry phase. It is also important to understand how the intense laser pulse melts the ground-state order because the timescale of such suppression often reveals crucial information about the microscopic mechanisms behind the formation of the order. To this end, Gedik group carried out UED studies on the photoinduced melting of charge density wave (CDW) order in $LaTe_3$ at the mega-electron-volt (MeV) beamline in SLAC National Accelerator Laboratory, in collaboration with Wen (Fig. 6). To characterize the overall temporal resolution, an intense, single-cycle terahertz (THz) pulse with a field strength of more than

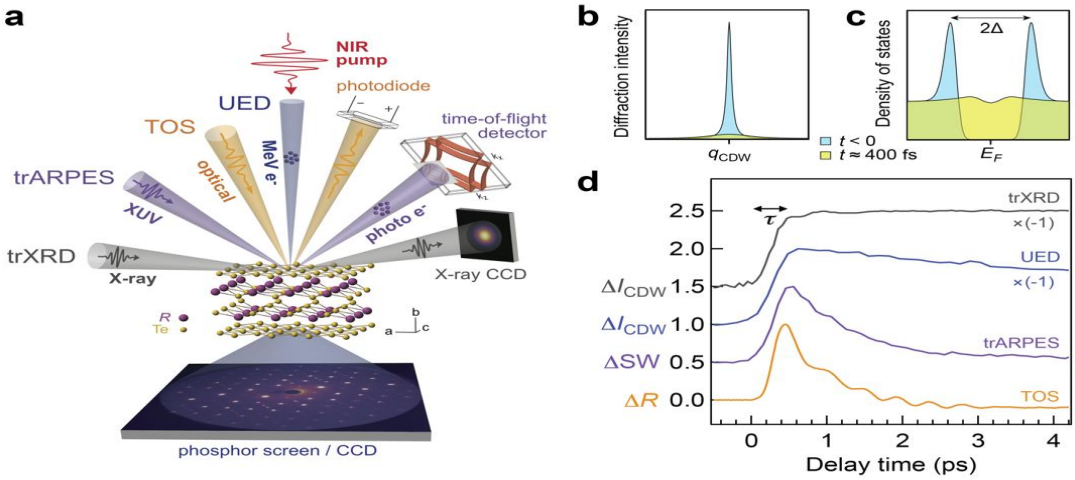

Fig. 6. a, Schematics of different time-resolved probes, including UED, transient optical spectroscopy (TOS), trARPES, and time-resolved X-ray diffraction (trXRD). **b**, **c**, Schematics of the superlattice peak and density of states before (blue) and after (yellow) photoexcitation. **d**, Normalized transient response of superlattice peak intensity (ΔI_{CDW}), in-gap spectral weight (ΔSW), and reflectivity (ΔR) probed by corresponding time-resolved techniques. ΔI_{CDW} are inverted for easier comparison. trXRD data is adapted from Moore *et al.*, *PRB* **93**, 024304 (2016).

500 kV/cm was incident on the sample surface, leading to a center-of-mass deflection of the MeV electron bunch. From the electron streaking pattern, a temporal resolution of less than 300 fs was obtained. The time evolution of the superlattice peak intensity measured in MeV UED is presented in Fig. 6d (blue curve) and is compared to other time-resolved techniques (Fig. 6a).[5] All traces exhibit a CDW melting timescale of 400 fs. This remarkable consistency among different time-resolved techniques indicates that the electronic and lattice subsystems are strongly coupled throughout the melting process. This result suggests the important role of electron-phonon coupling in the formation of the CDW phase in this compound, as opposed to alternative scenarios where electron-electron correlation induces the charge modulation state. The study therefore serves as an elegant demonstration where the synergy of several time-resolved techniques is capable of unveiling the microscopic driving forces behind the formation of broken-symmetry phases.

Terahertz-field-driven dynamics of charge density waves (Wen, Nuh, and Xu): In addition to optical excitation, Wen group explore a direct electric field control of CDW dynamics by a terahert (THz) field pulse, in collaboration with Gedik and Xu. In this case, a picosecond intense electric field modifies the charge density distribution via Coulomb interaction. We performed THz-pump, ultrafast electron diffraction measurement of CDW in thin $LaTe_3$ crystals at the UED facility of the SLAC National Lab (Fig. 7a). Upon the THz-field excitation with a peak field of 500 kV/cm, we recorded the electron diffraction patterns in transmission geometry (Fig. 7b). Figure 7c shows that the ultrafast melting of the CDW intensity upon THz field excitation is on the order of 400 fs, in agreement with melting time upon the optical excitation. The melting is followed by an exponential recovery with a time constant of 2.5 ps. The disordering and recovery of CDW redistributes the scattering intensity back to the zero-order diffraction, showing as a conjugate increase and decay of the direction beam intensity. The ps recovery of the CDW upon THz excitation is distinct from much slower (ms) recovery of sliding CDWs driven by a quasi-DC electric field. This disagreement indicates a new mechanism of CDW recovery upon an electric field excitation.

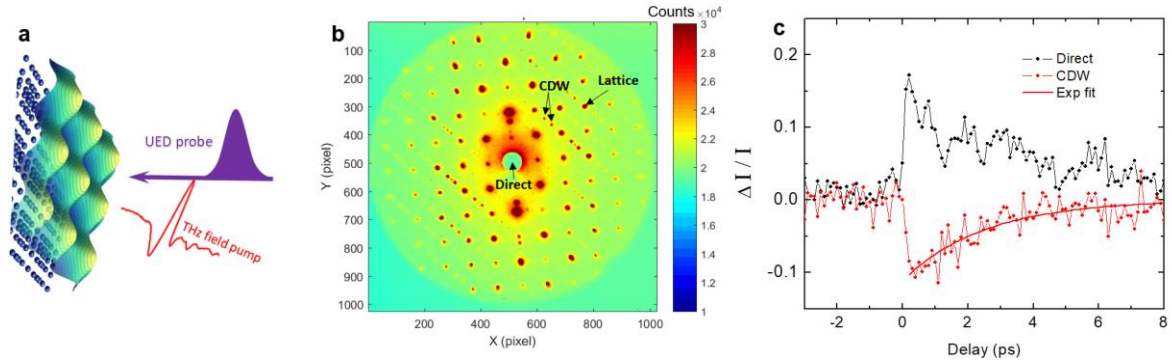

Fig. 7. (**a**) THz-pump electron-diffraction-probe measurements. (**b**) Electron diffraction pattern of $LaTe_3$. The diffraction intensity of CDW superlattice, lattice and direction beam (not shown) can be selectively probed. (**c**) Normalized diffraction intensity changes of the CDW peak and the direct beam as a function of delays.

Future Plans

Theoretical efforts (Xiao) include investigation the Berry phase effect in nonlinear optics and the ultrafast dynamics of spin-lattice coupled systems and understanding the emerging phenomena in experiments performed by team members. These experiential efforts include: (1) Gedik, Xu and Xiao will explore the highly excited exciton dynamics and their optical selection rules in

monolayer TMDs and interlayer exciton dynamics in heterostructures. (2) CDW in 2D quantum materials: In complementary to the THz-pump UED-probe measurements, Wen, Gedik and Xu plan to perform THz-pump, optical probe measurements to understand the dynamics of CDW upon THz excitation. In addition, in-situ x-ray diffraction microscopy measurement will be performed at the APS with enhanced spatial resolution and out-of-plane structural sensitivity to image the domain and domain wall structures in CDW. (3) Magnetic dynamics: Xu, Wen, and Xiao will further investigate the coupling between lattice and magnetic order, and realize the control via magnetic field and electric field. We have planned x-ray diffraction measurement at the APS to investigate the magnetostriction effect. We will also investigate possible higher order coupling effects, such as anharmonicity. In parallel, Wen and Xu will work on THz emission effects at 2D magnetic heterostructures.

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