X-ray Scattering
Principal Investigators' Meeting

Zoom Meeting
November 9–10, 2020

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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 via Zoom on November 9–10, 2020, 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.

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AGENDA

DOE BES DMSE X-ray Scattering Principal Investigators' Meeting

Via Zoom

November 9–10, 2020

Monday, November 9

12:00 – 12:15 **Greetings and business issues**

12:15 **Panel 1: XFEL, UF excited states, phase control**

Venkat Gopalan (Penn State)	David Reis (SLAC)
Keith Nelson (MIT)	Mariano Trigo (SLAC)
Riccardo Comin (MIT)	Matthias Hoffmann (SLAC)
Aaron Lindenberg (SLAC)	Wanzheng Hu (BU)
Haidan Wen (ANL)	Rohit Prasankumar (LANL)
John Freeland (ANL)	Andrej Singer (Cornell)

12:15 – 12:25 1-minute "hello" slides

12:25 – 1:15 50-minute Question & Answer discussion period

1:15 – 1:45 30 minutes of breakout discussions or time to review notes for the next panel

1:50 **Panel 2: Coherence and imaging, BCDI, nanobeams, XPCS**

Stephan Hruszkewycz (ANL)	William Chueh (SLAC)
Hoydoo You (ANL)	Paul Evans (Wisconsin)
Matt Highland (ANL)	Yue Cao (ANL)
Oleg Shpyrko (UCSD)	Simon Billinge (BNL)
Ian Robinson (BNL)	Emil Bozin (BNL)
Robert Suter (CMU)	Ray Osborn (ANL)
Tony Rollett (CMU)	Valeri Petkov (Cent. Mich.)

1:50 – 2:00 1-minute "hello" slides

2:00 – 2:50 50-minute Question & Answer discussion period

2:50 – 3:20 30 minutes of breakout discussions or time to review notes for the next panel

3:25 **Panel 3: Multi-modal UF, optical UED, high pressure**

Tony Heinz (SLAC)
Xiaodong Xu (Washington)
Tanja Cuk (Colorado)
John Harter (UCSB)
Naomi Ginsberg (UCB)
Feng Wang (LBNL)
Jing Tao (BNL)
Yimei Zhu (BNL)
Nuh Gedik (MIT)
Hemamala Karunadasa (SLAC)
Wendy Mao (SLAC)
Yu Lin (SLAC)
Brian Collins (Washington State)

3:25 – 3:35 1-minute "hello" slides

3:35 – 4:25 50-minute Question & Answer discussion period

4:25 – 4:55 30 minutes of breakout discussions or time to review notes for the General Discussion time

4:55 **General discussion and daily wrap-up**

Tuesday, November 10

12:00 – 12:15 **Greetings and business issues**

12:15 **Panel 4: Spin contrast, RIXS, XPCS**

Todd Hastings (Kentucky)
Sujoy Roy (LBNL)
Steve Kevan (LBNL)
Margaret Murnane (Colorado)
Henry Kapteyn (Colorado)
Kemp Plumb (Brown)
Peter Abbamonte (Illinois UC)
Georgi Dakovski (SLAC)
Mark Dean (BNL)
Wei-Sheng Lee (SLAC)
Y-D Chuang (LBNL)
Brian Stephenson (ANL)
Josh Turner (SLAC)

12:15 – 12:25 1-minute "hello" slides

12:25 – 1:15 50-minute Question & Answer discussion period

1:15 – 1:45 30 minutes of breakout discussions or time to review notes for the next panel

1:50 **Panel 5: Theory and synthesis for X-ray and UF**

Long-Qing Chen (Penn State)
Robert Konik (BNL)
Nicole Benedek (Cornell)
Jim Freericks (Georgetown)
Brian Moritz (SLAC)
Tom Devereaux (SLAC)
Hong-Chen Jiang (SLAC)
Joel Moore (LBNL)
Di Xiao (CMU)
David Limmer (UCB)
Lane Martin (LBNL)
Darrell Schlom (Cornell)
Ivan Bozovic (BNL)
Dmitri Talapin (Chicago)

1:50 – 2:00 1-minute "hello" slides

2:00 – 2:50 50-minute Question & Answer discussion period

2:50 – 3:20 30 minutes of breakout discussions or time to review notes for the next panel

3:25 **Panel 6: ARPES innovations**

Zahid Hasan (Princeton)
Patrick Kirchmann (SLAC)
Jonathan Sobota (SLAC)
ZX Shen (SLAC)
Donghui Lu (SLAC)
Makoto Hashimoto (SLAC)
Alessandra Lanzara (LBNL)
Kyle Shen (Cornell)
Tai Chiang (Illinois UC)
Jyoti Katoch (CMU)
Inna Vishik (UC Davis)
Alex Gray (Temple)
Zahid Hussain (LBNL)

3:25 – 3:35 1-minute "hello" slides

3:35 – 4:25 50-minute Question & Answer discussion period

4:25 – 4:55 30 minutes of breakout discussions or time to review notes for the General Discussion time

4:55 **General discussion and daily wrap-up**

Abstracts

Novel X-Ray Probes of Electronically Heterogeneous Quantum Materials

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Program Scope

The objective of this project is to define new approaches to studying the meV-scale dynamics of valence band collective phenomena in quantum materials that are intrinsically heterogeneous. Most of the fundamental properties of quantum materials are defined by their collective excitations at meV energy scales. The focus of this project is to develop new, fully momentum-resolved techniques for studying these dynamics.

Our approach will be to employ both time-resolved and frequency-resolved techniques, to bridge the full energy spectrum ranging from fractions of a meV to ~1 eV. In the near future, we will employ time-resolved IXS experiments at LCLS, as well as frequency-resolved IXS using the HERIX and MERIX spectrometers at APS and a new, meV-resolved EELS system in our laboratory. We will study a wide swath of quantum materials, including copper- and iron-based high temperature superconductors, polaronic materials such as $SrTi_{1-x}Nb_xO_3$, transition metal dichalcogenides, strange metals, and other, related materials of contemporary importance.

Recent Progress:

Diffusive dynamics and pump-induced Doppler recoil of charge order 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 showed that the charge order in prototypical $La_{2-x}Ba_xCuO_4$ exhibits transverse fluctuations at ps

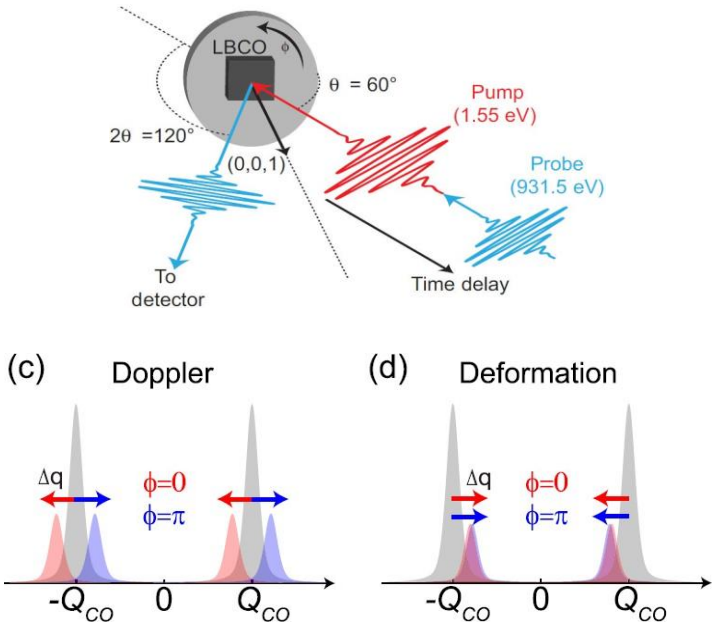

Figure 1 Time-resolved RIXS studies of charge order dynamics in $La_{2-x}Ba_xCuO_4$ measured at LCLS. (top) Schematic of the experiment. The angle ϕ denotes the azimuthal angle of the sample with respect to the IR pump beam. (bottom left) Expected peak shift if the charge order undergoes a Doppler recoil in response to the IR pump. (bottom right) Expected peak shift if the charge order periodicity is modified by the pump. Our experiments are consistent with a Doppler scenario, indicating that the IR pump generates a coherent recoiling in the collective stripe state in this material.

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 the movement is governed 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 (see **Publication #2**).

In a follow-up study, we also showed that the IR pump beam at LCLS can impart coherent dynamics on the charge order. By analyzing the time-resolved shift in the observed charge order wave vector, we showed that charge order undergoes a transient, coherent Doppler recoil in response to the IR pump (see Fig. 1). This measurement demonstrates that an ultrafast pulse can be used to coherently manipulate the charge order in cuprates, suggesting a new route to control the many-body behavior of these materials (see **Publication #3**).

Featureless M-EELS continuum in "strange metals"

A normal metal exhibits a valence plasmon, which is a sound wave in its conduction electron density. The mysterious "strange metal" is characterized by non-Boltzmann transport and violates most fundamental Fermi-liquid scaling laws. A fundamental question is, do strange metals have plasmons? Using momentum-resolved, low-energy electron energy-loss spectroscopy (M-EELS), we showed that, for nearly all of momentum space, the charge response of strange metals is independent of both frequency and momentum. This result, which has received most of its citations from string theorists, shows that strange metals exhibit "local scale invariance," a phenomenon conjectured in the late 1980's but not demonstrated until now (see Publication #4).

In a follow-up study, we identified how this continuum manifests in a material that is intermediate between a strange metal and a Fermi liquid. Applying M-EELS to the correlated metal, Sr_2RuO_4, we discovered that the broad strange metal continuum coexists with a dispersing, Fermi liquid-like collective mode. These features exhibited a spectral weight redistribution and velocity renormalization when we cooled the material through the quasiparticle coherence temperature. This result showed that strange metal and Fermi liquid phenomena can coexist, and that Sr_2RuO_4 serves as an ideal test case for studying the interaction between the two (see Publication #8).

Charge density waves in the nematic pnictide superconductor $Ba(Ni_{1-x}Co_x)_2As_2$

$Ba(Ni_{1-x}Co_x)_2As_2$ is a structural homologue of the pnictide high temperature superconductor, $Ba(Fe_{1-x}Co_x)_2As_2$, in which all the Fe atoms are replaced by Ni. Superconductivity is highly

suppressed in this system, reaching a maximum T_c = 2.3 K, compared to 24 K in its iron-based cousin, and the origin of this T_c suppression is not known. Using x-ray scattering, we show that $Ba(Ni_{1-x}Co_x)_2As_2$ exhibits a structural charge density wave (CDW) at its triclinic phase transition that forms by an unconventional mechanism. This CDW undergoes an incommensurate-to-commensurate transition at lower temperature, indicating the importance of lattice degrees of freedom. Co doping suppresses the CDW, paralleling the behavior of antiferromagnetism in iron-based superconductors (see **Publication #1**).

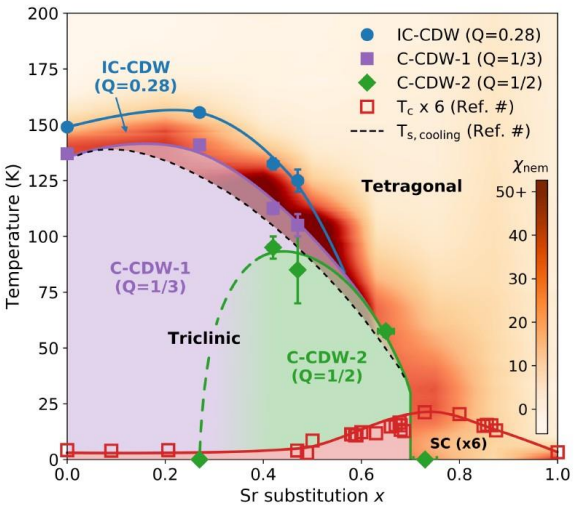

Figure 2 Phase diagram of $Ba_{1-x}Sr_xNi_2As_2$ showing three different charge density waves, denoted IC-CDW, C-CDW-1, and C-CDW-2, superconductivity, and fluctuating nematic order (color scale), all in the same material system.

In addition, in collaboration with J. P. Paglione at the University of Maryland, we performed a study of the Sr-doped variant, $Ba_{1-x}Sr_xNi_2As_2$, and found that it exhibits a giant nematic susceptibility that is connected with the melting of the CDW state. Using x-ray scattering, we showed that this material exhibits three distinct, competing CDWs with different wave vectors, as shown in Fig. 2. The nematic susceptibility is largest and exhibits hysteresis in the region in which the CDW is incommensurate, indicating that the CDW pins the nematic domains, making them static and thus trainable with an applied strain field. This study demonstrates direct interaction between CDW, nematic, and superconducting order in the same material system in which all three can be observed in detail (see **Publication #5**).

Future Plans: *Collective mode coupling and ferroelectricity in $SrTiO_3$*

We were fortunate to be part of a successful LCLS Campaign proposal, led by Mariano Trigo from SLAC, to study wave vector-resolved collective modes (phonons and magnons) of exotic transient phases of quantum materials, as well as the non-linear couplings among these modes. This Campaign was inspired, in part, by the discovery of light-induced ferroelectricity in the quantum paraelectric, $SrTiO_3$ – an effect attributed to nonlinear mode-mode coupling of phonons in this material. This Campaign will use time-resolved hard x-ray inelastic scattering techniques at LCLS to study the microscopic mechanisms of this coupling.

In addition to assisting with these experiments, we will perform conventional IXS experiments using the HERIX spectrometer at APS to determine the degree of mode-mode coupling in $SrTiO_3$ in the low-amplitude regime. Our strategy will be to measure the intensity of distinct phonons in many Brillouin zones to determine to what extent they are anharmonically mixed, by directly reconstructing the pattern of atomic displacements from the intensities of the phonons in different zones. This study will provide crucial complementary information that will

aid the interpretation of the LCLS Campaign, bringing conventional light sources to bear on interpreting state-of-the-art FEL experiments.

Publications (Oct. 2018 – present)

1. S. Lee, G. A. de la Pena, S. X.-L. Sun, M. Mitrano, Y. Fang, H. Jang, J.-S. Lee, C. Eckberg, D. Campbell, J. Collini, JP. Paglione, F. M. F. de Groot, P. Abbamonte, Unconventional Charge Density Wave Order in the Pnictide Superconductor $Ba(Ni_{1-x}Co_x)_2As_2$, Phys. Rev. Lett. **122**, 147601 (2019)
2. M. Mitrano, S. Lee, A. A. Husain, L. Delacretaz, M. Zhu, G. de la Peña, S. X. L. Sun, Y. I. Joe, A. H. Reid, S. F. Wandel, G. Coslovich, W. Schlotter, T. van Driel, J. Schneeloch, G. D. Gu, S. Hartnoll, N. Goldenfeld, P. Abbamonte, Ultrafast time-resolved x-ray scattering reveals diffusive charge order dynamics in $La_{2-x}Ba_xCuO_4$, Science Advances **5**, eaax3346 (2019)
3. M. Mitrano, S. Lee, A. A. Husain, M. Zhu, G. de la Peña, S. X. L. Sun, Y. I. Joe, A. H. Reid, S. F. Wandel, G. Coslovich, W. Schlotter, T. van Driel, J. Schneeloch, G. D. Gu, N. Goldenfeld, P. Abbamonte, Evidence for photoinduced sliding of the charge-order condensate in $La_{1.875}Ba_{0.125}CuO_4$, Phys. Rev. B **100**, 205125 (2019)
4. A. A. Husain, M. Mitrano, M. S. Rak, S. I. Rubeck, B. Uchoa, K. March, C. Dwyer, J. Schneeloch, R. Zhong, G. D. Gu, P. Abbamonte, Crossover of Charge Fluctuations across the Strange Metal Phase Diagram, Phys. Rev. X **9**, 041062 (2019)
5. C. Eckberg, D. J. Campbell, T. Metz, J. Collini, H. Hodovanets, T. Drye, P. Zavalij, M. H. Christensen, R. M. Fernandes, S. Lee, P. Abbamonte, J. Lynn, J.P. Paglione, Sixfold enhancement of superconductivity in a tunable electronic nematic system, Nature Physics **16**, 346 (2020)
6. Y. I. Joe, Y. Fang, S. Lee, S. X. L. Sun, G. A. de la Peña, W. B. Doriese, K. M. Morgan, J. W. Fowler, L. R. Vale, F. Rodolakis, J. L. McChesney, J. N. Ullom, D. S. Swetz, P. Abbamonte, Resonant soft x-ray scattering from stripe-ordered $La_{2-x}Ba_xCuO_4$ using a transition edge sensor array detector, Phys. Rev. Applied **13**, 034026 (2020)
7. Y. Y. Peng, A. A. Husain, M. Mitrano, S. Sun, T. A. Johnson, A. V. Zakrzewski, G. J. MacDougall, A. Barbour, I. Jarrige, V. Bisogni, P. Abbamonte, Enhanced electron-phonon coupling for charge-density-wave formation in $La_{1.8-x}Eu_{0.2}Sr_xCuO_{4+\delta}$, Phys. Rev. Lett. **125**, 097002 (2020)
8. A. A. Husain, M. Mitrano, M. S. Rak, S. I. Rubeck, H. Yang, C. Sow, Y. Maeno, P. E. Batson, P. Abbamonte, Coexisting Fermi Liquid and Strange Metal Phenomena in Sr_2RuO_4, arXiv:2007.06670 (submitted to Science; out for review).

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

PI: Tai Chang Chiang

Program Scope

This research program focuses on the physics of surfaces, interfaces, ultrathin films, and composite thin film structures that are promising for a wide range of scientific and technological advances in the quantum and nanoscale regimes. Measurements, modeling, and computation will be performed to determine and to understand the electronic, spintronic, and atomistic behavior of selected surface-based nanoscale systems prepared by deposition, self-assembly, and artificial layering. Electronic states in these systems, including quantum well states, surface states, interface states, and composite states, can be sensitive to the physical dimensions, layering configurations, and coupling at the boundaries. As a result, the electronic wave functions, total energy, charge distribution, spin texture, and density of states can exhibit substantial quantum variations as a function of system size and structural architecture. The system's atomic lattice responds to these changes in electronic structure, possibly leading to distortions and new structural phases with different symmetry types. These effects can be pronounced at the nanoscale because of quantum coherence, interference, entanglement, and the tendency for atomic reconstruction, relaxation, and rebonding at surfaces and boundaries. The resulting collective behavior involving coupled electronic, spin, and lattice degrees of freedom can deviate substantially from the bulk limit, thus giving rise to unusual and potentially useful emergent properties. Our main experimental methods include molecular beam epitaxy for sample growth and angle-resolved photoemission spectroscopy and x-ray diffraction for measurements of the electronic and atomic structures. Theory and modeling and complementary measurements using other techniques will also be performed in collaboration with others.

Recent Progress

We have performed research on a number of topics along the line described above. The progress is best illustrated by our recent publications as listed below. Two publications are highlighted here briefly.

For publication No. 7 (PRL Editor's Selection): Interfacing topological insulators with isotropic *s*-wave superconductors can initiate spin-helical Cooper pairing in the nontrivial surface states. Realizing this exotic phase depends on quantum-mechanical coupling between surface and bulk states, but the underlying physics remains under debate. Employing a novel cleavage-based flip-chip method, we have fabricated single-crystalline $(Bi_{1-x}Sb_x)_2Te_3$ films of predetermined layer thicknesses with a carefully chosen alloy ratio $x = 0.62$ on superconducting Nb substrates, which yields for the first time a bulk insulating topological insulator film on a superconductor even in the ultrathin-film limit. By using ultrahigh-resolution angle-resolved photoemission spectroscopy, we discover a remarkable attenuation of proximity-induced superconductivity for all films slightly n-doped by design, including for those two layers in thickness. Quantification of superconducting

gaps in these clean, nearly intrinsic systems with no bulk carriers and their contrast from heavily n-doped topological insulator films on Nb reveal superconductivity is strongly suppressed in bulk insulating topological films.

For publication No. 9: Single layers of materials, including numerous quasi-two-dimensional transition metal dichalcogenides, are of interest for emergent properties under extreme quantum confinement in reduced dimensions. A key issue, difficult to address and often neglected, is the influence of a substrate on the single-layer properties. We show that even weak van-der-Waals bonding between a single layer and its substrate can yield strong effects. Specifically, single-layer $TiTe_2$ shows a (2x2) charge density wave (CDW) below critical temperature T_C = 92 K if it is grown on a bilayer graphene. When the same single layer is grown on $PtTe_2$ films, its CDW T_C becomes suppressed and varies strongly with the $PtTe_2$ film thickness. This change in $PtTe_2$ thickness does not affect the interfacial epitaxial relationship, but the substrate transforms from a semiconductor with a sizable gap to a semimetal. The results demonstrate that interfacial electronic interactions are generally an integral part of single-layer physics.

Future Plans

Our planned research will be directed mainly at four areas: (1) surfaces, interfaces, and ultrathin films of interesting, functional, and nontrivial systems, including topological materials, charge density wave compounds, and superconductors, with an emphasis on the interplay of quantum confinement, reduced dimensions, spin texture, topological order, etc. as the film's thickness varies from a single layer, to a bilayer, … and to the thick film limit; (2) artificially stacked composite systems involving different quantum phases, where competitive or cooperative interactions between topological order, superconducting pair formation, charge order, spin polarization, lattice distortion, etc. can potentially lead to novel behavior and unusual properties; (3) studies of spin polarization effects based on angle-resolved photoemission spectroscopy using a spin detector and/or linearly and circularly polarized light, which will shed light on the spin degrees of freedom and provide valuable information relevant to spintronic applications; and (4) studies of dynamic effects in the above-mentioned systems for a thorough understanding of the physics of ultrafast excitation, relaxation, and driven behavior at time scales down to the femtosecond regime. The experimental work will include angle resolved photoemission at our home laboratory, the Advanced Light Source (ALS), and Synchrotron SOLEIL; x-ray diffraction and scattering at the Advanced Photon Source (APS); and dynamic pump-probe studies at Artemis, Central Laser Facility, Rutherford Appleton Laboratory, Institute of Solid State Physics at the University of Tokyo, and other facilities including free electron lasers. Modeling, simulation, and first-principles calculations will be performed as needed for comparison with experiment to gain a deeper understanding of the observed phenomena as well as insights for guiding further experimentation and model development.

Publications from Work Supported by the DOE Grant over the Previous Two Years

1. P. Chen, Y.-T. Chen, R.-Y. Liu, H.-D. Chen, D.-S. Lin, A.-V. Fedorov, and T.-C. Chiang, "Atomic-scale chemical conversion of single-layer transition metal dichalcogenides," ACS Nano **13** (5), 5611(2019). DOI: 10.1021/acsnano.9b00756
https://pubs.acs.org/doi/10.1021/acsnano.9b00756

Abstract: Chemical conversion by atomic substitution offers a powerful route toward the creation of unusual structures and functionalities. Here, we demonstrate the progressive transformation of single-layer $TiTe_2$ into $TiSe_2$ by reaction with a Se flux in vacuum. Angle-resolved photoemission spectroscopy and scanning tunneling microscopy reveal intriguing reaction patterns involving $TiSe_2$ island ingrowth starting from the $TiTe_2$ island edges, while the band structure and core level signatures of $TiSe_2$ grow in intensity at the expense of those corresponding to $TiTe_2$. Lattice mismatch between $TiTe_2$ and $TiSe_2$ results in misfit holes and lattice distortions over a distance behind a seamless fingerlike reaction front. The regions of $TiSe_2$ and $TiTe_2$ are distinguished by a height difference and a charge density wave (CDW) at different transition temperatures. The method of *in situ* chemical conversion offers opportunities for atomic-scale engineering of layered transition metal dichalcogenides that host useful properties arising from CDW, Dirac, Weyl, superconducting, spin-valley, and magnetic structures.

Acknowledgements: This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering, under Grant No. DE-FG02-07ER46383 (T.C.C.). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. D.S.L. acknowledges the financial support from the Ministry of Science and Technology of Taiwan under Grant No. MOST-106-2112-M-007-026.

2. Zhongzheng Wu, Fan Wu, Peng Li, Chunyu Guo, Yi Liu, Zhe Sun, Cheng-Maw Cheng, Tai-Chang Chiang, Chao Cao, Huiqiu Yuan, and Yang Liu, "Probing the origin of extreme magnetoresistance in Pr/Sm mono-antimonides/bismuthides," Phys. Rev. B **99**, 035158 (2019). DOI: 10.1103/PhysRevB.99.035158
https://journals.aps.org/prb/abstract/10.1103/PhysRevB.99.035158

Abstract: Combining angle-resolved photoemission spectroscopy and magnetotransport measurements, we systematically investigated the possible origin of the extreme magnetoresistance in Pr/Sm mono-antimonides/bismuthides (PrSb, SmSb, PrBi, SmBi). Our photoemission measurements reveal that the bulk band inversion and surface states are absent (present) in Pr/Sm antimonides (bismuthides), implying that topological surface states are unlikely to play an important role for the observed extreme magnetoresistance. We found that the electron-hole compensation is well satisfied in all these compounds and the bulk band structure exhibits no obvious temperature dependence from 10 up to 150 K. Simultaneous fittings of the magnetoresistance and Hall coefficient reveal that the carrier mobility is dramatically enhanced at low temperature, which naturally explains the suppression of extreme magnetoresistance at high temperatures. Our results therefore show that the extreme magnetoresistance in these compounds can be well accounted for by the two-band model with good electron-hole compensation. Finally, we found that both PrSb and SmSb exhibit highly linear bulk bands near the X point and lie close to the transition point between a topologically trivial and nontrivial phase, which might be relevant for the observed anomalous quantum oscillations.

Acknowledgements: This work is supported by the National Key R&D Program of the MOST of China (Grants No. 2017YFA0303100 and No. 2016YFA0300203), the National Science Foundation of China (Grants No. 11674280, No. 11274006, and No. U1632275), and the Science Challenge Project of China (Grant No. TZ20160004). T.C.C acknowledges support from the US Department of Energy under Grant No. DE-FG02-07ER46383. We thank P. Wang, Y. Wu, Dr. C. Chang, Professor D.-S. Lin for help during synchrotron ARPES measurements, and Professor H. Zhang, Professor Y. Zhou, and Professor F. Steglich for helpful discussions.

3. Meng-Kai Lin, Joseph A. Hlevyack, Peng Chen, Ro-Ya Liu, and T.-C. Chiang, "Comment on 'Chiral phase transition in charge ordered 1T-$TiSe_2$'," Phys. Rev. Lett. **122**, 229701 (2019). DOI: https://doi.org/10.1103/PhysRevLett.122.229701 https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.122.229701

Abstract: None

Acknowledgments: This work is supported by the U.S. Department of Energy (DOE), Office of Science (OS), Office of Basic Energy Sciences, Division of Materials Science and Engineering, under Grant No. DE-FG02-07ER46383.

4. Huanzhi Hu, Zhibin Shi, Peng Wang, Weiping Zhou, Tai-Chang Chiang, and Xiaoxiong Wang, "Transformation of the topological phase and the edge modes of double-bilayer bismuthene with inter-bilayer spacing," Crystals **9**, 266 (2019). DOI: 10.3390/cryst9050266 https://www.mdpi.com/2073-4352/9/5/266

Abstract: The transformations of the topological phase and the edge modes of a double-bilayer bismuthene were investigated with first-principles calculations and Green's function as the inter-bilayer spacing increased from 0 Å to 10 Å. At a critical spacing of 2 Å, a topological phase transition from a topological insulator to a band insulator resulting from a band inversion between the highest valence band and the second lowest conduction band, was observed, and this was understood based on the particular orbital characters of the band inversion involved states. The edge modes of double-bilayer bismuthene survived the phase transition. When d was 2 Å < d < 4 Å, the interaction between the edge modes of two separated bismuthene bilayers induced an anti-crossing gap and resulted in a trivial band connection. At and beyond 4 Å, the two bilayers behavior decoupled entirely. The results demonstrate the transformability of the topological phase and the edge modes with the inter-bilayer spacing in double-bilayer bismuthene, which may be useful for spintronic applications.

Acknowledgments: This work received support from the National Natural Science Foundation of China (No. 11204133 for XXW), the Fundamental Research Funds for the Central Universities (No.30917011338 for XXW), the US Department of Energy, Office of Science (Grant DE-FG02-07ER46383 for TCC), the National Natural Science Foundation of China (No. 11504207 for PW), the Shandong Province Natural Science Foundation of China (No. ZR2014AQ006 for PW).

5. Ro-Ya Liu, Meng-Kai Lin, Peng Chen, Takeshi Suzuki, Pip C. J. Clark, Nathan Lewis, Cephise Cacho, Emma Springate, Chia-Seng Chang, Kozo Okazak, Wendy Flave, Iwao Matsuda,

and Tai-Chang Chiang, "Symmetry-breaking and spin-blockage effects on carrier dynamics in single-layer tungsten diselenide," Phys. Rev. B **100**, 214309 (2019).
DOI: https://doi.org/10.1103/PhysRevB.100.214309
https://journals.aps.org/prb/abstract/10.1103/PhysRevB.100.214309

Abstract: Understanding carrier creation and evolution in materials initiated by pulsed optical excitation is central to developing ultrafast optoelectronics. We demonstrate herein that the dynamic response of a system can be drastically modified when its physical dimension is reduced to the atomic scale, the ultimate limit of device miniaturization. A comparative study of single-layer (SL) tungsten diselenide (WSe2) relative to bulk WSe2 shows substantial differences in the transient response as measured by time- and angle-resolved photoemission spectroscopy (TRARPES). The conduction-band minimum in bulk WSe2, populated by optical pumping, decays promptly. The corresponding decay for SL WSe2 is much slower and exhibits two time constants. The results indicate the presence of two distinct decay channels in the SL that are correlated with the breaking of space inversion symmetry in the two-dimensional limit. This symmetry breaking lifts the spin degeneracy of the bands, which in turn causes the blockage of decay for one spin channel. The stark contrast between the single layer and the bulk illustrates the basic carrier scattering processes operating at different timescales that can be substantially modified by dimensional and symmetry-reduction effects.

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Abstract: Platinum ditelluride ($PtTe_2$), a type-II Dirac semimetal, remains semimetallic in ultrathin films down to just two triatomic layers (TLs) with a negative gap of −0.36 eV. Further reduction of the film thickness to a single TL induces a Lifshitz electronic transition to a semiconductor with a large positive gap of +0.79 eV. This transition is evidenced by experimental band structure mapping of films prepared by layer-resolved molecular beam epitaxy, and by comparing the data

to first-principles calculations using a hybrid functional. The results demonstrate a novel electronic transition at the two-dimensional limit through film thickness control.

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Abstract: Interfacing bulk conducting topological Bi2Se3 films with s-wave superconductors initiates strong superconducting order in the nontrivial surface states. However, bulk insulating topological (Bi1−xSbx)2Te3 films on bulk Nb instead exhibit a giant attenuation of surface superconductivity, even for films only two layers thick. This massive suppression of proximity pairing is evidenced by ultrahigh-resolution band mappings and by contrasting quantified superconducting gaps with those of heavily n-doped topological Bi2Se3/Nb. The results underscore the limitations of using superconducting proximity effects to realize topological superconductivity in nearly intrinsic systems.

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work was also supported by a public grant by the French National Research Agency (ANR) as part of the "Investissements d'Avenir" (reference: ANR-17-CE09-0016-05).

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DOI: 10.1016/j.physleta.2020.126782
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Abstract: α-Sn is on the boundary of a couple of distinct topological phases. It will transform into a topological insulator under a suitable strain. However, a clear picture of its topological surface states (TSSs) is still lacking. Here we perform first-principles calculations on the electronic structure of α-Sn(111) surface to identify its TSSs and reveal their properties. The results show that the presence of valence band reorganizes the TSSs in the inverted *sp* gap into two Dirac cones. The lower one is in the valence band continuum; the upper one resides in the gap between the valence and conduction bands. We also demonstrate the transformation of the surface states by switching on or off of strain and/or spin-orbit coupling. Without spin-orbit coupling, only the TSSs associated with the lower Dirac cone survive, and they are spin unpolarized. The results are useful for understanding and engineering the topological properties of α-Sn.

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DOI: https://doi.org/10.1103/PhysRevLett.125.176405
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Abstract: Single layers of transition metal dichalcogenides are of interest for emergent properties. An often-neglected issue is substrate effects. Our experiments show that the charge density wave in a single-layer $TiTe_2$ grown on $PtTe_2$ films is strongly suppressed by increasing the $PtTe_2$ substrate thickness. Given the interfacial bonding remains of the weak incommensurate van-der-Waals type, the observed changes are correlated with a thickness-dependent metallicity transformation in the $PtTe_2$ substrate. The results illustrate the crucial role of the substrate in single-layer physics.

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Several other manuscripts have been submitted to journals and are currently under consideration.

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

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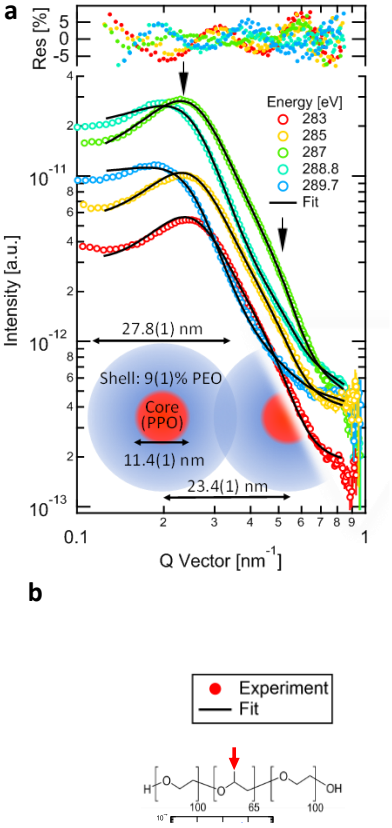
Program Scope

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 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 transistors, solar cells, and aqueous nanocarriers.



Recent Progress

Figure 1: **RSoXS spectral analysis can extract quantitative molecular composition inside nanostructures.** (a) Simultaneous multi-resonance fit to extract both structural statistics and molecular composition (inset) of a Pluronics F127 organic nanocarrier used in drug-delivery. (b) F127 dynamics captured in a dual-flow experiment fit to a double exponential model. Inset is the F127 molecular structure, highlighting the single identifying chemical moiety.

Three aims embody the program, each of which we report progress. ***Aim 1:*** *Establish a theoretical framework for resonant scattering.* In advancing analytical methods, we realized that achieving absolute scattering at the carbon absorption edge is critical for extracting quantitative chemical and orientational information on molecular ordering from RSoXS. This cannot be accomplished via scattering standards as they are too absorptive at these energies. Thus we developed and confirmed a simple method involving simultaneously measuring absorption and fluorescence intensities of polymer thin films to calibrate detector responsivities (Ferron 2020). Next we merged our spectral RSoXS model[1] with our recently developed microfluidic sample stage to quantify the spatiochemical structure of aqueous organic nanocarriers in-situ. Figure 1 shows how our spectral analysis encompassing both scattering angle (q) and photon energy now quantifies not only dimensions of micelle core, corona and closest approach, but also the chemical concentration of the polymers within each component – of particular use for measuring drug uptake and delivery in new smart medicine platforms or environmental oil-spill remediation solutions. The dual flow capabilities of the instrument also enabled a first demonstration of

nanocarrier dyanmics with the work currently under review (McAfee, 2020). This work also contributes toward ***(Aim 2:** Determine sensitivity limits)* because the only chemical difference between the two polymer components is a single methyl group with no elemental or density differences. Such sensitivity demonstrates the power of RSoXS to intrinsically distinguish molecular species without the use of laborious and disruptive labeling through, for example, deuteration in neutron scattering or fluorescent tags. In addition to this, we have begun testing sensitivity limits on measuring molecular orientation at buried interfaces through resonant X-ray reflectivity.[2] This project has been significantly delayed, however, due to the pandemic. ***Aim 3:** Develop optical models for organic molecules that enable quantitative measurement of molecular conformation.* We have developed algorithms to combine DFT calculations with angle-resolved NEXAFS spectroscopy measurements to construct a bond-resolved optical tensor for any target molecule. This will enable the quantitative measurement of molecular orientation and macromolecular conformation of critical importance to both organic electronic devices and peptide and protein structures.

Future Plans

Moving forward, we will further develop our analytical methods to enable characterization of molecular cargo within nanocarriers. Going beyond a 2-component system in this case will ensure the new method is robust for wide-spread use, will test the sensitivity limits further, and will potentially have a high impact on numerous applications. We will additionally continue our pursuit of quantifying molecular orientation at buried interfaces as applied to organic electronic devices fabricated in our lab. We hypothesize that molecules with conductive pi-orbitals aligned along the dielectric interface of a transistor channel will result in higher mobilities and on/off ratios in these devices. Finally, we will apply our converged optical tensor model to polarized RSoXS measurements of simple nanostructures such as polymer grafted nanoparticles to first demonstrate the power of these hyper-accurate models.

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Publications resulting from work supported by the DOE

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Presentation Video File: "Collins DOE X-ray Scattering PI 2020"

Dynamics and Control of Magnetic and Charge Order in Complex Oxides

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Brookhaven National Laboratory

PI meeting Presentations

Ian Robinson "Dynamics and Control of Magnetic and Charge Order in Complex Oxides"
Robinson_PI_meeting_ultrafast_2020.pptx

Mark Dean "Dynamics and control in complex oxides: resonant x-rays"
PI_meeting_2020_MPMD.pptx

Jing Tao "Dynamics and control in complex oxides: ultrafast electron diffraction"
Presentation_2020 Xray PI Meeting_JTao.pptx

Simon Billinge "Towards Pump-Probe femtosecond ultrafast PDF studies (ufPDF)"
PI_meeting_2020-SJB_ultrafast.pptx

Abstract

The main goal of the "Dynamics and Control" program at Brookhaven National Laboratory is to study charge, spin, lattice, and orbital dynamics using advanced x-ray and electron scattering techniques in order to better understand the electronic properties of complex oxides and how they can be manipulated. We have particular strengths in ultrafast Resonant Inelastic X-ray Scattering (ufRIXS), ultrafast Bragg Coherent Diffractive Imaging (ufBCDI) and ultrafast electron diffraction (UED) and are applying these techniques to several prototypical complex oxides such as cuprates and iridates. In the near future we are adding an ultrafast Pair Distribution Function (ufPDF) capability to focus particularly on the emergence of short-range order in d-band complex materials. We will image domains associated with magnetic, charge and orbital degrees of freedom with BCDI and use RIXS to provide a scattering vector, energy and ultrafast time-resolved view of short-range electronic correlations. The techniques complement each other by providing structure and excitation spectra of the same materials on different length scales and are supported by UED measurement of how the structure is changing. This program is intended to deliver measurements of short-range spin/charge correlations and charge and spin domains on a carefully-chosen series of prototypical Mott quantum materials. It is expected that these results will answer key questions about the manipulation of charge and spin degrees of freedom in transient states on both short and long length scales, providing "properties on demand" via strategic ultrafast excitation of quantum materials.

1. Recent Program Achievements

In order to clarify the interactions that stabilize the electronic order, we performed a comprehensive resonant inelastic x-ray scattering study of $La_{2-x}Sr_xCuO_4$ finding that charge-density wave effects persist up to a remarkably high doping level of x=0.21 before disappearing at x=0.25. The inelastic excitation spectra remain essentially unchanged with doping despite crossing a topological transition in the Fermi surface. This indicates that the spectra contain little or no direct coupling to electronic excitations near the Fermi surface, rather they are dominated by the resonant cross section for phonons and charge-density-wave-induced phonon softening. We interpret our results in terms of a charge-density wave that is generated by strong correlations and a phonon response that is driven by the charge-density-wave-induced modification of the lattice.

We performed temperature-dependent in situ TEM and MeV UED experiments under various pump fluences on Fe_3O_4 single-crystal samples. With the help of dynamic electron diffraction simulations, we found a symmetry breaking in the charge and lattice structures in Fe_3O_4 at temperatures far above the Verwey transition. Furthermore, UED results indicate a significant role of X3 phonon mode in the structural phase transition during photoexcitation. One manuscript is under preparation.

We used Bragg coherent diffractive imaging (BCDI) to image the low-temperature structural domain walls in $La_{1.875}Ba_{0.125}CuO_4$ (LBCO), which are hypothesized as nanometer-scale pinning sites for the CDWs. The domain structures associated with these symmetry changes were imaged directly during phase transition. This work brings BCDI into the cryogenic regime where most phase transitions in quantum materials reside. We imaged the structural evolution during the high-temperature tetragonal to low-temperature orthorhombic (LTO) phase transition. Our results showed the formation of LTO domains close to the transition temperature and followed how the domain size decreases with temperature.

Coherent X-ray diffraction patterns were recorded by using an X-ray free-electron laser to illuminate barium titanate nanocrystals as a function of time delay after laser excitation. Rather than seeing any significant thermal expansion effects, the diffraction peaks were found to move perpendicular to the momentum transfer direction. We invoked a laser driven rotation of the crystal lattice, which is delayed by the aggregated state of the crystals. Internal deformations associated with crystal contacts were observed, which confirms the model.

2. Future Plans

We have had a long-term interest in performing ultrafast PDF (ufPDF) experiments, but until now none of the XFEL facilities has been able to produce high enough energy X-rays. LCLS-II will start operations during FY20 with 24keV photons, which will be attractive for PDF at least in favorable cases. We have already put together a “campaign proposal” to prepare a team of ufPDF users interested to participate. Although the campaign was not selected, we are still planning the first experiments at the MFX station of LCLS, which will be equipped with a laser and large area detector. We also identified the thiospinel, $CuIr_2S_4$, as the most interesting

material to start with. We will investigate the time scale of the melting and reformation of the Ir-Ir dimers responsible for the ODL fluctuations.

A major challenge for ufBCDI, is that conventional iteration methods for phase retrieval are very computationally intensive and sensitive to their initial guess due to their iterative nature. This makes on-the-fly visualization of dynamics at XFEL experiments very challenging. We plan to develop a deep neural network model to give fast and accurate estimates of the complex single-particle image in the form of a universal approximator learned from synthetic data. We will explore ways to combine the deep neural network model with conventional iterative methods to refine the accuracy of the reconstructed results.

We will extend our successful studies of ultrafast magnetism in iridates to probe spin-lattice and spin-charge coupling in transient states with the long-term goal of controlling magnetism via ultrafast photo-excitation. To achieve this, we are developing a new frequency-domain RIXS spectrometer at the SACLA facility and are collaborating with Hasan Yavas at SLAC to develop analyzer technology for Fourier Transform RIXS.

Bragg geometry X-ray ptychography images of the domain structure of the charge-density wave "stripes" in the prototypical cuprate high-temperature superconductor, $La_{2-x}Ba_xCuO_4$ close to optimum doping, x=0.125 will be analyzed. A pinhole can be scanned over the domains on resonance at the Cu L_3 edge at 931eV to produce a series overlapping coherent diffraction patterns which will be used to reconstruct images of the domains. These will be analyzed for expected inhomogeneities, attributed to pinning of the stripes to underlying twin domains in the parent crystal. Related stripe-ordered nickelate materials (at Ni L_3) will be studied to help isolate effects that are associated with superconductivity.

In the upcoming beamtime at the European XFEL, we will make XPCS measurements on selected relaxor ferroelectric materials, such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN). The available 220ns pulse spacing is well-matched to the expected spontaneous fluctuation time of the "polar nano regions" believed to be responsible for the frequency-dependent dielectric function. We will also investigate these materials using traditional synchrotron XPCS at NSLS-II.

We will continue performing TEM and UED investigations of magnetite Fe_3O_4 single-crystal samples prepared by FIB to answer a few remaining open questions: Can we excite a particular phonon mode (it would be X_3 optical phonon in this case) to drive the structural phase transition by a THz laser pump? If so, do we expect to see two timescales from superlattice and Bragg peak measurements? Can we obtain ultrafast observations of the charge ordered peak above the Verwey transition? Can we apply magnetic field during UED experimental operations? There has been debate about the origin of very strong diffuse scattering at the temperatures right above Verwey transition. Is this related to phonon modes or a short-range order in the structure? Can we understand the origin of this strong diffuse scattering by ultrafast dynamic observations? The answers to these questions will lead to better understanding of the charge-lattice interactions in complex oxides.

In addition, we plan to study the effect of collective vibrations (phonons and Debye-Waller factors) using UED techniques. SnSe, grown by Cedomir Petrovic (BNL) is a good quantum

material candidate for this study. It was reported to have anisotropic phonon softening and condensation that could give rise to its outstanding thermoelectricity. Our preliminary UED data and data analysis show anisotropic lattice dynamic processes in this crystal. In the future, more analysis will be performed to link the observed anisotropic lattice dynamics to the anisotropic phonon behaviors in order to establish a structure-property relationship in this material.

Moreover, we plan to explore the charge density wave (CDW) peak in $La_{1.875}Ba_{0.125}CuO_4$ (LBCO) superconductor. The CDW, seen using x-ray and neutron scattering, is considered to bridge between the superconducting and higher-temperature phases. It has long been proposed using electron probes to investigate charge order in LBCO but so far failed in conventional electron diffraction. High electron dose rate is one of the key factors suspected to suppress the charge order. Indeed, electron dose rate in UED technique is lower than the conventional electron diffraction by a few orders in magnitude, so it is worth trying as we mature our UED sample prep methods on single-crystal bulk. We will compare the UED observations from LBCO bulk (sample from Genda Gu at BNL) and thin films on substrate (sample grown by MBE methods from Ivan Bozovic in the Dynamic & Control team) to study the strain effect in this material.

We will investigate the same FIB-cut Fe_3O_4 as well as Sr_2IrO_4 and $Sr_3Ir_2O_7$ samples with X-ray BCDI to learn about the formation of domains. We will also try to develop magnetic BCDI for imaging magnetic domain structures in both materials, although the signal level is a significant challenge, which can be overcome by using resonant BCDI methods.

A device for applying external strain on pregrown LSCO films will be tested for looking at the influence of strain on nematicity. The time scale of nematic fluctuations is unknown and may be accessible in ultrafast diffraction experiments. External strain may also couple to potential CDW ordering ins LSCO and this will be investigated with synchrotron experiments.

We have been performing first-principles-based investigation of the ultrafast experiments and in particular the two-step structural relaxation seen in many samples we have probed with UED. We aim at unveiling how photoinduced electronic excitations drive transitions from infrared phonon modes to Raman modes and the resultant exotic physical properties.

3. Recent Publications

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Dynamics of Complex Magnetic and Ferroelectric Polarization Configurations

Paul G. Evans, University of Wisconsin-Madison, pgevans@wisc.edu, November 2020.

I. Program Scope

There is a challenging nanoscale characterization problem associated with understanding the interaction between atomic-scale structural features, nanoscale ferroicity, and the dynamics of these features. Ferroic nanomaterials (e.g. in ferroelectric and ferromagnetic nanostructures) occupy tiny nanoscale volumes and possess a range of excitations that extends to picosecond timescales that are outside the range of conventional microscopy techniques. Ferromagnetic order presents particularly challenging problems, including the need to characterize phenomena at low temperature, with elemental sensitivity, and in cases where there are ions of the same elements in the substrates supporting the nanostructure. Our recent work has focused on developing novel x-ray methods and using them to understand the coupling of structural features and nanoscale ferroic order, and to understand the dynamics of ferroelectrics (and multiferroics). Our activities in the last two years have resulted in a series papers that are published [1-13] or are submitted or in preparation [14-17] as well as a web-based nanobeam dynamical diffraction calculator.[18]

Ferroelectric and ferromagnetic materials have important similarities with respect to the design of new structures and in the experimental tools employed to characterize them. *Ferroelectric* thin films and superlattices (SLs) host exotic polarization configurations that result from a competition of nanoscale structural, electrical, and elastic effects. The lattice distortion induced by the optical excitation, resulting can directly modify the polarization of ferroelectrics or can lead to the distortion of key structural parameters such as the rotation angles of oxygen octahedra. *Ferromagnetic* materials, in comparison with ferroelectrics, are at an earlier stage with respect to understanding the effects of nanoscale stress and in the role of structural effects in magnetic dynamics. In part, these challenges have persisted because structural techniques employing hard x-rays have lacked magnetic sensitivity. Magnetic insulators such as the magnetic rare-earth ion garnets $Re_3Fe_5O_{12}$ (where Re can be one of many ions, e.g. Ho or Gd) are particularly important and particularly challenging because the volume of present devices of interest is orders of magnitude smaller than has been previously probed.

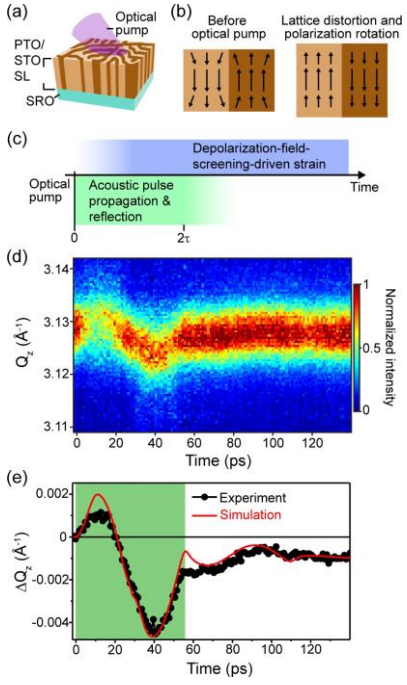

Fig. 1: Photoinduced picosecond dynamics in SL nanodomains. (a) Experimental arrangement. (b) Lattice distortion in a perovskite unit cell and the corresponding change in the out-of-plane scattering vector Q_z. (c) Acoustic and screening phenomena in SL thin film and intensity distribution of domain scattering as a function of Q_z following optical excitation at t=0. (d) Measured shift ΔQ_z of the out-of-plane wave vector of domain diffuse scattering (points) and simulation of strain propagation (lines).

II. Recent Progress

This section highlights progress in (i) probing, understanding, and manipulating nanoscale polarization domain configurations and their dynamics, (ii) developing nanobeam magnetic nanobeam diffraction imaging methods, and (iii) developing and applying coherent x-ray nanobeam diffraction techniques incorporating dynamical diffraction simulations.

II.1. FEL-based studies of the dynamics of nanoscale ferroelectricity

Our series of studies employing ultrafast diffraction have been included two experiments at the PAL XFEL, one at LCLS, and one at SACLA. Optical absorption perturbs the energy balance leading to mesoscale phenomena in ferroelectrics. These experiments used the experimental arrangement illustrated in Fig. 1(a). We highlight here a study of the perturbation of ferroelectricity in a $PbTiO_3/SrTiO_3$

(PTO/STO) SL, following up our prior discovery of the optically driven domain transformation.[19] The effect of the acoustic perturbation on the domain diffuse scattering distribution is shown in Figs. 1(c) and (d).[3] The intensity and reciprocal-space location of the domain scattering are consistent with an optically driven rotation of the ferroelectric polarization near nanodomain boundaries, which we have reported in a submitted publication.[14] We have also probed the optically induced acoustic transient in PTO/STO SLs to characterize the vibrational modes and found an anomalous speed of sound and acoustic mode frequencies not predicted by continuum models.

II.2. Magnetic nanobeam diffraction imaging of nanoscale layers of magnetic insulators

With collaborators working at the European Spallation Source, the CNRS, and the ESRF, we have developed a novel approach to magnetic nanobeam diffraction imaging and used it to probe the magnetism and structure within a $Gd_3Fe_5O_{12}$ (GdIG) garnet thin film.[1] Relatively little nanomagnetic information is available about GdIG and related materials because appropriate imaging techniques for nanoscale buried layers have not previously existed. The nanobeam diffraction experiment included of the construction of an x-ray quarter-wave plate to be used with the x-ray nanobeam diffractometer at station ID-01 of the ESRF. The x-ray magnetic resonant scattering nanobeam microscopy studies probed a 25 nm-thick GdIG layer.[1] Before our experiments, few details were known about magnetic scattering in GdIG, with an exception of Fe-K-edge resonant scattering studies conducted probing GdIG single crystals.[20] Our experiments thus included a series of basic measurements of the magnetic scattering properties at the Gd L2 resonance. Key features of magnetism of the GdIG layer at low temperature are revealed in the x-ray nanobeam maps shown in Fig. 3. The imaged area consists of a lithographically defined square that appears as an area of lighter contrast in Fig. 3(a). The GdIG thin film surrounding this area has been removed. Maps of the flipping ratios F_{cir} and F_{π} in Figs. 3(b) and 3(c) show the distribution of magnetic domains within the GdIG layer. The point-to-point variation of F_{cir} and F_{π} in Figs. 3(b) and 3(c) is on the order of 1% and exhibits complementary contrast between the two flipping ratios that is distinct from the intensity variation in the structural image. π polarization is useful at large angles between the incident and diffracted beams, e.g. those of Bragg reflections. π polarization, does not, however, provide magnetic contrast for small scattering angles and thus has not been considered in previous studies employing only absorption contrast or small-angle scattering contrast mechanisms.[21]

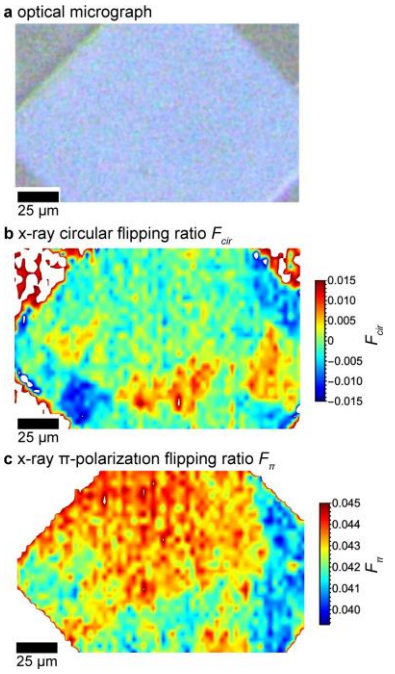

Fig. 2: Domain imaging in GdIG SSE devices. (a) Ppatterned GdIG layer from which GdIG has been removed in the area outside the light square. X-ray nanobeam diffraction maps of (b) circular-polarization flipping ratio F_{cir} and (c) linear π-polarization flipping ratio F_{π}.[1]

II.3. Nanobeam methods: dynamical diffraction and novel ptychography approaches

We have incorporated dynamical diffraction effects into simulations of the diffraction patterns produced in experiments using Fresnel zone plate focusing optics.[5,11,13,18] The dynamical diffraction methods have been incorporated within a nanobeam diffraction simulation framework that we developed earlier in kinematical diffraction with convergent x-ray beams.[22,23] The experiments in Fig. 3 also revealed that the formation of metal gate electrodes on AlGAs-GaAs creates mechanical distortion that is an important source of electronic disorder in quantum electronic devices.[5,13] Studies of $SrTiO_3$ sheets enabled by these methods allow the stress in nanoscale sheets to be determined precisely.[10] In considering the section of reciprocal space that is probed in nanobeam diffraction studies, we have found that a 90 deg.-exit-angle

geometry can have important advantages in studying thin-film structures with in-plane features. We have acquired the demonstration data using PTO/STO SLs and are now preparing the results for publication.[17]

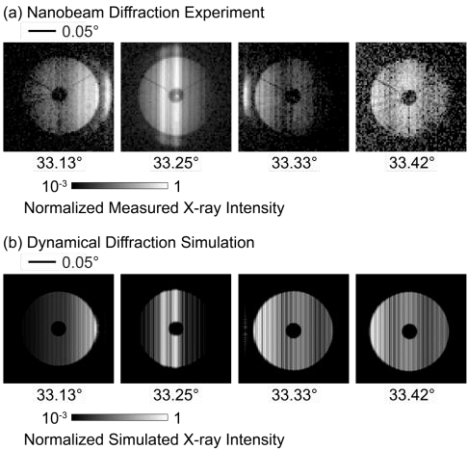

Fig. 3: Nanobeam dynamical diffraction experiment and simulation. (a) Observed and (b) simulated focused-beam dynamical diffraction patterns for a GaAs-AlGaAs heterostructure, at different values of the x-ray incident angle.

III. Future Directions

(1) Characterization of nanoscale structural and magnetic coupling in magnetic insulators. The x-ray nanobeam magnetic diffraction and nanobeam imaging methods that we have developed will allow us to address unanswered questions in the nanoscale magnetism of thin-film magnetic insulators. X-ray magnetic diffraction techniques provide precise local magnetic information from materials and devices with nanoscale dimensions, a regime in which combined structural and magnetic information has not been previously available. The research directions, including investigations of magnetic nanobeam diffraction ptychography methods, benefit from the dramatic improvement in the brilliance of synchrotron light sources.

(2) Understanding and controlling the dynamics of structural features associated with nanoscale ferroelectricity: Recent developments in materials design and epitaxial synthesis techniques have made it possible to create systematic variations in the orientation of oxygen octahedra with perovskite oxide thin films. Control of the octahedral orientation promises to yield a new approach to the control of functional properties such as ferroelectricity and magnetism, but systematic exploration faces artifacts due to subtle variations among substrates with different strain and symmetry. We are using ultrafast time-resolved diffraction techniques to probe the rotation of octahedra systematically as a function of ultrafast optically induced distortion in $BiFeO_3$, a model perovskite for which octahedral rotation predictions are already available. The resulting structural probe promises to be widely applied to problems associated with octahedra in thin films and at interfaces, including in improper ferroelectricity in SLs.

(3) Dispersion of magnetic excitations in magnetic garnets: We are developing methods to characterize the magnetic excitations of thin-film magnetic materials using a novel combination of the developments in x-ray magnetic diffraction and ultrafast methods described in the previous two activities. Our previous work has shown that the acoustic phonon dispersion can be accurately measured using high-dynamic range thin-film diffraction techniques. We will combine this ultrafast scattering approach with magnetic diffraction in order to measure the dispersion of spin waves in magnetic garnets. The dispersion and lifetimes of these excitations are key components underpinning models of spincaloritronic devices based on the spin-Seebeck effect but are presently out of reach for optical probes and inelastic x-ray or neutron scattering techniques.

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Ultrafast Electronic and Structural Dynamics in Quantum Materials

DE-FG02-08ER46521

Nuh Gedik, MIT

1. Program Scope

Discovery and control of novel phases of quantum materials has been a long-standing goal in condensed matter physics. Historically, a plethora of exotic phenomena has been realized by inducing phase transitions in thermal equilibrium through chemical substitution or via the application of external stimuli such as pressure or magnetic field. With the advent of time resolved techniques based on ultrafast laser pulses, realizing novel phases through nonequilibrium phase transitions induced by light has become a hotly researched frontier. These "light-induced phase transitions" can lead to new states that may or may not exist in thermal equilibrium.

Despite several examples of this phenomena in different systems, there are still many unanswered questions and the overarching principles (if any) that govern these phase changes are still not well known. For example, what are the similarities and differences in terms of physical mechanisms between the regular phase transitions and the ones that are induced by light? How do the properties of new phases created by light compare to the equilibrium phases that may exist in different parts of the equilibrium phase diagram? What determines the relaxation timescales and under what circumstances can these phases be made metastable? Could the coherence of light be utilized to engineer new band structures to facilitate these phase transitions?

The goal of this proposal is to answer these and related questions in light induced phase transitions and optical manipulation of order parameters. This will be done by using and developing advanced time resolved optical and electron based spectroscopies. Our scientific program will be focused on studying photoinduced phase transitions in model charge density wave systems, using light to optically manipulate order parameters of complex phases, and realizing Floquet topological phases. In terms of technique development, we will significantly improve the capabilities of our high harmonic generation based time and angle resolved photoemission spectroscopy (trARPES) setup by increasing the repetition rate and extending the pump excitation frequency range and fluence. We will also develop a new capability of measuring phase shifts in trARPES experiments with energy and momentum resolutions and apply this to problems in condensed matter physics.

2. Selected Recent Progress

2.1. Evidence for topological defects in a light-induced phase transition (Nature Physics 2019)

The understanding of equilibrium phase transitions caused by spontaneous symmetry breaking is a hallmark achievement of 20th-century physics. When these transitions are induced by adiabatically cooling from a disordered to an ordered phase, they are marked by a diverging correlation length and correlation time of equilibrium fluctuations at the transition temperature [1]. Much less is understood about non-adiabatic transitions, or quenches, where fluctuations are not expected to exhibit a diverging correlation length and time, preventing the onset of long-range order (LRO). This absence of critical behavior is often linked to the creation of topological defects in the ordered phase [2,3]

Photoinduced phase transitions present a unique platform whereby non-adiabatic phenomena can be explored. They have emerged as an intense research field in recent decades as a consequence of the technological advances offered by ultrafast lasers. During these transitions, the initial state appearing immediately after photoexcitation, out of which order recovers, is far from equilibrium. Moreover, topological defects in this case are not necessarily generated through a complete melting of the broken-symmetry phase but may also arise within the ordered state as a result of spatially-localized absorption of high-energy photons.

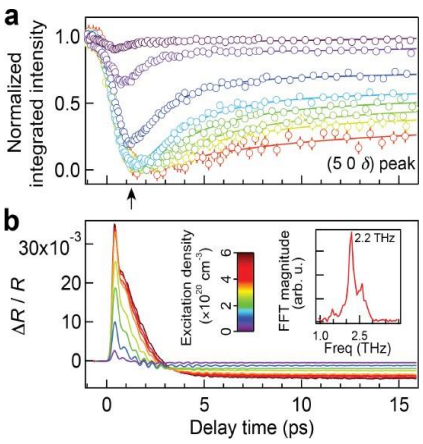

Figure 1 a, Time evolution of the superlattice peak integrated intensity in $LaTe_3$ upon photoexcitation at different excitation densities**. b,** Transient reflectivity as a function of delay time at different excitation densities. The color scale is the same in both panels. Inset: Fourier transform of the oscillatory component.

Recently, we showed that these concepts play an important role in the light-induced melting of a CDW order. Using a suite of time-resolved probes, we independently tracked the amplitude and phase dynamics of the CDW order parameter in the prototypical material $LaTe_3$ [4]. We found that a quick (~1 ps) recovery of the CDW amplitude was followed by a slower re-establishment of phase coherence. This longer timescale was dictated by the presence of topological defects: indeed, LRO was inhibited in the material and only restored when the defects annihilated.

In these experiments, we tracked the CDW amplitude using time- and angle-resolved photoemission spectroscopy (trARPES) and transient optical spectroscopy (TOS), and the CDW phase coherence using ultrafast electron diffraction (UED). Figure 1a shows the CDW diffraction peak intensity at several photoexcitation densities, as measured in our UED setup. Noticeably, the characteristic time it took for the CDW peak to recover to a quasi-equilibrium value was much longer at higher excitation densities (red curve). This relationship is mimicked in the TOS data presented in Figure 1b, with one major difference: the characteristic recovery times observed in the TOS traces are much shorter. The short recovery

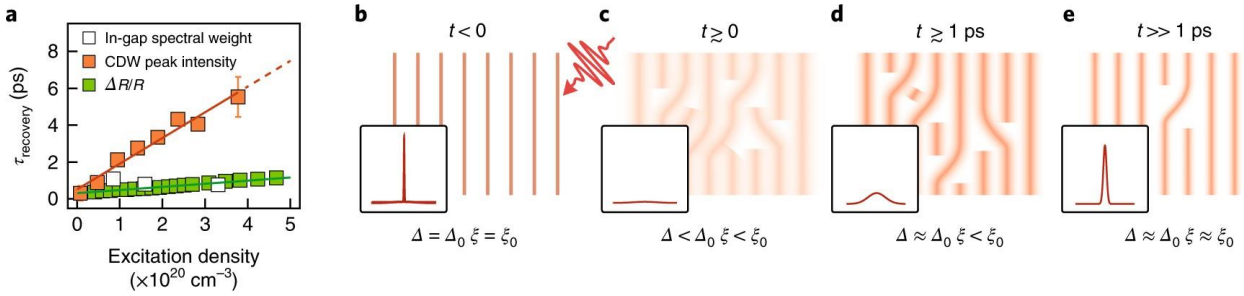

Figure 2 a Characteristic recovery times across three probes as a function of excitation density. Lines are linear fits. **b–e,** Schematic illustration of the CDW evolution after photoexcitation. In each image, the unidirectional charge density modulation is depicted as stripes in real space. Stripe 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. CDW amplitude recovers on a fast (~ 1ps) timescale, whereas the phase coherence recovers slowly as the topological defects heal.

time is also confirmed by our trARPES measurements, which measure the dynamics of the gap. Because TOS and trARPES are sensitive to the CDW amplitude, while UED is sensitive to both the CDW amplitude and phase coherence, we attribute the discrepancy in time scales to the longer recovery of the phase coherence. The difference in recovery timescales is summarized in Figure 2a. Interestingly, we also observe that the CDW peak broadens and narrows as the CDW is suppressed and then recovers, where the broadening is a hallmark of the appearance of topological defects in the system. We also find that the inverse of the peak width, the correlation length, recovers on a similar timescale compared to the CDW peak intensity. This relationship further demonstrates that it is the existence of topological defects that prevents the phase coherence of the CDW order parameter from recovering quickly. The recovery of CDW amplitude and phase is schematically illustrated in Figure 2b-e. Recently, the topological defects in equilibrium were also successfully visualized in the real space by scanning tunneling microscopy of palladium-intercalated $ErTe_3$ [5].

2.2. Light-induced CDW in $LaTe_3$ (Nature Physics 2020)

Another major theme in modern condensed matter physics is the relationship between proximal phases of matter, where one ordered ground state gives way to another as a function of some external parameter such as pressure, magnetic field, doping, or disorder. In our investigations, we asked whether, by lifting the restrictions placed by equilibrium thermodynamics and driving a system into a non-equilibrium state, a material could gain access to a nearby non-equilibrium ordered phase of matter. In this regard, photoexcitation provides a viable path to enter the out-of-equilibrium regime, where excited electrons can alter the free energy landscape and access phases of matter that are beyond reach in thermal equilibrium. This accessibility becomes of vast importance in the presence of phase competition, when one state of matter is preferred over another by only a small energy scale that, in principle, is surmountable by light.

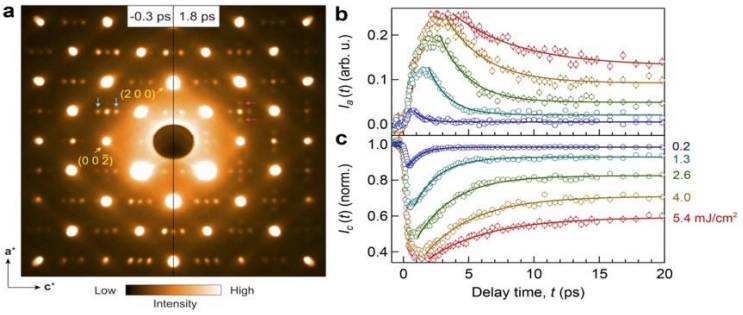

Figure 3 Light-induced CDW observed by ultrafast electron diffraction. a, Electron diffraction patterns before (left) and 1.8 ps after (right) the arrival of an 80-fs, 800-nm laser pulse, taken at 3.1 MeV electron kinetic energy. Blue and red arrows indicate the equilibrium CDW peaks along the *c*-axis and the light-induced CDW peaks along the *a*-axis, respectively. $a^* \equiv 2\pi/a$ and $c^* \equiv 2\pi/c$ are reciprocal lattice units. b-c, Time evolution of integrated intensities for the transient *a*-axis CDW peaks and the equilibrium *c*-axis CDW peaks, respectively. Each color denotes an incident fluence. Curves are single-exponential fits to the relaxation dynamics. Adopted from [6]

In this respect, the layered CDW compound $LaTe_3$ again presents an excellent opportunity, since its small lattice anisotropy dictates that the equilibrium CDW always form along the crystallographic *c*-axis instead of the nearly-equivalent *a*-axis [7]. Using UED, we found [6] that after photoexcitation, the equilibrium *c*-axis CDW is suppressed and a different competing CDW rapidly emerges along the *a*-axis Figure 3(a). The timescales characterizing the relaxation of this transient *a*-axis CDW and the re-establishment of the original *c*-axis CDW are nearly identical (Figure 3b), which points towards a strong competition between the two orders and a common microscopic mechanism behind the phenomenology along the two axes.

To explain all of these observations within a consistent framework, the existence of topological defects turned out again to be an important aspect. Indeed, the non-equilibrium CDW arises due to the topological defects in the *c*-axis CDW. In the spatial regions where the dominant *c*-axis order is suppressed (such as in topological defects), the sub-dominant *a*-axis phase can develop. The benefit of this picture is that it can explain several observations in a consistent manner. First, the transient CDW forms despite only a partial suppression of the *c*-axis CDW. From equilibrium, we know that any finite *c*-axis CDW amplitude necessarily forbids the presence of an *a*-axis CDW in $LaTe_3$. The presence of topological defects, however, explains this apparent puzzle considering that it allows for the local suppression of the *c*-axis CDW. Furthermore, the coincidence of relaxation timescales is naturally explained in this scenario: as the defects annihilate, the transient CDW can no longer be sustained and the equilibrium *c*-axis CDW necessarily recovers. We expect the mechanism of seeing competing states near topological defects to be general, and that other ordered states of matter will exhibit a similar phenomenology under the influence of photoexcitation. Not only does this result provides a path toward the discovery of other states of matter in the presence of phase competition, it also enables the manipulation and control of other ordered phases with light.

3. Future Plans

PI's group at MIT has been working on photoinduced phase transitions [4,6,8,9] and coherent phenomena [10–13] in quantum materials for more than a decade. To visualize the dynamics of different degrees of freedoms, we have been developing advanced spectroscopic tools [4,14–17] to selectively probe and control electronic and structural excitations. Building upon these, we will attempt a set of novel experiments that are aimed at achieving a fundamental understanding of light induced phase transitions and optical manipulation of complex orders. Our efforts will be organized in five directions: (i) Upgrades to our high harmonic generation (HHG) based time and angle resolved photoemission spectroscopy (trARPES) setup, (ii) Experiments on model charge-density wave (CDW) systems to study light induced phase transitions. (iii) Investigating ultrafast control of complex orders with light. (iv) Search for light-induced topological phase changes and (v) Building a new beamline to measure the phase shifts in photoemission process with high energy and momentum resolution

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3. "*Room Temperature Terahertz Electroabsorption Modulation by Excitons in Monolayer Transition Metal Dichalcogenides*" Jiaojian Shi, Edoardo Baldini, Simone Latini, Shunsuke A. Sato, Yaqing Zhang, Brandt C. Pein, Pin-Chun Shen, Jing Kong, Angel Rubio, Nuh Gedik, and Keith A. Nelson, ***Nano Lett. 20,*** 5214–5220, (2020)

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6. "*Light-Induced Charge Density Wave in $LaTe_3$*" Anshul Kogar*, Alfred Zong*, Pavel E. Dolgirev, Xiaozhe Shen, Joshua Straquadine, Ya-Qing Bie, Xirui Wang, Timm Rohwer, I-Cheng Tung, Yafang Yang, Renkai Li, Jie Yang, Stephen Weathersby, Suji Park, Michael E. Kozina, Edbert J. Sie, Haidan Wen, Pablo Jarillo-Herrero, Ian R. Fisher, Xijie Wang, Nuh Gedik, ***Nature Physics 16,*** 159 (2020)

7. "*Time-resolved XUV ARPES with tunable 24–33 eV laser pulses at 30 meV resolution*" Edbert J. Sie*, Timm Rohwer*, Changmin Lee*, Nuh Gedik, ***Nature Communications 10***, 3535 (2019)

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13. " *Evidence for topological defects in a photoinduced phase transition*" Alfred Zong*, Anshul Kogar*, Ya-Qing Bie, Timm Rohwer, Changmin Lee, Edoardo Baldini, Emre Ergeçen, Mehmet B. Yilmaz, Byron Freelon, Edbert J. Sie, Hengyun Zhou, Joshua Straquadine, Philip Walmsley, Pavel E. Dolgirev, Alexander V. Rozhkov, Ian R. Fisher, Pablo Jarillo-Herrero, Boris V. Fine, Nuh Gedik, ***Nature Physics 15***, 27–31 (2019)

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Elucidating Emergence in Multiscale Driven Systems

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Collaborators: Samuel Teitelbaum, Arizona State University; Andrei Fluerasu, Brookhaven National Lab; Christopher Tassone, SLAC; Chenhui Zhu, Lawrence Berkeley Laboratory; Garth Williams, Brookhaven National Lab

Program Scope

The goal of this 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.

In particular, we previously showed that new colloidal suspension of nanoparticles in polar and ionic media can form strongly-coupled superlattices mediated by unusual, Coulomb-dominated inter-nanoparticle interactions due to the use of short ionic ligands.[1–3] The initial agglomeration of nanoparticles sets the stage for subsequent ordering but its mechanisms remain to be characterized and optimized. Furthermore, the process works for conducting nanoparticles but not yet for dielectric ones. Our goal is to resolve the complex, multiscale dynamics of agglomeration and subsequent annealing for this novel class of materials, measuring the nanoparticle diffusion and agglomeration as a function of time following introduction of destabilizing excess ionic ligands that trigger the process, and manipulating the annealing process to elucidate its mechanisms. To do so, we use a combination of coherent and incoherent X-ray scattering approaches, resolving the kinetics and dynamic fluctuations associated with agglomeration through ordering. Varying ligand concentrations will modulate the driving force for assembly, and comparing metallic and semiconducting properties will identify the role of nanoparticle free charge density in modulating inter-nanoparticle interaction strength. We will thus elucidate the mechanisms for strongly coupled nanoparticle superstructure formation to open promising applications in energy science.

Recent Progress

A primary activity has been to elucidate the mechanism of the superlattice self-assembly of an initially colloidal suspension of 4-5 nm Au nanoparticles decorated with thiostannate $(Sn_2S_6)^{4-}$ ligands in a (polar) hydrazine solvent. We studied this crystallization process with *in situ* small angle X-ray scattering (SAXS), X-ray photon correlation spectroscopy (XPCS), and simulation to yield new insights into the assembly process. We find that particles first agglomerate into a dense amorphous phase and then rearrange into an ordered lattice, which we refer to as a two-step crystallization process.

The process is induced by mixing the colloidal suspension with a solution of additional thiostannate $(Sn_2S_6)^{4-}$ ligands, to increase the overall ligand concentration and therefore also to increase

the ligand coverage at the surface of the nanoparticles. To do so, we developed a sophisticated gas-tight, capillary-based injection reactor for studying superlattice formation *in situ* at storage rings that is compatible with future XFEL experiments. Because of their negative charge and the associated increased surface charge on the nanoparticles, the interparticle interaction potential becomes more repulsive at short range. Altering this interaction effectively quenches the nanoparticle suspension to drive the 'bonding' of particles to one another.

Self-assembly kinetics: By time-resolving the kinetics of self-assembly using *in situ* SAXS and fitting the SAXS 1D patterns, we were able to gain mechanistic insight. We simulated structures of the possible species formed in the experiment: mass-fractal diffusion-limited aggregates, disordered compact aggregates, and ordered FCC superlattices. The *in situ* SAXS patterns are well fit by a linear combination of completely disordered compact aggregates and FCC superlattices, with no evidence for the formation of fractal diffusion-limited aggregate.

The timescales on which these compact aggregates and FCC superlattices form yield insight into the mechanism of self-assembly. Nucleation of a condensed phase (ordered superlattice or compact, disordered aggregate) occurs within the 30 seconds it takes for the injected solution of reagents to reach the X-ray beam spot in the capillary. Subsequent growth of the condensed phase occurs within ten minutes, although we distinguish between disordered aggregate (broad peaks) and ordered superlattice (sharp Bragg peaks) in the time evolution. In particular, we observe a delayed onset of superlattice growth relative to compact aggregate growth. Furthermore, superlattices appear on a $\sim$ 6 minute timescale, and the lattice appears to contract on a time scale of $\sim$ 20 minutes. Our results are consistent with a two-step nucleation mechanism, in which the two order parameters are density and order. While ordered superlattices nucleate within the compact aggregates, the latter are the only species to form directly from the colloidal suspension.

Microscopic dynamics during self-assembly: We carried out synchrotron coherent SAXS and XPCS experiments to identify the microscopic fluctuations associated with the self-assembly process. By measuring coherent scattering speckle patterns, we observed correlation times of 0.1-1 s in the low-q range. This time scale could be associated with mesoscale rearrangements within an aggregate that consists of multiple supercrystalline domains in the 100 nm range. At higher q, we readily observe isolated superlattice Bragg peaks and also speckle patterns attributable to similarly oriented superlattices, or a high degree of strain in the sample. Already, the information gleaned from coherent scattering is helpful as we prepare for future experiments at LCLS and euXFEL.

Simulating self-assembly in silico: We have also developed a novel molecular simulation algorithm to enable the study of rare assembly dynamics in solution under arbitrary nonequilibrium environments. This algorithm was derived from a variation principle on the space of stochastic trajectories that identified an optimal control force that guides complex interacting systems to exhibit rare fluctuations as typical. The optimal control force is that which does not introduce a bias in the way in which the assembly is formed. To find the optimal force numerically requires solving an optimization problem. This was made tractable through the derivation of explicit gradients that determine how the dynamics of a system responds to changing its interaction and external forces. This was demonstrated in models of drive colloids, which exhibited condensed and hyperuniform phases.[4]

Future Plans

Self-assembly kinetics in various material systems: We plan to do more *in situ* SAXS measurements to clarify the self-assembly mechanism. We have developed a new sample reactor for SAXS experiments that enables more controllable initiation of the self-assembly process. The new reactor

will enable us to accurately quantify the concentration of aggregates and superlattices in our reactor. So doing would further support the hypothesis that superlattice assembly involves a two-step process of aggregation followed by superlattice growth. Additionally, our new sample reactor will allow detection of the colloidal dispersion prior to injecting the excess ligand that initiates self-assembly, which will allow us to resolve nucleation events and early-time ordering.

At upcoming beamtimes, in addition to beginning with the Au nanoparticles with thiostannate ligands in hydrazine, we will progress to test CdSe and PbS semiconducting particles with other chalcogenidometallate ligands and move toward more benign solvents such as n-methylformamide. We will vary the degree of ionicity of each nanoparticle-solvent system, which allows us to tune the range of the nanoparticle interactions and observe the effects on self-assembly. This includes transitioning to using molten salts with chalcogenidometallate ligands and ionic liquids such as 1-butyl-3-methyliimidazolium halide instead of polar solvents.

Coherent diffractive imaging of annealing events: We discovered through our modeling to fit 1D SAXS patterns that broadening of the peaks in the structure factor due to compact aggregates can potentially mask the presence of smaller polycrystalline domains which lead to similar types of broadening. Although we are unable to definitively identify the composition of the disordered precursors via SAXS, our upcoming beamtime at LCLS will aim to resolve the particle-by-particle structure of the disordered precursors as they anneal into more ordered superlattices.

Specifically, we will use coherent diffractive imaging (CDI) on individual Au superlattices to resolve defect annealing, unperturbed and with ultrafast optical excitation, as a function of ionicity of the solvent. With laser irradiation we will watch how nanoparticle heating and surface polarization change the surrounding solvent's charge density, allowing us to characterize and modulate inter-nanoparticle interactions. All of the prior SAXS and XPCS experiments, analysis, and related simulations are becoming increasingly helpful in preparing for this beamtime, since we are developing more specific models of the structures that we might expect to see with CDI.

To perform time-resolved CDI, superlattices must be fixed in place. To ultimately watch the nucleation and growth of such structures, we will develop ways to nucleate heterogeneously on surfaces compatible with XFEL experimental conditions, for example on deliberate 'defects' or templates. In particular, we will take advantage of two-dimensional materials on surfaces to nucleate self-assembly, holding the superlattices in a fixed orientation, affording a higher degree of structural information to be obtained from scattering experiments.

Resolving microscopic fluctuations: W**e** also intend to perform XPCS experiments at the EuXFEL MID instrument to complement the synchrotron XPCS experiments by probing a different timescale regime capable ultimately of resolving nanoparticle diffusion in suspension prior to the self-assembly process. At NSLS-II (CHX), we were able to obtain high-quality correlations with a photon flux of 10^{10} photons/sec on target, observing down to ~100 ms correlation times at low wavevector. Our goal in experiments at the MID instrument is to have similar average flux, but concentrated into microsecond-scale bursts. Diffusion timescales of the gold and semiconducting nanoparticles are predicted to be on the order of hundreds of nanoseconds to microseconds, ideally matched to the MID instrument capabilities. This will still enable us to access sub-microsecond motions of the gold nanoparticles in solution that ultimately result in aggregate formation and critical nucleation predicted by theory. We will repeat these experiments with semiconducting nanoparticles, (e.g. PbS), to establish differences in interactions that lead to variable ordering in the conducting vs semiconducting systems.

Simulating non-classical self-assembly pathways: We have begun to develop a model for gold colloids with tunable ranged attractions that will enable the study of superlattice formation. We will employ state of the art computational techniques to tease out the free energetics and kinetics of

superlattice formation and how each depends on the formation pathway. With the coincident development of an underlying microscopic model for the emergent effective interactions of gold nanoparticles in ionic solutions, we will be able to rationalize how varying experimental solution conditions result in varying super lattice formation dynamics. We are testing this framework against our SAXS data to confirm an accurate representation of the time dependent structure factor and the time-dependent pair distribution function. This will enable us to posit novel solution conditions to study in future beamline experiments.

Design principles for colloidal assembly: We are also working towards a set of basic design principles for the formation of finite colloidal clusters. The formation of self-limiting structures is often difficult to achieve, as near equilibrium surface free energies tend to drive aggregation. Away from equilibrium these energetic constraints can be mitigated in principle, but there is currently little understanding regarding the form of nonequilibrium driving protocols that can lead to such structures. We recently developed a variational theory for pattern formation in nonequilibrium systems that can be used to address this problem. First we are focusing on the formation of small compact and nonrigid clusters of particles interacting with short ranged pairwise additive potentials and under shear flows. Using our variational theory will optimize the interaction matrix, achievable experimentally through DNA coated colloids, as well as the features and extents of the shear flow. We aim for this study to seed the design of subsequent experiments, where the nonequilibrium driving protocols are not generated through flows but rather by photoexcitation.

Fully ionic solutions: As we press toward studying superlattice self-assembly and interparticle interactions in fully ionic solutions (i.e. without any polar molecules), such as molten salts or room temperature ionic liquids, we anticipate the interaction potentials to become oscillatory and much longer range.[1–3] The persistent charge correlations surrounding nanoparticle surfaces may frustrate the ability for 3-dimensional assembly, and all of the expertise that we are developing to resolve microscopic dynamics in our currently studied systems with polar/electrolytic solvents will prove extremely useful toward elucidating the correlations associated with nanoparticle interactions in ionic solutions. We anticipate that there may be substantial advantages to working with interacting components with higher dimensionality than nanoparticles, for example by examining interactions between two-dimensional sheets, such as MXenes.

We will investigate the role of molten salts in MXene surface functionalization.[5] By understanding the mechanism of surface reactions, we expect to develop new fundamental knowledge of MXene surfaces and identify the factors controlling reaction kinetics and selectivity. There is no experimental evidence for complete delamination of MXene sheets during surface functionalization—at the end of the reaction, we observed perfectly stacked materials instead of randomly aggregated 2D sheets. We, therefore, hypothesize that the reaction pathway may include the transition state with partially unstacked MXene sheets, with their surfaces sterically accessible to the exchange of functional groups. Stabilization of this transition state can be assisted by the interaction of molten salt with the MXene surface, in a similar way to the interactions responsible for colloidal stabilization of nanoparticles in molten salts investigated in this project for Au nanoparticles.

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Transient and Metastable Order Created by Ultrafast Light

V. Gopalan (PI), L-Q. Chen (Penn State), J. W. Freeland, H. Wen (ANL), L. W. Martin (U.C. Berkeley and LBNL), A. M. Lindenberg (Stanford and LCLS). Collaborators: D. Zhu, M. Hoffmann, J. Turner, P. H. Fuoss (LCLS), R. Ramesh (Berkeley), V. Stoica (Penn State), L. Bellaiche (U. Arkansas), Y. Cao (ANL). **Funding:** DE-SC-0012375 & LCLS Campaign LW00

Abstract:
The central goal of this grant is to *probe fluctuations, the emergence of order from disorder, and the coherent collective dynamics of complex topological objects created by design*. It builds upon our recent successes in designing and demonstrating polar supercrystals [1], vortices [2], and skyrmions [3,4] that span the sub- Å-to-10's nm scale. We focus on three interconnected science foci: Collective modes, driven transition pathways, and the emergence through fluctuations of these structures. All three foci inform the central theme of how to create, stabilize, deform, destroy, and re-create complex topological polar textures. It requires high-Q (wavenumber) metrology, resonant ultrafast pump probe, and X-ray photon correlation spectroscopy (XPCS). Such complex extended structures are ubiquitous in condensed-matter physics. The high-impact showcase science proposed here focuses on polar vortices, skyrmions, and supercrystals and involves a comprehensive program integrating theory, computation, synthesis, and ultrafast X-ray and optical characterization.

Table of Content for the Talks:

Filename: Talks 1_V_Gopalan & L-Q. Chen (Penn State)_PIMeeting2020_DE-SC0012375
Fluctuations, Emergence and Dynamics of Complex Topological Superstructures by Design: Introductory talk by V. Gopalan that includes the central theme of the project, the different types of complex polar textures to be studied, the scientific questions to be addressed, and a one slide preview of the other talks to follow.

Filename: Talks 2_J. Freeland (ANL)_PIMeeting2020_DE-SC0012375
Ultrafast Transformation Pathways to Form Complex Polar Textures: This talk will cover the ways in which we are probing the ultrafast transformation mechanism for the creation of a supercrystals and Skyrmions using XFEL and ultrafast optics.

Filename: Talks 3_Haidan_Wen_ANL_PIMeeting2020_DE-SC0012375
Driven Collective Mode Dynamics of Complex Polar Textures: This talk will discuss a new vortexon mode[5] discovered in THz driven polar vortex dynamics, and plans to study similar dynamics in skyrmions and supercrystals.

Filename: Talks 4_Lindenberg (Stanford) & Martin (Berkeley)_PIMeeting2020_DE-SC0012375
Role of Fluctuations and Disorder in Topological Superstructures: This talk will cover the XPCS experiments aimed at probing fluctuations in the polar order in vortices, skyrmions, and supercrystals using XPCS.

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

Alexander Gray, Department of Physics, Temple University

Program Scope

This research program aims at addressing the scientific questions related to time-dependent emergence and control of non-equilibrium electronic phases of matter in strongly-correlated Mott oxides and their interfaces. We are focusing specifically at exploiting the interfaces in heterostructures and superlattices containing strongly-correlated manganites and nickelates because, in such systems, precise control of electronic and magnetic structure in the ground state can be achieved through dimensionality, heterostructuring, interface termination, and lattice strain [1-3].

One of the main objectives of this program is to develop a suite of complementary ultrafast x-ray scattering techniques which probe the three-dimensional nanoscale evolution of materials' properties as the electronic and spin states are driven out of equilibrium by ultrafast external stimuli such as intense THz electric fields [4]. Ångstrom-level depth resolution in such measurements is achieved by utilizing the x-ray standing-wave method, wherein the intensity profile of the probing x-ray radiation is tailored and translated vertically within the sample [5]. As a key part of this project, we are working to marry this methodology, which is presently being utilized only in equilibrium, with the ultrafast FEL- and synchrotron-based pump-probe techniques. This will result in the development of a powerful new experimental platform that can be used to study electronic systems driven out of equilibrium with depth resolution. The new depth-resolved ultrafast x-ray scattering techniques and instrumentation developed in the course of this program will be generalizable for immediate use at the DOE's synchrotron and FEL facilities.

Recent Progress

Over the past two years, we have demonstrated the capability to probe the momentum-resolved electronic structure of a quasi-2D oxide layer buried underneath several unit-cells of an insulator [6]. These results mark a significant milestone in the progress of this project because they demonstrate an effective way of investigating the electronic structure of matter with exotic order in a few buried layers. We are currently applying these techniques to the Mott oxide systems that are of direct relevance to the major goals of this project ($CaMnO_3/LaNiO_3$ and $CaMnO_3/CaRuO_3$).

Additionally, we have demonstrated a single-unit-cell resolution in the depth-dependent probing of the electronic structure in oxide superlattices [7]. This new capability made possible by the use of soft x-rays and standing-wave excitation, present significant advances from the point of view of technique development and will be critical for our planned studies of buried interfaces at FELs.

More recently, we have continued our investigations of strongly-correlated Mott oxides and interfaces that are of direct relevance to the major goals of the project. We have addressed these goals by carrying out comprehensive synchrotron-based measurements of the $CaMnO_3/CaRuO_3$ superlattices that exhibit emergent interfacial ferromagnetism. We have also carried out extensive ultrafast ***THz-pump*** optical-probe measurements at the LCLS Research Laser Lab using ultrathin epitaxial Mott oxide VO_2 as a model system. These measurements mark the beginning of the ultrafast activities that are relevant to the major goals of the project and the shift to the planned FEL-based activities.

Finally, we have completed construction and *commissioning* of the first laboratory-based hard/tender x-ray angle-resolved photoemission spectrometer in the U.S. It is currently being utilized for depth-sensitive studies of a aide variety of materials systems that are relevant to the major goals of this project.

Future Plans

During the next reporting period, we are planning to continuously shift the emphasis of our research efforts toward the lab- and FEL-based ultrafast THz studies of the electronic, magnetic, and structural properties of the strongly-correlated materials and superlattices. Specifically, we are planning to continue our ultrafast THz-pump optical probe experiments at the LCLS Research Laser Lab at SLAC, while actively preparing for the future ultrafast x-ray scattering experiments at LCLS, which will likely resume normal operation in early 2021.

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Synchrotron X-ray based study of novel quantum materials & ultrafast study and control of novel topological matter

M. Zahid Hasan (Princeton University)

Program Scope

Our program is focused on discovery and understanding of quantum materials (topological insulators, magnets, superconductors and chiral materials) using advanced spectroscopic techniques. We combine FP-DFT calculation techniques (related to spectroscopic methods) to discover novel topological phases harboring new protected quantum properties then probe and explore suitable materials primarily via spin-ARPES, X-ray and Ultrafast (including ARPES) spectroscopic techniques including photogalvanic effects in some compunds. Currently we are also working on developing a novel ultrafast-laser-ARPES technique suitable for the study of photo-induced changes (including the control of Weyl fermions) in topological magnetic materials. The general focus of this proposal is to carry out novel and potentially high-impact experiments to advance the fundamental science of quantum materials.

Recent Progress

Novel quantum materials: Our recent progress [1-12] include identification and exploration of topological magnets, novel Weyl semimetals, topological Fermi arc states including weakly and strongly Lorentz-violating Weyl metals, topological nodal-line states, quantum properties of chiral crystals and many-body spin–orbit tunability in correlated kagome magnets. We have also developed a novel artificial condensed matter lattice which will be able to explore tunable topological magnetic phases of matter.

Technique development: We are making progress in developing a novel ultrafast-ARPES technique (as originally proposed) aimed at controlling Weyl and nonlinear optical properties of topological magnetic materials (currently not accessible by existing techniques) relevant for developing spintronics and topotronics. This technique will also allow us to explore photo-induced changes on the surface of chiral (nonmagnetic) topological matter for which we have developed a theory (Chang, Hasan *et.al.*, PRL 2020). We have set-up the ultrafast laser/optical system in our Princeton laboratory and working on developing a cryogenic manipulator. An essential component of our ultrafast-ARPES setup is the Spin-TOF analyzer (key collaborator Dr. Z. Hussain of Berkeley Lab). We are currently waiting for the ARTOF analyzer/detector system (experiencing vendor delay due to the COVID-19 shutdown). The development of this instrument has also been slowed down due to the shutdown of our labs at Princeton for several months (COVID emergency including identification of a positive case in the lab building).

Future Plans

Knotted topological magnets : Quantum magnets with Chern or Knot-theory invariants are of great recent interest. Current topological magnets have very complex band structures containing multiple intertwined Weyl or nodal-linked loops [3,6,7,11]. Therefore it is of great interest to the entire physics community to discover the simplest versions of such novel quantum matter. We are currently working on both theoretical and experimental search algorithms for this. Recently we have developed a collaboration with knot theorists at Princeton mathematics department. To be specific, utilizing Knot theory we would like to understand the invariant structure of Co2MnGa series of compounds that we have experimentally discovered to be topological magnets, then use that guideline to extend the search to other magnets that exhibit anomalous Hall conductivity in the quantum geometry limit. We will also explore our search for chiral conductor materials since they are of great interest due to the quantization of circular photogalvanic effect in optical/THz/X-ray regimes that we have predicted (see, *Chang et.al., Phys. Rev. Lett. 119, 156401 (2017)*) and which also feature unconventional (topological) photocurrents from Fermi arcs as we have shown in other recent theory papers (*Chang et.al., Nature Mat. 17, 978 (2018) and Phys. Rev. Lett. (2020)*). We plan to explore highly exotic photogalvanic effects and study of the dynamics of chiral (non-linear) materials.

Spin-TOF and Ultrafast technique development: This technique will also allow us to explore photo-induced changes on the surface of chiral materials including allowing ultrafast control of Weyl fermions as our theory has demonstrated (*PRL 2020*). We have set-up the ultrafast laser/optical system but the essential component - the Spin-TOF analyzer is missing. We are currently waiting for the TOF analyzer/detector system (experiencing vendor delay due to the COVID-19 shutdown). If things go well we hope to receive the analyzer sometime mid or late next year. Hopefully, starting next summer (2021) we will be working on integrating the existing ultrafast laser pump-probe optics, manipulator and spin-TOF together. Our longer-term 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 instrumentation 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 articles in Nature News (homepage, July 2017), Scientific American (July, 2017) and Discover magazine (October, 2018). These news articles cite our works on

topological matter supported during the past cycles of this DOE grant. (Key collaborator: Dr. Z. Hussain (Berkeley Lab)).

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6). Topological Hopf and Chain Link Semimetal States and Their Application to Co2MnGa
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10). Giant and anisotropic spin–orbit tunability in a strongly correlated kagome magnet
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11). Topological quantum properties of chiral crystals
G. Chang et.al., *Nature Materials 17, 978–985 (2018)*

12). Chiral Fermion Modes on the Surface of Superconducting Topological Insulators
C.-K. Chiu et.al., *Europhys. Letters 123, 47005 (2018)*

Publications (2018-2020)

Work supported by grant #DE-FG-02-05ER46200 (M.Z. Hasan)

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

Guoqing Chang, Bahadur Singh, Su-Yang Xu, Guang Bian, Shin-Ming Huang, Chuang-Han Hsu, Ilya Belopolski, Nasser Alidoust, Daniel S Sanchez, Hao Zheng, Hong Lu, Xiao Zhang, Yi Bian, Tay-Rong Chang, Horng-Tay Jeng, Arun Bansil, Han Hsu, Shuang Jia, Titus Neupert, Hsin Lin, M Zahid Hasan

Physical Review B 97, 041104(R) (2018)

2. ***Giant and anisotropic many-body spin–orbit tunability in a strongly correlated kagome magnet***

Jia-Xin Yin, Songtian S. Zhang, Hang Li, Kun Jiang, Guoqing Chang, Bingjing Zhang, Biao Lian, Cheng Xiang, Ilya Belopolski, Hao Zheng, Tyler A. Cochran, Su-Yang Xu, Guang Bian, Kai Liu, Tay-Rong Chang, Hsin Lin, Zhong-Yi Lu, Ziqiang Wang, Shuang Jia, Wenhong Wang & M. Zahid Hasan

Nature 562, 91–95 (2018)

3. ***Topological quantum properties of chiral crystals***

Guoqing Chang, Benjamin J. Wieder, Frank Schindler, Daniel S. Sanchez, Ilya Belopolski, Shin-Ming Huang, Bahadur Singh, Di Wu, Titus Neupert, Tay-Rong Chang, Su-Yang Xu, Hsin Lin, M. Zahid Hasan

Nature Materials 17, 978–985 (2018)

4. ***Chiral Majorana Fermion Modes on the Surface of Superconducting Topological Insulators***

Ching-Kai Chiu, Guang Bian, Hao Zheng, Jia-Xin Yin, Songtian S. Zhang, D. S. Sanchez, I. Belopolski, Su-Yang Xu and M. Zahid Hasan

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5. ***Discovery of topological Weyl fermion lines and drumhead surface states in a room temperature magnet***

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6. Quantum phase transition of correlated iron-based superconductivity in LiFe1-xCoxAs

Jia-Xin Yin, Songtian S. Zhang, Guangyang Dai, Yuanyuan Zhao, Andreas Kreisel, Gennevieve Macam, Xianxin Wu, Hu Miao, Zhi-Quan Huang, Johannes H. J. Martiny, Brian M. Andersen, Nana Shumiya, Daniel Multer, Maksim Litskevich, Zijia Cheng, Xian Yang, Tyler A. Cochran, Guoqing Chang, Ilya Belopolski, Lingyi Xing, Xiancheng Wang, Yi Gao, Feng-Chuan Chuang, Hsin Lin, Ziqiang Wang, Changqing Jin, Yunkyu Bang, M. Zahid Hasan

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7. Magnetic-field control of topological electronic response near room temperature in correlated Kagome magnets

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8. Topological Chiral Crystals with Helicoid Arc Quantum States

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10. Crystal growth and quantum oscillations in the topological chiral semimetal CoSi

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11. Unconventional Scaling of the Superfluid Density with the Critical Temperature in Transition Metal Dichalcogenides

F. O. von Rohr, J. -C. Orain, R. Khasanov, C. Witteveen, Z. Shermadini, A. Nikitin, J. Chang, A. R. Wieteska, A. N. Pasupathy, M. Z. Hasan, A. Amato, H. Luetkens, Y. J. Uemura, Z. Guguchia

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12. Nodeless superconductivity and its evolution with pressure in the layered dirac semimetal 2M-WS2

Z. Guguchia, D. Gawryluk, M. Brzezinska, S. S. Tsirkin, R. Khasanov, E. Pomjakushina, F. O. von Rohr, J. Verezhak, M. Z. Hasan, T. Neupert, H. Luetkens, A. Amato

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13. Observation of Weyl fermions in a magnetic non-centrosymmetric crystal (Magnetic Weyl Semimetal)

Daniel S. Sanchez, Guoqing Chang, Ilya Belopolski, Hong Lu, Jia-Xin Yin, Nasser Alidoust, Xitong Xu, Tyler A. Cochran, Xiao Zhang, Yi Bian, Songtian S. Zhang, Yi-Yuan Liu, Jie Ma, Guang Bian, Hsin Lin, Su-Yang Xu, Shuang Jia, M. Zahid Hasan

Nature Commun. 11, 3356 (2020)

14. Observation of sixfold degenerate fermions in PdSb2

Xiàn Yáng, Tyler A. Cochran, Ramakanta Chapai, Damien Tristant, Jia-Xin Yin, Ilya Belopolski, Zijia Chéng, Daniel Multer, Songtian S. Zhang, Nana Shumiya, Maksim Litskevich, Yuxiao Jiang, Guoqing Chang, Qi Zhang, Ilya Vekhter, William A. Shelton, Rongying Jin, Su-Yang Xu, and M. Zahid Hasan

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15. Many-body Resonance in a Correlated Topological Kagome Antiferromagnet

Songtian S. Zhang, Jia-Xin Yin, Muhammad Ikhlas, Hung-Ju Tien, Rui Wang, Nana Shumiya, Guoqing Chang, Stepan S. Tsirkin, Youguo Shi, Changjiang Yi, Zurab Guguchia, Hang Li, Wenhong Wang, Tay-Rong Chang, Ziqiang Wang, Yi-Feng Yang, Titus Neupert, Satoru Nakatsuji, M. Zahid Hasan

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16. Spin-orbit quantum impurity in a topological kagome magnet

Jia-Xin Yin, Nana Shumiya, Yuxiao Jiang, Huibin Zhou, Gennevieve Macam, Songtian S. Zhang, Hano Omar Mohammad Sura, Zijia Cheng, Zurab Guguchia, Yangmu Li, Qi Wang, Maksim Litskevich, Ilya Belopolski, Xian Yang, Tyler A. Cochran, Guoqing Chang, Qi Zhang, Brian M. Andersen, Zhi-Quan Huang, Feng-Chuan Chuang, Hsin Lin, Hechang Lei, Ziqiang Wang, Shuang Jia, M. Zahid Hasan

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17. Unconventional photocurrent responses from chiral surface Fermi arcs in topological semimetals (Theoretical prediction)

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Physical Review Letters 124, 166404 (2020)

PREPRINT (relevant for this report)

Photocurrent-driven transient symmetry breaking in the Weyl semimetal TaAs

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

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Program Scope

The program seeks to understand fluctuations and phase transitions in artificial spin ices (ASIs), and to use this knowledge to study X-ray orbital angular momentum (OAM) generated by these structures. ASIs consist of patterned arrays of nanomagnets, as shown in Fig. 1(a), whose properties can be tuned based on geometry and competing interactions. ASIs are often designed to realize systems not readily accessible in nature [1,2] such as geometrically frustrated magnetic lattices [3–5]. ASIs can be reconfigured through a variety of field [6,7], temperature [8,9], and direct writing approaches [10,11]. Control of these processes and the introduction of defects may allow ASIs to be programmed into states with useful functions such as magnetic logic [12–16] or generation of X-ray OAM as discussed below. OAM is a topological property of light for which the photon phase has a helical structure around its propagation axis [17–19]. Interest in optical OAM is rapidly increasing in the X-ray regime where it could provide a selective probe of electronic and magnetic systems [20–29]. ASIs can be patterned with topological defects and reconfigured dynamically. As a result, they offer a pathway to X-ray metamaterials for programmable OAM generation and a platform to deepen understanding of photon interactions with 2D magnetic lattices.

Recent Progress

Superdomains in Artificial Spin Ices

Square ASIs have an antiferromagnetically ordered ground state as shown in Fig. 1(b). Regions of the ground state (superdomains) can be separated by boundaries (superdomain walls) as shown in

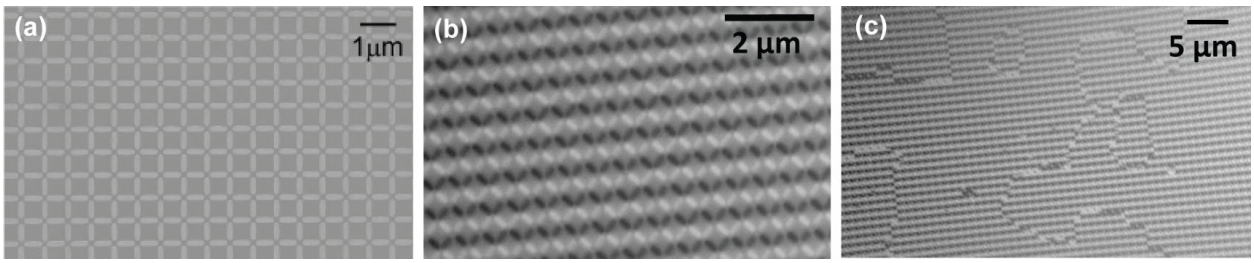

Figure 1. (a) Scanning electron micrograph of a square artificial spin ice fabricated from ≈3-nm thick permalloy. (b) Anti-ferromagnetic ground state imaged by x-ray magnetic circular dichroism photoemission electron microscopy (XMCD-PEEM). (c) Superdomains of the AF ground state separated by superdomain walls.

Fig. 1(c). We previously used coherent, resonant x-ray scattering to study the antiferromagnetic (AF) order parameter as a function of temperature though the ASI's antiferromagnetic to paramagnetic phase transition. We also used x-ray photon correlation spectroscopy (XPCS) to characterize the equilibrium dynamics of superdomain walls in square ASI and found a transition from low-temperature ballistic to high-temperature diffusive motion as we approached the AF-to-PM phase transition. These findings showed that superdomain-wall nucleation, annihilation, and motion are important for understanding the complex equilibrium fluctuations of ASIs. [30]

Recently, we have used Bragg Coherent Diffraction Imaging (BCDI) to reconstruct the real-space behavior of ASI superdomains. 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 materials can be revealed. To further study superdomain wall motion in square ASIs, we used resonant, coherent X-ray scattering to obtain diffraction patterns at a time scale of 100 ms as shown in Fig. 2(a,b). The superdomain structure was reconstructed from the speckle pattern at the AF Bragg condition for each time step as shown in Fig 2(c). Square ASIs are ideal to commission this technique because of their known lattice structure and strong AF peaks. Moreover, the real-space reconstruction can provide additional insight into domain wall nucleation, annihilation, and interactions at time scales not easily accessible with XMCD-PEEM.

X-ray OAM from Topological Defects in Artificial Spin Ices

We have recently shown that a square ASI with a programmed topological defect, a double edge dislocation as shown in Fig. 3(a), imparts orbital angular momentum to scattered X-rays. Unlike a single dislocation [31], a double dislocation does not introduce magnetic frustration, and the ASI equilibrates to its AF ground state as shown in Fig. 3(b). The topological charge of the defect differs with respect to the structural and magnetic order; thus, X-ray diffraction from the ASI

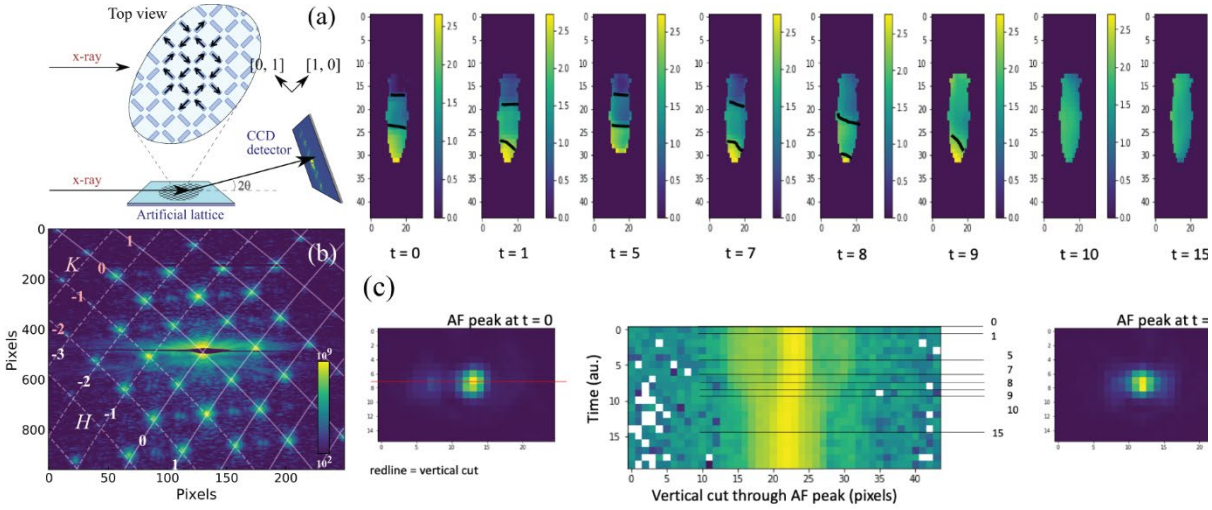

Figure 2. Bragg coherent diffraction imaging of magnetic superdomains using coherent soft x-rays. (a) Experimental configuration. (b) Diffraction pattern showing structural peaks and anti-ferromagnetic peaks broken into speckle patterns. (c) Reconstruction of superdomains in an elongated square ASI. Superdomain walls move through the samples as the structure transitions from three superdomains to a single-domain ground state. (Times are in seconds.) A cut through the speckle pattern at the AF Bragg condition also shows the transition from a multi-domain (three speckles) to a single-domain (one peak) state.

produces photons with even and odd OAM quantum numbers at the structural and AF Bragg conditions, respectively. In the off-resonance x-ray diffraction pattern of Fig. 3(c), vortex beams are clearly visible at each Bragg condition for the ASI lattice. These beams carry even order x-ray OAM. Critically, the on-resonance diffraction pattern of Fig. 3(d) reveals vortex beams at each antiferromagnetic Bragg condition. These beams carry odd-order OAM and should be sensitive to temperature and applied magnetic fields. The lack of speckle in these beams indicates that the sample is in a nearly single-domain ground state.

The polarization sensitivity of X-ray scattering [32] also enables direct determination of the phase progression of the OAM beams and thus the OAM quantum numbers. Fig. 4 shows the difference between right and left circularly polarized illumination for the first three AF vortex beams. The fringe patterns arise from interference between charge and magnetically scattered X-rays. The increasing number of fringes with diffracted order is consistent with increasing OAM and thus an increasing number of phase windings. [33,34] Plotting the difference between the circular polarizations vs. azimuthal angle for the first three AF beams gives the number of fringes as $\ell = 1$, 3, and 5 which confirms the predicted OAM quantum numbers.

The temperature and magnetic field dependence of the AF order provides control of the AF-scattered OAM beams. As temperature increases toward the AF-to-PM transition of our ASI, the intensities of the OAM-beams at the AF Bragg condition weaken until they are extinguished above $T_N \approx 380$ K as shown in Fig. 5(a). If we apply an in-plane magnetic field to the sample, instituting an AF-to-FM transition, the AF OAM beams are also extinguished, as shown in the first frame of Fig. 5(b). If we maintain the sample temperature slightly below T_N and remove the magnetic field, the sample relaxes into disordered AF superdomains within seconds as evidenced by the speckle

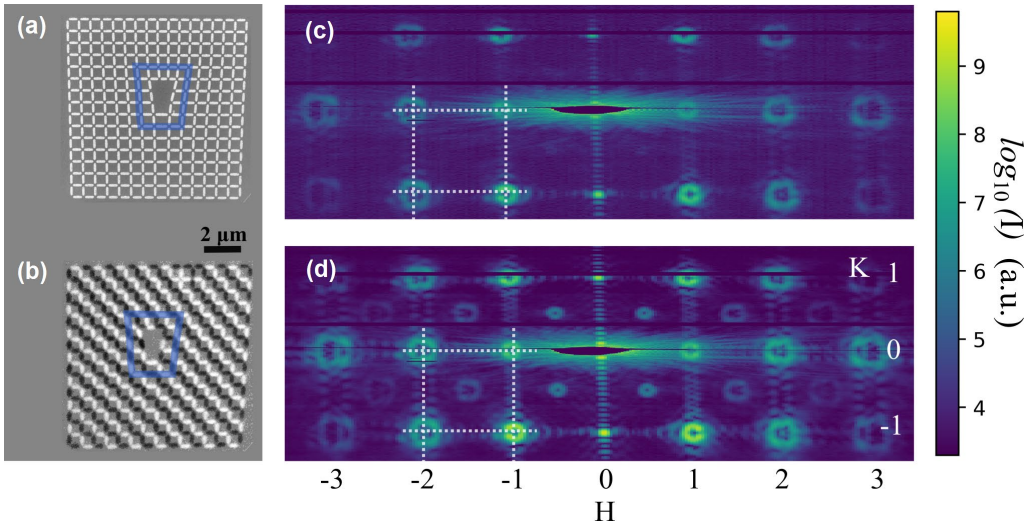

Figure 3. Experimental realization of a single-domain AF ground state in a square ASI with a double edge dislocation and resulting X-ray diffraction. (a) Scanning electron micrograph of a permalloy ASI with a topological defect consisting of a double edge dislocation. (b) XMCD-PEEM micrograph revealing the single-domain AF ground state order. The blue boxes trace out a Burgers circuit. (c) Off-resonance diffraction produces X-ray vortex beams carrying even order orbital angular momentum at the structural Bragg conditions. (d) Diffraction at the resonance condition dramatically enhances vortex beams at the AF Bragg conditions (half-integer values of H and K) which carry odd-order OAM.

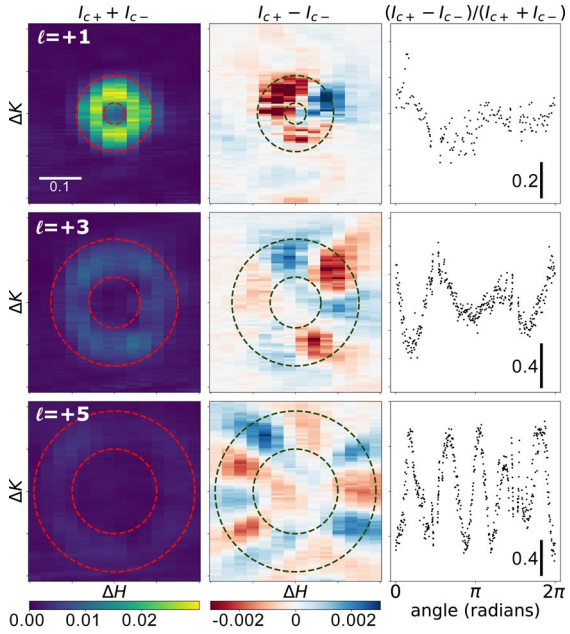

Figure 4. Determination of the AF OAM quantum number from interference between charge and magnetically scattered X-rays. First column: Vortex beam at first three antiferromagnetic Bragg conditions. Second column: Difference between diffraction of left and right circularly polarized illumination. Within the vortex ring, the number of interference fringes corresponds to the OAM quantum number. Third column: Ratio of column 2 to column 1 versus azimuthal angle. The approximately sinusoidal oscillation is consistent with the OAM phase progression.

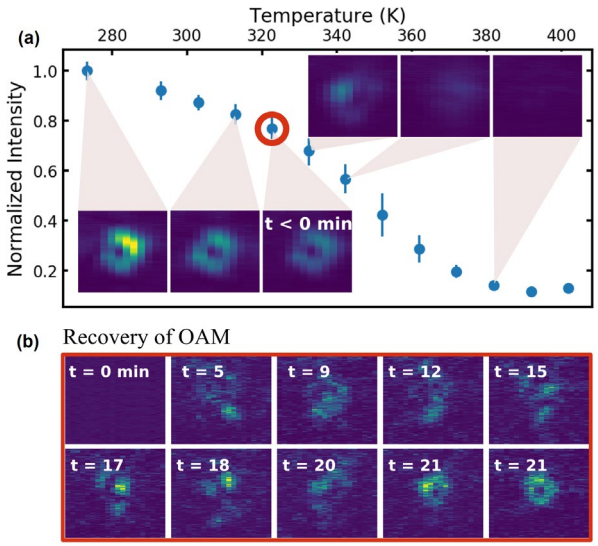

Figure 5. Response of the ASI to temperature and applied magnetic field. (a) Temperature dependent X-ray intensity of the magnetically scattered OAM beam with $\ell = 1$. The beam is extinguished as the sample approaches the antiferromagnetic-to-paramagnetic transition temperature. (b) Time dependence of intensity after the beams are switched off using a magnetic field. The speckle pattern at early time points indicates that disordered AF domains form first. Afterwards, the sample relaxes to its AF ground state and the OAM vortex beam is restored. Times are in minutes.

patterns at short time scales of Fig. 5(b). Eventually, the sample relaxes to the AF ground state over several minutes, as shown in the last frame of Fig 5(b). Thus, the AF OAM beams can be switched on and off with small changes in temperature and applied field. These findings represent a first step toward realizing reconfigurable optics for the generation and analysis of soft X-ray orbital angular momentum. More broadly, these studies show that engineering defects in nanoscale magnetic lattices offers a powerful tool for designing X-ray metasurfaces.

Future Plans

With regard to magnetization dynamics in ASI, we are currently extending our PEEM and XPCS investigations to understand how defects in *frustrated* magnetic lattices (triangular or honeycomb) alter dynamics. In parallel, we are continuing development of BCDI for imaging magnetic textures using resonant soft x-rays. 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. It may be possible to switch between OAM states by moving superdomain walls through the dislocation region with a suitable field protocol. Additional control may be obtained from thermally static

edge segments that can be switched with larger fields to seed one of the two degenerate AF textures. Even more fine-grained control can be achieved using magnetically programmable ASIs developed at Argonne National Laboratory. [10] From a more fundamental perspective, we plan to study magnetic fluctuations, and the resulting fluctuations in X-ray OAM, as function of the topological charge of the defect. We expect marked differences in the fluctuations and relaxation between lattices with defects of odd (frustrated) and even (non-frustrated) topological charge. We also expect to observe X-ray vortices with fractional topological charge depending on the defect's topological charge and the presence of superdomains.

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Bidirectional Manipulation of Phase Transitions by Laser Excitation of Optical Phonons

DE-SC0021305

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1. Program Scope

Dynamical manipulation of quantum materials by femtosecond laser is an emerging technique with wide applications including high-temperature superconductivity, ultrafast information processing, and quantum computation. Strong-field mid-infrared or terahertz laser pulses tuned to specific infrared-active phonons can directly modify structural parameters which are crucial to the physical properties of quantum materials.

This research aims at ultrafast and bidirectional manipulation of ordered phases in quantum materials using laser excitation of optical phonons. Different to previous works, here we will focus on laser manipulation which can flip switching direction, i.e., an ultrafast switching back and forth from one state to another. The goal is to steer quantum materials towards desirable states on demand and ultimately stabilizing novel quantum phases.

We will work on two objectives:

(1) Dynamical bidirectional tuning of nematicity in complex oxides and high-temperature superconductors.

We will use off-resonance phonon excitations to tune nematicity in high-temperature superconductors and complex oxides. It is predicted that electronic nematicity in tetragonal materials can be either suppressed or enhanced by laser pulses, depending on the laser frequency with respect to an infrared-active E_u phonon which couples quadratically to the electronic nematic degrees of freedom [1]. We will use mid-infrared and terahertz lasers for blue and red tuning of nematicity in $BaTi_2As_2O$ and iron-based superconductors. Our goal is to identify an efficient knob to manipulate the nematic phase, and to investigate the relationship between nematicity and interrelated orders, such as superconductivity and charge ordering in quantum materials.

(2) Ultrafast bidirectional switching of ferroelectric polarization in ferroelectrics.

We will use on-resonance phonon excitations to explore bidirectional switching of ferroelectric polarization. We will use mid-infrared lasers to drive the highest frequency infrared-active phonon in $BiFeO_3$ and $BaTiO_3$. The switching is predicted to be bidirectional, with a long-lived switched state [2]. Ultrafast switching of ferroelectric polarization is appealing for developing non-volatile ultrafast memory unit. Our research may also enable multi-bit information encoding in a single ferroelectric domain.

2. Recent Progress

We received $BaTi_2As_2O$ samples. The equilibrium optical characterization is ongoing. Equilibrium measurements will pin down the frequency of the Eu phonon mode, its width, and its splitting upon cooling down below the nematic transition temperature. These are important information for further investigating the effect of off-resonance phonon pumping on nematicity in $BaTi_2As_2O$.

3. Future Plans

We will use our mid-infrared pump light source to study blue detuning of electronic nematic ordering in $BaTi_2As_2O$. If successful, we need to upgrade the light source to generate laser pulses lower than the E_u phonon frequency to study red detuning of nematic ordering in $BaTi_2As_2O$. The following step is to investigate bidirectional tuning of electronic nematic phases in iron-based superconductors.

4. References

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Tunable Energy Landscape, Non-trivial Band Topology, and Electric Field Driven Phenomena in Low-Dimensional Materials as Probed by Localized Photoemission Spectroscopy

DE-SC0020323
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1. Program Scope

The ability to obtain atomically thin two-dimensional (2D) sheets from bulk layered crystals and engineer atomically precise van der Waals (vdW) based superlattices of 2D materials give us a unique opportunity to explore emergent physical phenomena in reduced dimensionality. The physical properties of the 2D systems are easily manipulated by the external perturbations such as underlying substrate, adatoms, defects, quantum confinement (layer thickness), and external electromagnetic field. Thus, it is imperative to directly probe the intrinsic band structure and the effects of external perturbations on electronic band structure of 2D systems because the quasi-particle band structure is responsible for bestowing the 2D systems with exotic properties such as dissipation-less particle propagation, fractional quantum Hall states, bound quasiparticles, correlated insulating phase, and superconductivity. Angle-resolved photoemission spectroscopy (ARPES) on mesoscopic sized 2D systems and their devices can directly probe, with no assumptions, the complex interplay of quasi-particle interactions that are responsible for novel emergent phenomena in quantum materials. Especially, the spatially resolved ARPES technique will allow direct mapping of the electronic dispersion of 2D systems with the momentum-resolved information to study the non-trivial band topology; investigate competing phases in highly correlated states of matter in precisely assembled vdW heterostructures; and probe non-equilibrium phenomena-driven dynamical band structure of the 2D quantum materials.

The central theme of the proposed research is to employ a localized photoemission spectroscopy technique to develop a comprehensive understanding of intrinsic electronic band structure of novel two dimensional (2D) quantum materials and the tunability of the electronic states of quantum matter by extrinsic controlled nanoscale perturbations. To investigate the dynamically driven quasiparticle band structure of quantum systems under non-equilibrium conditions, we will develop the experimental capability of in-operando nanoARPES. This capability will enable direct investigation of the electronic states and chemical potential in quantum material-based nanoscale devices when driven to non-equilibrium using an external electric field.

2. Recent Progress

2.1. Momentum-resolved view of highly tunable many-body effects in a graphene/h-BN field-effect device (PRB, Rapid Comm. 2020)

The union of nanoscale phenomena and macroscopic properties of 2D material devices is of great importance and must be understood to complete the picture of an operating device. Here, we employ micron-scaled ARPES on a functional graphene field-effect device to understand the many-body effects as we apply a gate voltage. For the first time ever, we extract rich quasiparticle dynamics that renormalize the Dirac cone and give insight on how this affects the transport in the device. Previously, studying the effect of varying carrier concentration under ARPES has been performed by adding alkaline atoms to the sample surface [1, 2]. This technique achieves carrier concentrations larger than electrostatic gating but has major drawbacks because it is difficult to control, nearly irreversible, and can influence the ARPES signal by adding scatterers which disrupts interactions. With gating, none of these drawbacks are present; the carrier concentration is finely and reversibly tuned, giving control of the reconstruction of the band structure.

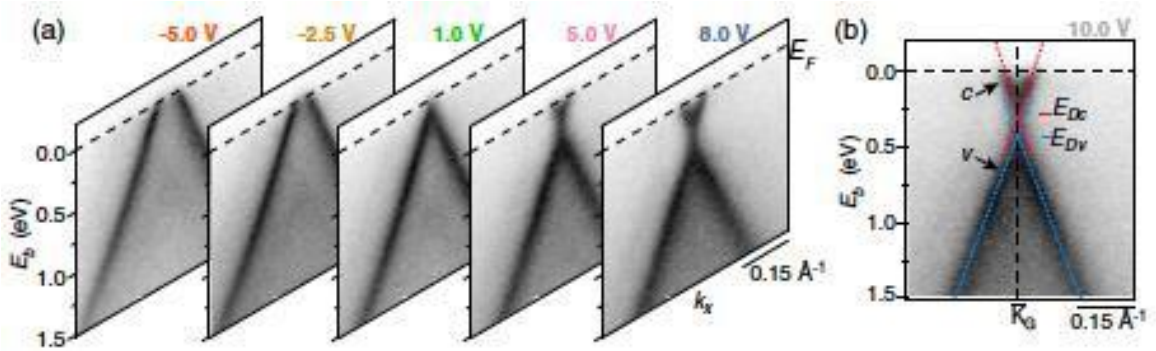

Fig. 1: (a) Snapshots of Dirac dispersion at the given gate voltages. (b) Dirac cone at the highest achieved gate voltage for n-type doping. The branches below (above) the Dirac crossing are labeled v (c). The dashed curves represent linearly extrapolated bands determined from momentum distribution curve (MDC) fits to the v branches (blue dashed bands) and c branches (red dashed bands). The v (c) branches cross at E_{Dv} (E_{Dc}).

For this ARPES study the device fabrication process was carried at the PI's home institution (CMU) and in-operando ARPES measurements were carried out at the MAESTRO facility at the Advanced Light Source, Lawrence Berkeley National Laboratory. The detailed measurements of the E(k) dispersion of the Dirac cone as a function of gate voltage (V_G) in our device are presented in Fig. 1. The series of snapshots around $\bar{K}$ in Fig. 1(a) and (b) demonstrate excellent control of both p- and n-type fillings of the Dirac cone, thereby giving access to the valence (v) and conduction (c) bands defined in Fig. 1(b). By combining the momentum distribution curve (MDC) fits at E_F with a more detailed analysis over a binding energy range of 1 eV measured from the Fermi level, we extract the doping dependent many-body interactions in our device. At large carrier concentrations, the Dirac point becomes ill-defined as the top and bottom Dirac cone become separated by a diamond-shaped feature. To study this, we track the binding energy of the Dirac point of the conduction and valence cones, denoted as E_{DC} and E_{DV} respectively as shown in Fig. 2 (a). Both E_{DC} and E_{DV} follow a $\sqrt{n}$ dependence. The separation grows as a function of carrier concentration and vanishes at charge neutrality demonstrating the existence of electron-plasmon coupling.

Next, from our quality data we can extract parameters such as band velocities (Fig. 2(b)) and scattering rates (Fig. 2(c)) as a function of carrier concentration. The band velocities' response to carrier concentration is investigated by measuring the curvature in two places: 300 meV below E_{DV} and at the fermi-level,

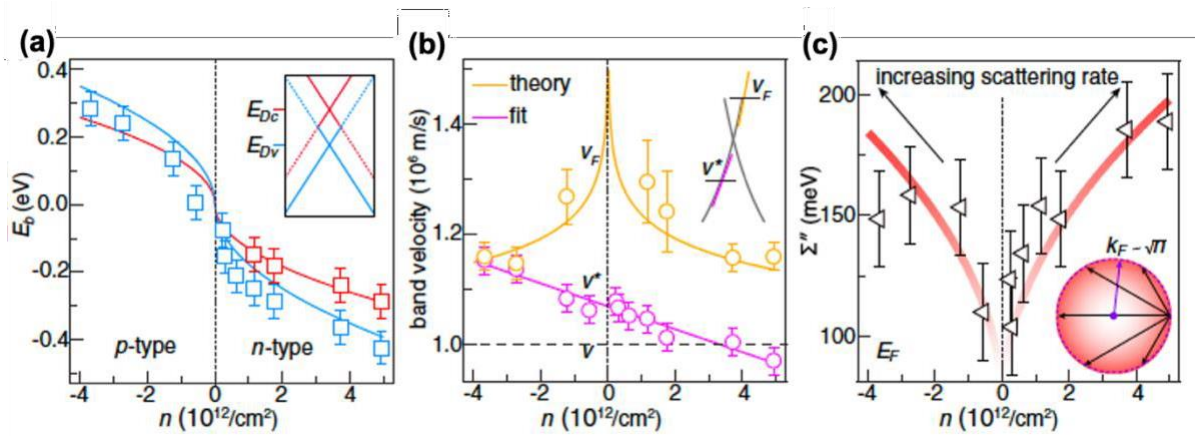

Fig. 2: (a) Binding energy positions of EDv and EDc determined by extrapolating the linear dispersion from below (blue squares) and from above (red squares) the Dirac point region, respectively. The curves are fits to √n-dependent functions. (b) Band velocities v_F and v^* measured at the Fermi level (orange circles) and 300 meV below E_{Dv} (purple circles), respectively. (c) Imaginary part of the self-energy determined from the linewidth of Lorentzian fits to MDCs at the Fermi level. The curve is a fit to a √n dependence, which follows from scattering processes that scale with the size of the Fermi surface k_F as illustrated in the inset.

denoted as V* and V_F respectively. Considering a non-interacting electron model of graphene, there should be no change in the linear bands. We find the evolution of the measured regions is drastically different from each other and the non-interacting case. First, V* shows a linear response to carrier concentration where the highest band velocity is in the heavily hole-doped regime. The curvature at the fermi level reveals severe and symmetric sharpening centered at charge neutrality. The findings here affirm the quasiparticle dispersion is heavily influenced by coulomb interactions. Finally, the doping dependent scattering is investigated by extracting band line widths at the fermi-energy, which best describes the scattering rates of the charge carriers participating in conduction. We find a near-symmetric dip in the scattering rate centered around charge neutrality. This dip is fitted to a $\sqrt{n}$ dependence which is indicative to electron-phonon coupling which dominates the short-range scattering process and leads to the reduced mobility in our device.

This work, the first of its kind, demonstrates the power of operating a device as we perform ARPES; the union of global transport measurements and ARPES helps complete the picture of the underlying physics dictating the operation of the device. By careful tuning of the carrier concentration, modify the band velocities and scattering rates of the charge carriers that participate in conduction. This technique can be utilized to understand the quasiparticle dynamics in complex phases of matter such as high-temperature superconductivity. The intrinsic doping dependence of the spectral function holds the key to fully understanding the physics of these phenomena.

2.2. Observation of electrically tunable van Hove singularities in twisted bilayer graphene from nanoARPES (Advanced Materials 2020)

Since graphene was first experimentally isolated, it has displayed exciting novel physics from its unique electronic structure [3]. An unexpected and impactful finding was that stacking two sheets of graphene with a relative twist angle lead to a superconducting phase [4]. The two Dirac cones hybridize and form a van Hove singularity (vHs) at a binding energy that decreases as the twist angle decreases. At the "magic angle," 1.1 degrees, the vHs appears at the fermi-energy which forces the electrons available for transport into correlated phases [4]. The electronic structure of twisted bilayer graphene (TBG) has been directly observed recently, through ARPES, for small [5, 6] and large [7, 8] twist angles but the effect of electrostatic gating on the spectral function has not been explored.

In this work carried out at Diamond Light Source, UK, we utilize nano-focused ARPES on a back gated TBG device with a twist angle of 12.2 degrees (samples prepared in PI's lab at CMU) and support our experimental findings with density functional theory (DFT) on a 13.17 degree TBG. First, the system is understood with its intrinsic carrier concentration with no gate voltage applied (Fig. 3a). The electronic dispersion is characterized by three main features: two flat bands at binding energies of 0.95eV and 2.48eV (designated low and high respectively) and a mini gap 0.3eV, as shown in Fig. 3(b). The gap is considerably larger than what is reported by experiments reported by TBG on hydrogen-terminated SiC, which is likely due to the h-BN flake our sample is on which weakly interacts with the TBG and allows for stronger hybridization between the two Dirac cones.

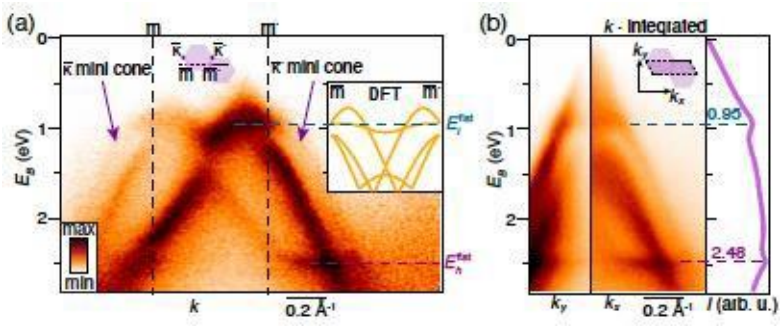

Figure 3: Observation of flat band segments at multiple energies. a) ARPES intensity cut along a line that connects $\bar{m}$ and $\bar{m}'$ as shown in the sketch of neighboring mini BZs. b) Photoemission intensity integrated over the k_x-direction (left panel), k_y-direction (middle panel) and (k_x; k_y)-plane (right panel) of a full mini BZ as sketched by the dark purple area enclosed by dashed lines in the mini BZ diagram in the middle panel.

The most interesting results come from the behavior of the system when the gate voltage is applied (Fig. 4); the bottom graphene sheet receives more carriers and receives a larger overall energy shift in comparison to the top graphene. This causes the features within the band structure shift as we apply a voltage. Between the largest negative and positive voltages, the lower and higher binding energy vHs move 400meV and 800meV respectively. This realizes a fine control over the location of the vHs and points at the possibility of superconducting phases in TBG systems with twist angles larger than the "magic angle." We finish our study by constructing a phase diagram that predicts the location of the vHs with respect to the fermi energy.

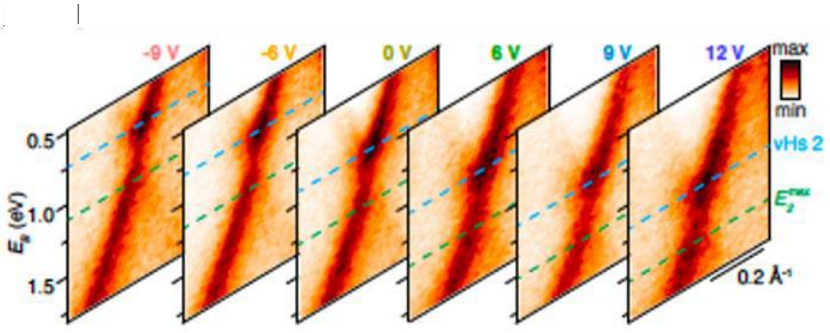

Figure 4: Doping dependence of at band segments and van Hove

To summarize, we have identified two vHs within the mini Brillouin zone (BZ) of a TBG with a twist angle of 12.2 degrees. Electrostatic gating of the system allows for fine control of the vHs location on the order of hundreds of meV. This points to the prospect that TBG systems with twist angles above the "magic angle" could have their vHs pushed into the fermi energy, forcing the conducting electrons into highly correlated phases. Our results lead to the tantalizing prospects of triggering novel interactions for larger twist angles and thereby larger mini BZs that can be fully explored in E- and k-resolving experiments combined with electron transport, as well as in optical studies where an excitation can be resonantly tuned with the energy of the vHs. Most importantly, our work establishes a route forward for accessing emerging phenomena associated with vHs physics for a wider range of superlattice heterostructures.

2.3. Accessing the spectral function in a current-carrying device

The presence of an electrical transport current in a material is one of the simplest and most important realizations of non-equilibrium physics. The current density breaks the crystalline symmetry and can give rise to dramatic phenomena, such as sliding charge density waves, insulator-to metal transitions or gap openings in topologically protected states. Until now, very little is known about the effects of current on the electron dispersion. In this work, we utilize nano-focused ARPES to investigate the spatial variance of the quasiparticle dispersion of a current carrying graphene-based device.

By scanning the 500nm diameter x-ray beam across the sample (graphene/hBN device), we can locate spatial variations of the electronic structure (Fig. 5). Directly extracted parameters are the fermi energy (Fig. 5a), location (in both energy and momentum) of the Dirac point (Fig. 5b), and the line widths which are proportional to the scattering rate (Fig. 5c). The shifts in momentum of the Dirac cone is attributed to rotated regions of graphene that most likely occurred during

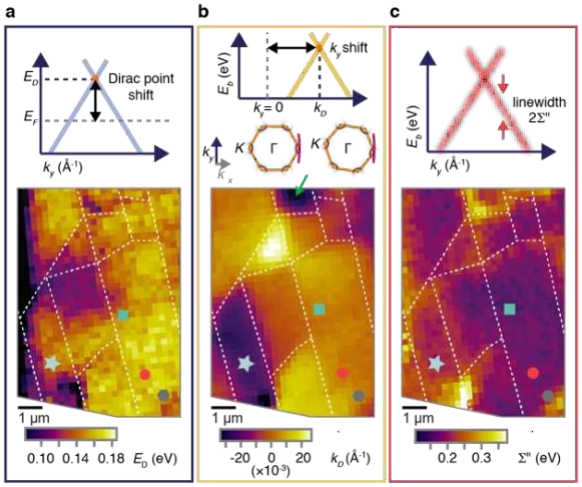

Figure 5: Detailed characterization of the device properties obtained by scanning the light spot across the device and ftting the spectra measured at every point. a) Energy of the Dirac point ED, corresponding to the local variation in doping across the device. b) Position of the Dirac cone in k_y. A shift is primarily assigned to azimuthal rotations between domains on the sample. c) Imaginary part of the self energy measuring the width of the spectra or, equivalently, the inverse lifetime of the state.

the mechanical stacking process. These rotational domains align with what is seen in an atomic force microscope (AFM) image.

When considering the line widths of the spectra, there exists extra broadening around the edges of the wrinkle. This is not attributed to an increase in scattering, rather it is an effect of capturing two separate regions spectra and averaging over the two. For a further analysis of the extracted parameters we calculate the electric potential, electric field, conductivity, and mobility of our device. The potential drops linearly, as expected, across the device, and with this we can measure the contact resistance to be 14 kΩμm. The position dependent fermi energy is used to determine the localized electric potential which is visually smooth. Taking the gradient determines the electric field, where more structure is seen, where a lack of electrical contact is seen between the graphene and electrode. The electric field is then used to determine the conductivity where the high electric field strength corresponds to a low conductivity. There is a close relationship between the AFM image which shows the wrinkles and the electric field/ conductivity map where the location of the wrinkle in the AFM matches the location of low conductivity. There exist techniques to map these extracted parameters, but no other technique simultaneously retrieves them along with the band structure. This provides a link between the transport related properties and localized many-body effects of a device. Moving forward, this could lead to understanding many-body physics within current-related phenomena such as the valley-hall effect.

3. Future Plans

The PI will continue to probe the electronic band structure of novel quantum states induced by superlattices in 2D heterostructures, which are formed by stacking various combinations of graphene and transition metal dichalcogenides (TMDCs) at different twist angles: 1) graphene/graphene/h-BN; 2) graphene/MX_2(M=Mo, W; X=S, Se)/h-BN; 3) MX_2/MX_2/h-BN. The PI has been working to fine-tune the methods to fabricate heterostructures at precise twist angle and will explore the correlated states resulting as a function of twist angle between different TMDCs. The PI will utilize a custom-built vacuum suitcase for transportation of air-sensitive and open surface 2D samples prepared in her lab to the MAESTRO beamline. In the next reporting period, we will complete the construction and commissioning of the vacuum suitcase at CMU and make arrangement for its attachment at MAESTRO beamline. In the same heterostructures, we will explore the lateral landscape of band gap, spin-orbit coupling, band alignment, and band bending phenomena by probing spatially resolved electronic band structure. We will carry out the *in-situ* doping of these 2D heterostructures with alkali metals, hydrogen atom flux, and vacancies by low energy ions, at liquid helium temperatures to examine the changes in the electronic structure of 2D heterostructures.

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5. Publications in the past one year

1. "*Momentum-resolved view of highly tunable many-body effects in a graphene/hBN field-effect device*", **Ryan Muzzio**[+], Alfred J.H. Jones[+], Davide Curcio, Deepnarayan Biswas, Jill A. Miwa, Philip Hofmann, Kenji Watanabe, Takashi Taniguchi, Simranjeet Singh, Chris Jozwiak, Eli Rotenberg, Aaron Bostwick, Roland J. Koch, Soren Ulstrup[*], and **Jyoti Katoch**[*], **Physical Review B Rapid Communications** 101, 201409(R) (2020). [*] Corresponding authors, [+] Equal contributing authors.

2. "*Observation of Electrically Tunable van Hove Singularities in Twisted Bilayer Graphene from NanoARPES*", Alfred J.H. Jones[+], **Ryan Muzzio**[+], Paulina Majchrzak[+], Sahar Pakdel, Davide Curcio, Klara Volckaert, Deepnarayan Biswas, **Jacob Gobbo**, Simranjeet Singh, Jeremy T. Robinson, Kenji Watanabe, Takashi Taniguchi, Timur K. Kim, Cephise Cacho, Nicola Lanata, Jill A. Miwa, Philip Hofmann, **Jyoti Katoch**[*], and Soren Ultrup[*], **Advanced Materials 32, 2001656 (2020).**
   [*]Corresponding authors, [+] Equal contributing authors.
3. "*Accessing the spectral function in a current-carrying device*", Davide Curcio, Alfred J. H. Jones, **Ryan Muzzio**, Klara Volckaert, Deepnarayan Biswas, Charlotte E. Sanders, Pavel Dudin, Cephise Cacho, Simranjeet Singh, Kenji Watanabe, Takashi Taniguchi, Jill A. Miwa, **Jyoti Katoch**, Soren Ulstrup and Philip Hofmann, **arxiv:2001.09891v1., (under review)**.

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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Josh Turner (DOE EC awardee 2018) and Matt Seaberg, LCLS, SLAC
Ben McMorran, Physics Department, University of Oregon
Karin Dahmen, Physics Department, University of Illinois, Urbana
Milan Sanyal, Saha Institute of Nuclear Physics, HBNI, Kolkata, India
Todd Hastings, Physics Department, University of Kentucky

Scientific scope

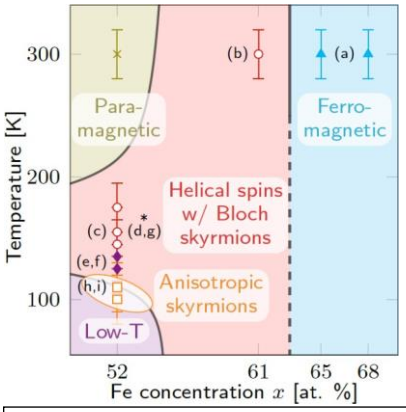
This program is part of the BES funded FWP **Non-Equilibrium Magnetic Materials (NEMM)** in the Materials Science Division at LBNL. The broader mission of NEMM is to understand the fundamental science of magnetic materials and phenomena enabled by interfaces and spin-orbit coupling (SOC). Our work inside NEMM utilizes unique capabilities at the Advanced Light source at LBNL and the LINAC Coherent Light Source at SLAC, and focuses on applying 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. 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.

An important recent NEMM focus has been materials in which several spin/magnetic interactions have 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 and phenomena. We are particularly interested in magnetic alloy films, since their properties can be easily tuned by varying the film thickness and composition, and moreover they are readily deployed in functional thin film structures. Below we briefly explore two recent sets of experiments done in the NEMM collaboration, and then briefly list relevant collaborations with PIs outside of the NEMM group.

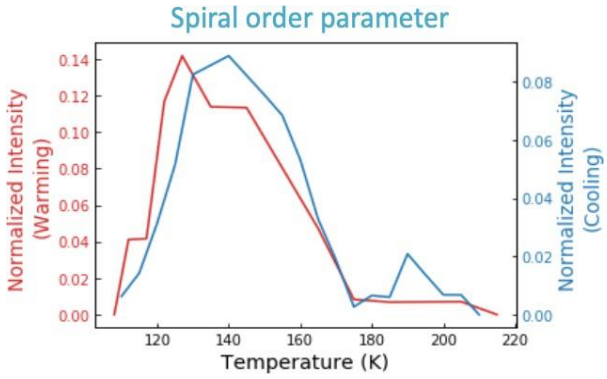
Spin structures and motion in amorphous FeGe alloy films

There is currently broad interest in utilizing the interesting properties of materials that exhibit topological solitary fields like skyrmions for advanced low power microelectronic applications. A prototypical skyrmion phase in *crystalline* FeGe is driven by the Dzyaloshinskii-Moriya vector spin exchange interaction, and persists to nearly 280 K.[1] The NEMM group has applied a battery of tools to study *amorphous* Fe_xGe_{1-x} films, which are magnetic for x greater than ~0.43. In particular, varying the composition allows the average scalar exchange interaction to be tuned relative to the spin frustration in a disordered alloy, while energetically both interactions are of order k_BT. We have probed the magnetic phase behaviors of these films with Fe L-edge resonant soft x-ray scattering, Lorentz TEM (in collaboration Ciston and Ercius at the Molecular Foundry), and magnetic measurements with x-ray magnetic circular dichroism (in collaboration with N'Diaye at the ALS).

A schematic of the measured x-T phase diagram (below, left) exhibits a helical phase and skyrmions in the region where the scalar and vector exchange and dipolar interactions are small and of comparable magnitude. The temperature dependence of the Bragg peak intensity in the helical striped phase at x=0.53 (below, right) exhibits a maximum between phase lines at higher temperature, where a paramagnetic phase exists, and at lower temperature where (probably) a longitudinal ferromagnetic phase is stable. We observe with LTEM disordered arrays of skyrmions having different chirality and topological charge.



Schematic of the x-T magnetic phase diagram in a-Fe_xGe_{1-x} films.



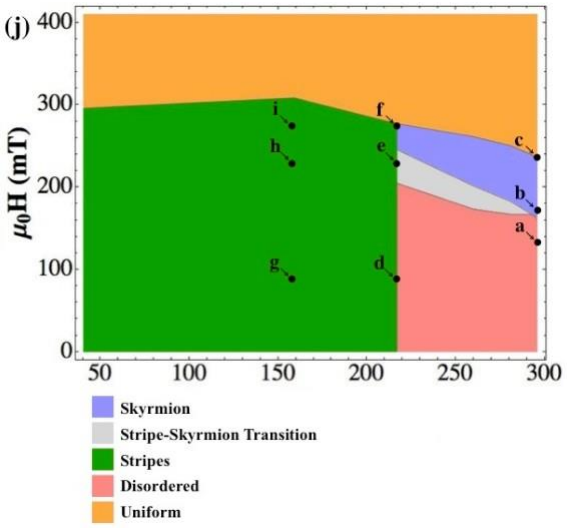
Bragg peak intensity/order parameter of the spin spiral phase in x-0.53 a-Fe_xGe_{1-x} films.

Fluctuations in the helical spin and skyrmion phases have been studies with LTEM, where switching between two discrete states in N=2 skyrmions was observed, and x-ray photon correlation spectroscopy, where larger-scale motion in these phases was mapped between the two phase lines. These results are being prepared for publication.

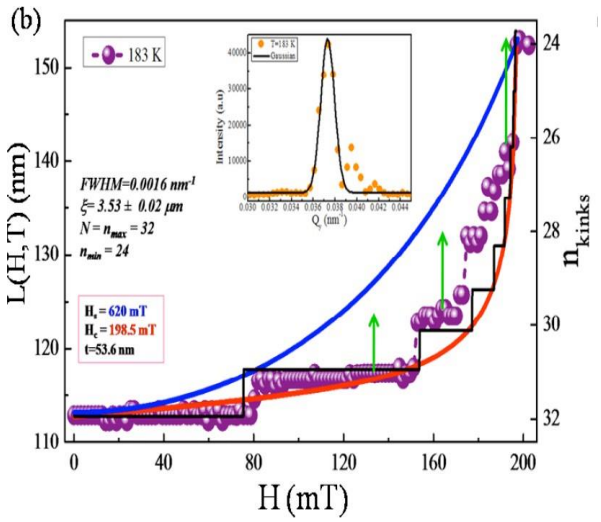
Spin structures and motion in amorphous FeGd alloy films

We have continued our previous studies of the unusually rich phase diagram of ferrimagnetic a-Fe_xGd_{1-x} films to further understand the role of topology, dimensionality, and microscopic interactions in skyrmion stability and motion. In this case the interesting region occurs for composition near magnetic compensation, where the Fe and Gd moments nearly cancel and the average magnetization is small, and over a narrow range of film thickness where the magnitudes of the surface and volume anisotropies are also comparable. In previous years we have reported a complicated phase diagram that includes weakly perpendicular ordered and disordered stripe phases, which transition to a lattice of bound skyrmions/skyrmion pairs at higher field (see below, left).[2] Our recent work has focused on the identification and understanding of other more subtle features in the phase diagram. Firstly, we used a coherent soft x-ray scattering metrology technique to measure the statistics of Barkhausen (magnetization) cascades as a function of (T,H). This has now been extensively studied and modeled, and we demonstrated the existence of transitions and underlying critical points in the stripe and skyrmion phases. We found that distinct scaling and universality classes are associated with these domain topologies.[3]

We have also observed that stripes in a-Fe-Gd films behave like finite-sized chiral soliton lattice, exhibiting discrete jumps in periodicity (see below, right), and that the orientation in the film plane of the disordered stripe phase rotates abruptly at characteristic values of (T,H), suggesting there are other hidden phase line in the a-FeGd phase diagram shown below. We are presently doing micromagnetic simulations to understand this unusual phenomenon.



Schematic (T,H) phase diagram of an a-Gd(0.4 nm)/Fe (0.36 nm)] x 80 film.



Quantization of stripe domain periodicity in the strip a-FeGd phase due to a finite sized 1D soliton lattice.

Instrumentation development to harness unique opportunities at LCLS-II and ALS-U

In the context of the NEMM science focus, we are actively planning for future developments in coherence resonant soft x-ray scattering techniques :

- In collaboration with Josh Turner at LCLS, we have helped develop the 2-pulse XPCS approach at LCLS and, soon, LCLS-II (some of which will be presented by Josh in this PI meeting).[4,5] We have measured ns-scale fluctuations through the skyrmion phase in a-FeGd, and have observed an unusual transition from oscillatory motion deep in the phase to highly damped motion near the phase boundaries.
- Complementing this 2-pulse XPCS program at LCLS, Sujoy Roy is leading the commissioning a new XPCS beamline and end station at the ALS. 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, after ALS-U, probe the entire second-to-nanosecond XPCS time domain. This will be of major benefit to this task in the NEMM program, and will take full advantage of the ALS upgrade to diffraction limited operation through the soft x-ray regime.
- In collaboration with Todd Hastings, we have an emerging interest in topological spin structures in systems with spin frustration such as artificial and natural spin ices (some of these results will be reported by Todd in this PI meeting). We have recently studied superparamagnetic fluctuations in these systems near the antiferromagnetic – paramagnetic transition, and look forward to extending those studies to natural spin ice and quantum spin liquid materials.[6] We have also made a defective artificial spin ice that, through magnetic scattering, produces diffraction orders with controlled orbital angular momentum.
- 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 to study topological spin structures.[7]

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FWP Title: Ultrafast Materials Science Program
Lawrence Berkeley National Laboratory

Lead PI: Alessandra Lanzara,
Co-PI: Robert Kaindl, Joel Moore*
** up to 2020*

Program Scope: The Ultrafast Materials Science program focuses on interrogating and manipulating quantum materials via short and intense pulses of light to unravel the intrinsic forces that drive strongly correlated ground states, as well as to generate novel phases that have no equivalent in thermal equilibrium. The program is focused on two fundamental questions: (i) How can we unravel competing phases in strongly correlated materials; and (ii) how can we manipulate and eventually control new quasiparticle distributions and topologies in quantum materials with ultrashort, intense and tailored light fields? The research approach consists of a closely coordinated effort between experiment and theory and state-of-the-art advanced ultrafast spectroscopic tools, such as time, spin, and angle-resolved photoemission spectroscopy, with spin detection of unprecedented sensitivity and with a unique extreme-ultraviolet source yielding access to electronic dynamics across the full Brillouin zone and ultrafast optical and broadband THz setups enable excitation and time-resolved studies of fundamental excitations and low-energy collective modes. Experiments will be guided by advanced theory of non-equilibrium dynamics. Materials of current interest include the creation, interrogation and control of quasiparticles distributions and topologies in unconventional superconductors and topological phases of matter.

Present Work:

* **High harmonic tr-ARPES on charge density wave materials [1]:** We have commissioned a new setup for extreme-UV (XUV) trARPES at high repetition rates. The high sensitivity, energy resolution and momentum access throughout the Brillouin zone allows us to map the entire evolution of the electronic structure in k space of a variety of materials. We have used it to study the origin of the CDW formation in TiSe2, whose nature is still debated after a decade, and to study how the electronic structure of monolayer transition metal dichalcogenides is modified by exciton formation.

* **Tracking and manipulation of long-lived surface photovoltage in TI [2,5]:**

Topological insulators (TI) are ideal systems for generated strong surface photovoltages (SPV). The necessary ingredient for a SPVs is surface band bending, which is only possible with a bulk insulator with in gap surface states. By tuning the chemical potential into the bulk gap, such that the bulk is insulating, we discover the appearance of a long lived (>10ns) surface photovoltage effect (SPV) in bulk-insulating Bi_2X_3 topological insulators (TI). Specifically, we looked at both bulk conductive and both p-type (Mg doped Bi2Se3) and n-type (Sn doped Bi2Te3) bulk insulating samples.

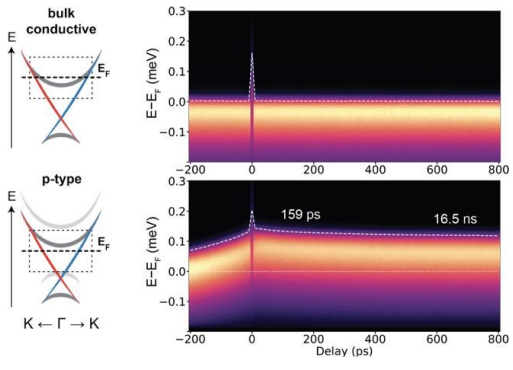

Figure 1. Time resolved spectra for conductive and insulating Tis, showing existence of long lived states.

We demonstrate that the required ingredients for the existence of an SPV state are the presence of an insulating bulk and an in-gap surface state. A wide-range of tunability of its magnitude and lifetime is also demonstrated.
We describe a qualitative and quantitative model for the long-lived SPV that is consistent with SPVs in semiconducting systems. The intrinsic band bending of the material causes photoexcited holes to drift into the bulk and get trapped by their own dipole field. We demonstrate that a rate equation model based on this description captures the fluence dependence of the SPV amplitude as well as the temperature dependence of the amplitude.

* **A new AI-based toolkit for real time data acquisition and data analysis [4]:**
The availability of large quantities of data has enabled powerful new consumer technologies to better understand individual and collective behaviors, from traffic predictions to understanding of the continued inflation of the universe.
Crossover opportunities exist for machine learning and the application of big data analysis techniques to the study of the individual and collective behavior of *electrons* in material physics. We have developed a new data analysis framework based on workflow automation and machine learning (PyARPES), to facilitate extracting novel conclusions from growing datasets of ARPES experiments. This framework enables rapid, reproducible and automated data analysis, as well as the possibility to optimize experimental outcomes in real time. PyARPES is suited for large nanoARPES and time-resolve ARPES data sets.

* **Spin momentum locking in cuprates superconductors [9]**: Development of new experimental tools is at the core of pushing forward understanding and design of new materials. Within this program we have developed an ultra-high-resolution spin resolved photoemission systems that allow to perform high resolution spin resolved measurements and to extend them also in the time domain. By applying this tool for the first time to high temperature superconductors, we have revealed a completely unexpected spin momentum locking, with a spin texture that orbits around the Gamma point. The spin polarization is of the order of 30% and displays very interesting energy, momentum and layer dependence. We argue that a local electric field within the unit cell might be responsible of the observed effect. Its implication for superconductivity, its dynamics, as well as its doping evolution will be topics of further studies.

* **Theory of second-harmonic generation in superconductors [6]:** A major challenge in the ultrafast field has been to interpret optical experiments on ultrafast modification of superconducting states. We sought to understand, for application to time-domain measurements, how linear and nonlinear optical measurements differ in a simple superconducting state. The basic result is that nonlinear optics, when allowed, arises much more rapidly below an equilibrium superconducting transition than does linear optics, suggesting that nonlinear optics might be a more sensitive probe, especially when inversion symmetry is broken so that second-harmonic generation is allowed. Even if a material does not break inversion symmetry in equilibrium, it can be broken by an applied current (current-induced second-harmonic generation), and we believe that our theory explains some experiments at Caltech by D. Hsieh et al.

* **Super diffusive transport in quasi-1D systems for spatially resolved ARPES [4]**: Motivated by efforts to develop some degree of real-space resolution in tr-ARPES, we considered problems where the system is out of local equilibrium and has time-dependent spatial variation on the

micron scale. We showed that heat and charge transport induced by spot heating in cold coupled-chain materials realizes a new kind of super-diffusive hydrodynamics, where tr-ARPES could have unique insight by showing the non-equilibrium nature of the electron distribution. The main idea, verified by a combination of analytical arguments and density-matrix renormalization group calculations, is that current relaxation does not take place fast enough, compared to the spreading of the current, for the local distribution to be in equilibrium, even for long times. This leads to a spread that is more rapid than conventional diffusion even for long times, and can best be seen experimentally with a combination of moderate space and momentum resolution consistent with the uncertainty principle.

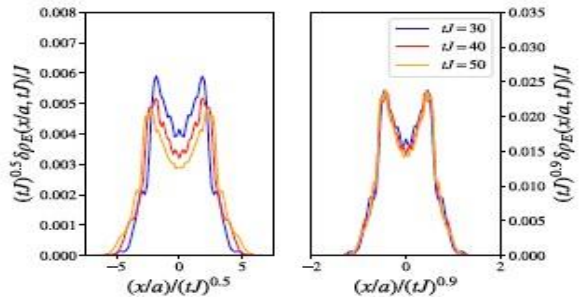

Figure 2. Theoretical calculations showing superdiffusive spread of energy in a realistic 1D system from a hot spot.

Future Plans:

Our plan is to continue investigating the role of spin orbit coupling in cuprates superconductors and its relation to local symmetry breaking. We plan to expand the current studies to the time domain and combine them with ultrafast diffraction measurements to investigate the relation between lattice distortion and spin orbit coupling.

Another focus of our future research is to use light polarization to couple and change the symmetry of a material's ground state to drive new phases. For example, we plan to utilize circularly polarized light to induce a time reversal symmetry breaking in the superconductors and enhance those phases, such as CDW that appear to coexist with superconductivity. This provide a clean way to disentangle order parameters. Similarly, choosing linearly polarized light we can couple to nematic order and disentangle its role in superconductivity.

Similarly, we plan to drive new topological phases through chiral symmetry breaking. Example include to drive the transition from a nodal semiline to Weyl and Dirac and viceversa.

Another important aspect of our future research is to combine coherent excitation with nano-ARPES capabilities to be able to resolve spatial dynamical fluctuations of the order parameter, evolution of different underlying orders and how the heterogeneous superconducting landscape influences the ultrafast evolution of the excited state. We plan to perform these experiments for both superconductors and topological superconductors, to search chiral Majorana fermions at the boundary between superconducting and AQH domains, while informing about their formation, dynamics and propagation.

Our future effort on theory for tr-ARPES experiments involves extending the Keldysh formalism developed in this program to incorporate self-consistent response to changes in the gap and to model more complicated initial states, such as those created by circularly polarized pumping,

which are analogous in symmetry terms to magnetic perturbations. These studies build on our previous work in developing a non-equilibrium formalism to study gap dynamics [7].
We are continuing to investigate how pump light of different symmetries can be used to modify other kinds of order also, or to create non-equilibrium states such as exciton condensates in topological insulators, possibly relevant to experiments in the team.

Publications in the past two years

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Structural Dynamics in Functional Materials

Principle Investigators: Aaron Lindenberg, David Reis, William Chueh, Mariano Trigo

Program Scope:
Our FWP is focused on understanding the role structure and dynamics play in the functionality of materials. It is divided into two main interconnected areas: 1) Probing dynamic microscopic interactions including the role of anharmonicity and ion motion in the functional properties of materials and 2) Synthesis of metastable phases driven by light, fields, or intercalation. Together these focused areas, combined with unique tools at SLAC and close theoretical collaborations, represent a new means of probing and understanding how the functional properties of materials arise from atomic-scale and meso-scale motions, processes typically blurred in time and in space by prior experimental approaches. This FWP makes central use of the user facilities at SLAC including the Linac Coherent Light Source as well as the Stanford Synchrotron Radiation Laboratory and the Advanced Light Source. Experiments within this FWP inherently involve studies of non-equilibrium metastable phases and materials at phase boundaries, dynamic transition states, and the role of heterogeneity. Measurements of the energy barriers which separate these phases and the first atomic/ionic steps associated with how these transformations occur are key to understanding these intrinsically dynamic processes.

Presentations included:

Talk 1: Introductory overview talk (Lindenberg)

Talk 2: Probing dynamic microscopic interactions (Reis, Lindenberg)

Talk 3: Synthesis of metastable structures using light and electric fields (Trigo, Lindenberg)

Talk 4: Synthesis of metastable phases by intercalation (Chueh)

Recent Progress (FY2019-2020)

1) We have discovered a means of synthesizing and switching metastable phases of matter via the application of electrical bias fields to 2D materials, focusing on the material WTe_2. In work published in *Nature Physics*, we show that this enables a new type of electrically-controlled, low energy, non-volatile topological memory functionality, with non-destructive readout enabled by the large and switchable Berry curvature, itself linked to the intrinsic out-of-plane ferroelectricity of this material. This switching is enabled by electrical driving of interlayer in-plane shear modes which we showed last year (Sie. et al., Nature (2019)) could be driven at THz frequencies. A combination of transport, optical spectroscopy, and ultrafast pump-probe studies in combination with first principles theory enabled this work, carried out collaboratively with FWP 10017.
2) We have investigated intercalation-driven transformations in 2D materials using a combination of *in-situ* x-ray scattering, impedance spectroscopy, optical linear and nonlinear optical spectroscopy, and UED. In work now submitted, we show that electrochemical insertion of lithium in WTe_2 induces a novel Td' structural phase with symmetry different from any known TMD. Using concurrent single-flake electrochemistry and operando XRD experiments, we demonstrate reversible control over the Td $\Leftrightarrow$ Td' phase transition, as well as over the composition-dependent lattice parameters of the Td' phase which can be modulated at frequencies faster than 1 Hz. Td'-Li_xWTe_2 holds promise as a low-voltage (<1.5 V) nano-actuator for strain engineering of two-dimensional (2D) materials, and exhibits giant in-plane electrochemical expansion coefficients, larger than any known single-phase lithium-insertion material.
3) Following up on Trigo and Reis's work on the ultrafast photo-induced switching dynamics of VO_2 (Science 2018), Chueh and Lindenberg have led studies probing the pathways and time-scales for

the electrically-driven metal-insulator transition using in-situ UED experiments. This work, currently in review, reports the discovery of an electrically-triggered transient isostructural state, demonstrates universal features in the transition spanning >8 orders of magnitude in timescale, and opens up new routes for uncovering non-equilibrium metastable phases in correlated materials. Meanwhile Trigo has led low temperature experiments on VO_2 at SACLA that exhibits a surprising disorder-driven transition between the insulating monoclinic phase and a metastable metallic state on a time-scale of order one phonon period with a surprising temperature dependence.

4) Trigo and Lindenberg, following experiments at LCLS and the European XFEL in 2018 and 2019, have collaborated on an effort visualizing for the first time dynamic polaronic responses in the hybrid perovskites. In this work we use femtosecond x-ray diffuse scattering approaches to resolve the local strain fields that accompany free carriers in these materials. Quantitative estimates of the magnitude and shape of this polaronic distortion are obtained. These studies provide a unified picture of the coupled structural and electronic dynamics that underlie the unique optoelectronic properties of these materials and can be applied widely to material systems exhibiting localized distortions or dynamic structural heterogeneity. This work is in press at Nature Materials. In 2020 we also carried out complimentary UED studies on hybrid perovskite nanocrystals showing strong exciton-lattice coupling and enabling a new understanding of the unique optoelectronic properties of these materials.
5) Ultrafast experiments led by Trigo at LCLS show that ultrafast excitation of the CDW of $SmTe_3$ induces a domain wall configuration that is not accessible in equilibrium. This order parameter configuration is relatively stable, lasting for nanoseconds. This finding is enabled by the extremely high wavevector and time resolution of the FEL, and provides a way to visualize the coupling to the order parameter of the secondary CDW in $SmTe_3$.
6) Following up on prior work on WTe2 by this FWP, Lindenberg and Chueh collaborated on work demonstrating that this anisotropic semimetal exhibits the largest terahertz frequency birefringence of any known material. This work shows that a 50 nm thick layer acts as a broadband quarter waveplate. This work defines a promising new way to enhance control over optoelectronic devices at the nanoscale using anisotropic semimetals and is currently in review.
7) Transition-state theory relates the diffusion coefficient for ion hopping to an apparent activation enthalpy of migration, and a vibrational attempt frequency for each individual hop. To achieve a mechanistic understanding of transport starting at individual hops, Lindenberg and Chueh combined time-resolved THz pump-probe experiments with large-scale molecular dynamics simulations of model "superionic" ion conductors β-aluminas, layered 2D superionic conductors with mobile ions Na, K, and Ag. We directly pump the vibrational resonances associated with the attempt frequencies for ion hopping, driving them beyond the small-perturbation regime. We report the first relaxation dynamics of the mobile ions in superionic conductors, their coupling to transport, and interpret the experimental results in conjunction with molecular dynamics simulations.
8) Building on our success in mapping Li intercalation in $LiFePO_4$, we have now developed a multi-modal imaging platform that combines X-ray ptychography (COSMIC at ALS) and scanning probe microscopy to image proton intercalation in binary oxides. In a manuscript under review, we provide the first mesoscale imaging of electrochemically-driven de-protonation of layered cobalt hydroxide. Through spectro-imaging at tens of nanometer resolution, we resolve the transition from Co(II) to Co(III) in real time, and definitely rule out the presence of Co(IV), which has been under debate. The edge plane of single crystallites are preferentially more oxidized, which we attribute to the disorder in the stacking sequence. We successfully integrated X-ray ptychography with scanning probe microscopies to elucidate the evolution of chemistry, morphology and reactivity at the nanoscale.
9) Trigo, Reis, and Lindenberg have led experiments combining XFEL, UED, and optical/THz spectroscopy on the family of IV-VI compounds, a class of materials exhibiting resonant bonding

and known to exist at the boundary of various lattice instabilities. These materials are known to host a variety of functional properties stemming from the interplay between the electronic and lattice degrees of freedom, leading to enhanced electron phonon interactions, large phonon anharmonicities, and intrinsic ferroelectric responses. Most recently, in the case of SnSe a high temperature transition from Pnma to Cmcm structure is thought to be responsible for the enhanced thermoelectric figure of merit. Like SnTe it has also recently been discovered to have a topological crystalline insulating phase, with mirror symmetry protected metallic surface sites. In our experiments, we measure the internal distortions associated with photoexcitation from measurements of the different Ag modes and find that photoexcitation drives the system towards a less distorted structure that notably differs from that of the high temperature Cnmn phase.

Future Plans:

- Correlated optical, x-ray FEL, and UED studies on the broad family of monochalcogenides, investigating light-driven and field-driven control of phase diagram and associated ferroelectric and optoelectronic functionalities.
- Building on ongoing work, in-situ UED experiments probing pulsed electric-field-driven and intercalation-driven structural dynamics.
- Building on our success in THz pump-probe measurements of ionic transport in beta alumina superionic conductor, we will develop XFEL experiments with structural and chemical specificity. A new collaboration with the LCLS accelerator group will enable >10 MV/cm THz pump experiments generated by the LCLS e-beam and coupled to femtosecond soft x-ray spectroscopy as a probe of the local structural dynamics of Na ions during an ionic hop.
- While ionic hopping occurs on the picosecond time second, intercalation at interfaces occur at the sub-microsecond and the nanoscale time scale. We will continue to develop frequency-resolved microscopy and spectroscopy approaches to perform locked-in detection the intercalation reactions at the solid-liquid interface. In particular, we will investigate protonation reaction of 2-D hydroxides in an aqueous environment.
- THz-pump-driven ionic hopping in intercalated WTe2 coupled to UED experiments to probe associated transition state.
- Nonlinear optical studies of non-equilibrium intercalated topological phases.

FY 2019-2020 Journal Publications:

1. **Visualization of dynamic polaronic strain fields in hybrid lead halide perovskites.** B. Guzelturk, T. Winkler , T. Van de Goor , M. D. Smith , S. A. Bourelle , S. Feldmann , M. Trigo, S. Teitelbaum, H-G. Steinrück , G. A. de la Pena , R. Alonso-Mori , D. Zhu , T. Sato , H. I. Karunadasa , M. F. Toney, F. Deschler, A.M. Lindenberg. Nature Materials (in press) (2020).

2. **Berry curvature memory via electrically driven stacking transitions**. Jun Xiao, Ying Wang, Hua Wang, C. D. Pemmaraju, Siqi Wang, Philipp Muscher, Edbert J. Sie, Clara M. Nyby, Thomas P. Devereaux, Xiaofeng Qian, Xiang Zhang, Aaron M. Lindenberg. *Nature Physics* (2020). Doi: 10.1038/s41567-020-0947-0

3. **Light-Induced Currents at Domain Walls in Multiferroic $BiFeO_3$**. Burak Guzelturk, Antonio Mei, Lei Zhang, Liang Tan, Patrick Donahue, Anisha Singh, Darrell Schlom, Lane Martin, Aaron M. Lindenberg, *Nano Lett.,* **20**, 145 (2020).

4. **Interpreting Tafel behavior of consecutive electrochemical reactions through combined thermodynamic and steady state microkinetic approaches**. J. T. Mefford, Z. Zhao, M. Bajdich, W. C. Chueh. *Energy Environ. Sci*. **13,** 622 (2020).

5. **Hydroxylation and Cation Segregastion in (La0.5Sr0.5)FeO3-δ Electrodes**. D. Zhang, M. L. Machala, D. Chen, Z. Guan, H. Li, S. Nemsak, E. J. Crumlin, H. Bluhm, W. C. Chueh. *Chem. Mater.* **32**, 2926 (2020).

6. **Synthesis of Macroscopic Single Crystals of $Ge_2Sb_2Te_5$ via Single-Shot Femtosecond Optical Excitation**. M. Zajac, A. Sood, R. Kim, M. Mo, M. Kozina, S.Park, X. Shen, B. Guzelturk, M. Lin, J. Yang, S. Weathersby, X. Wang, A. M. Lindenberg, *Crystal Growth and Design* (2020). Doi: 10.1021/acs.cgd.0c00816.

7. **Tuning electrochemically-driven surface transformation in atomically-flat $LaNiO_3$ thin films for enhanced water electrolysis**. C. Baumer, J. Li, Q. Lu, A. Liang, L. Jin, T. Duchon, H. Rations, M. Glob, S. Gericke, M. Wohlgemutrh, M. Giesen, E. Penn, R. Dittmann, F. Gunkel, R. Waser, M. Bajdich, S. Nemsak, J. T. Mefford, W.C. Chueh. *Nature Materials* (in press) (2020).

8. **Electrochemical Ion Insertion: Defects, Interfaces, Phase Transformations, and Device Applications**. Aditya Sood, Andrey D. Poletayev, Dan A. Cogswell, Peter M. Csernica, J. Tyler Mefford, Michael F. Toney, Aaron M. Lindenberg, Martin Z. Bazant, William C. Chueh. *Nature Reviews Materials* (2020) (Invited review, to be published).

9. **An ultrafast symmetry switch in a Weyl semimetal.** Edbert J. Sie, Clara M. Nyby, C. D. Pemmaraju, Su Ji Park, Xiaozhe Shen, Jie Yang, Matthias C. Hoffmann, B. K. Ofori-Okai, Renkai Li, Alexander H. Reid, Stephen Weathersby, Ehren Mannebach, Nathan Finney, Daniel Rhodes, Daniel Chenet, Abhinandan Antony, Luis Balicas, James Hone, Thomas P. Devereaux, Tony F. Heinz, Xijie Wang, Aaron M. Lindenberg, *Nature*, **565**, 61 (2019).

10. **Coherent order parameter dynamics in SmTe3**, M. Trigo, P. Giraldo-Gallo, M. E. Kozina, T. Henighan, M. P. Jiang, H. Liu, J. N. Clark, M. Chollet, J. M. Glownia, D. Zhu, T. Katayama, D. Leuenberger, P. S. Kirchmann, I. R. Fisher, Z. X. Shen, and D.A. Reis Phys. Rev. B **99** 104111 (2019)

11. **Ultrafast disordering of vanadium dimers in photoexcited VO2**. Simon Wall, Shan Yang, Luciana Vidas, Matthieu Chollet, James M. Glownia, Michael Kozina, Tetsuo Katayama, Thomas Henighan, Mason Jiang, Timothy A. Miller, David A. Reis, Lynn A. Boatner, Olivier Delaire, Mariano Trigo, Science (362) 572 (2018).

12. **Direct Measurement of Anharmonic Decay Channels of a Coherent Phonon**, Samuel W. Teitelbaum, Thomas Henighan, Yijing Huang, Hanzhe Liu, Mason P. Jiang, Diling Zhu, Matthieu Chollet, Takahiro Sato, Éamonn D. Murray, Stephen Fahy, Shane O'Mahony, Trevor P. Bailey, Ctirad Uher, Mariano Trigo, and David A. Reis, Phys. Rev. Lett. **121**, 125901 (2019)

13. **Frequency-selective excitation of high-wavevector phonons**, Samuel W. Teitelbaum, Thomas Henighan, Hanzhe Liu, Mason P. Jiang, Michael Kozina, Diling Zhu, Matthieu Chollet, Takahiro Sato, James M. Glownia, Mariano Trigo and David A. Reis, Appl. Phys. Lett. **113**, 171901 (2018).

14. **Fluid-enhanced Surface Diffusion Controls Intra-particle Phase Transformations.** Y. Li, H. Chen, K. Lim, J. Lim, D. Fraggedakis, P. M. Attia, S. C. Lee, N. Jin, Z. Guan, J. Hong, Y. S. Yu, M. S. Islam, M. Z. Bazant, W. C. Chueh. *Nature Mater*. **17**, 915 (2018).

15. **Electrochemical Reactivity of Faceted β-Co(OH)2 Single Crystal Platelet Particles in Alkaline Electrolytes**. J. T. Mefford, A. R. Abkashev, L. Zhang, W. C. Chueh. J. Phys. Chem. C. 123, 18783 (2019).

X-ray studies of complex materials at high pressure

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Project Scope

The theme of our FWP is manipulating the ground and excited states of complex materials by understanding their atomic and electronic structures at high pressure. Here, high pressure studies inform synthetic design towards improved materials and novel lattice architectures enable the realization of unprecedented high-pressure phenomena. The overarching goal of this research program is to disentangle the local and long-range structural response to pressure and understand how their cooperative interactions contribute to the macroscopic behavior of complex materials. Our proposed research program relies on our ability to characterize materials using a suite of *in situ* techniques – in particular X-ray probes – at the relevant energy, spatial, and temporal scales. As an archetypal materials family to pursue these fundamental studies, halide perovskites are an ideal platform of crystalline semiconductors to demonstrate how both thermodynamic properties and excited-state dynamics can be systematically tuned through mechanical compression. Our activities will be closely tied to SLAC facilities, and we will leverage expertise at SLAC through existing and new collaborations with the many groups within the Division of Materials Science working in condensed matter physics, ultrafast science, and theory.

Our research portfolio is organized under three main research thrusts: 1) Controlling lattice heterogeneity and electronic dimensionality – to understand how lattice compression affects the local structural heterogeneity (i.e. defects, disorder, and dynamics) and orbital interactions across ordered lattice vacancies; 2) Creating emergent electronic states – to generate itinerant electrons at high pressure, which can lead to interactions that yield novel electronic phenomena; 3) Accessing metastability and beyond equilibrium matter – to characterize and control matter away from equilibrium and find pathways to novel phases not accessible otherwise. For all three research thrusts, it is crucial that we continue to develop and enhance *in situ* and *in operando* X-ray diagnostics along with extreme environment capabilities for the characterization and study of these complex materials.

Recent Progress

Some highlights of the synergistic work among PIs, including developing high-pressure capabilities and instrumentation for X-ray characterization will be presented as well as some proposed work and future outlook for our project.

Dramatically enhanced electronic conductivity in copper-halide perovskites: We previously demonstrated the first example of conductivity in two-dimensional (2D) copper-chloride perovskites, but at very high pressures (10^4 S/cm at > 50 GPa). Building on these results, we showed this year that analogous copper-bromide perovskites are conductive at much lower pressures (10^3 S/cm at < 3 GPa) (A. Jaffe *et al,* 2020). This dramatic improvement in pressure response is due to increased orbital overlap from the higher-energy, more diffuse Br orbitals. DFT calculations show loss of ferromagnetism at pressures where we see appreciable electronic conductivity, consistent with the loss of orthogonality between half-filled orbitals and the formation of an electronic band.

Pressure-induced preservation of a metastable $CsPbI_3$ perovskite phase to ambient conditions: Replacing volatile MA^+ with Cs^+ should improve the heat and moisture stability of lead-iodide perovskites. But $CsPbI_3$ perovskite phases are not stable at ambient conditions and spontaneously convert to a yellow, non-perovskite δ phase. We demonstrated the preservation of a black γ-$CsPbI_3$ perovskite phase to room temperature by subjecting the δ phase to moderate pressure, followed by heating and rapid cooling (F. Ke *et al, Nature Comm.* in review). Thus γ-$CsPbI_3$ can be retained at ambient conditions; up to ten days at 35%

relative humidity. DFT calculations indicate that compression directs the out-of-plane tilt between Pb-I octahedra, which relatively stabilizes the energy of the γ phase over the δ phase. This motivates our plans to study other novel pathways for synthesizing metastable phases**.**

High-pressure X-ray technique developments: We performed time-resolved X-ray diffraction (XRD) with μs time resolution for simultaneous high pressure-high temperature studies using a pulsed laser-heating system that was synchronized with a synchrotron X-ray source and a time-gated detector (S. Park *et al*, 2020). We also developed a workflow for collecting, processing, and analyzing high-pressure pair distribution function (PDF) data extracted from X-ray total scattering measurements, which has allowed us to decipher the local structure of $Cs_2AgBiBr_6$, a Ag-Bi double perovskite. Members of our team introduced $Cs_2AgBiBr_6$ to the photovoltaic community as an environmentally benign solar absorber with long carrier lifetime and high stability. Powder and single-crystal XRD measurements show that it remains in the $Fm\bar{3}m$ structure up to 2.4 GPa. Surprisingly, within this pressure range, atomic PDF data reveal that the cubic structure poorly describes the local structure at unit-cell length scales. This indicates that local disorder is intrinsic to $Cs_2AgBiBr_6$ even at ambient conditions, and is enhanced upon compression. Importantly, disorder can explain the unexpectedly broad emission linewidth and large Stokes shift seen in $Cs_2AgBiBr_6$. Progress in high-pressure nanoscale transmission X-ray microscopy (nanoTXM) experiments and analysis (with spectroscopic capabilities) has enabled high spatial resolution elemental and chemical mapping during structural and electronic transitions, allowing for studies on poorly crystalline materials. We are also using the partial coherence of synchrotron X-ray sources like APS to develop high-pressure Bragg coherent diffractive imaging (BCDI).

Future Plans

Controlling lattice heterogeneity and electronic dimensionality

Probing local disorder in single and double perovskites: Static and dynamic (local) structural disorder have significant influence on the optoelectronic properties of halide perovskites. We will continue to utilize PDF measurements for understanding the local structural deviations that could be ubiquitous in halide perovskites, particularly at high pressure. Some target materials for study include $(MA)PbI_3$ and its analogs ($(FA)PbI_3$, $(MA)PbBr_3$, $CsPbBr_3$) with and without photoexcitation. These perovskites were reported to enter pressure-induced, partially amorphous phases wherein exciting electronic states were realized. The nature of this partial amorphization in 3D halide perovskites and how it contributes to the electronic states at high pressure is not understood. Our DFT calculations on $(MA)PbI_3$ suggested that strong intra- and inter-octahedral distortions develop within the high-pressure phase, leading to new bonding interactions that explain the pressure-induced metallization. However, DFT calculations, using the average structure, predict a significantly higher metallization pressure than experiments and cannot explain the onset of a more rapidly decreasing bandgap above 35 GPa. Probing the local structural disorder would be critical for shedding light on the partially amorphous structure.

Controlling electronic dimensionality through compressing vacancies: We have explored the pressure response of double perovskites where one B site is vacant. Such B-site vacancies disrupt the corner-sharing network of metal-halide octahedra, making $A_2B\square X_6$ (□ = vacancy) structurally zero-dimensional (0D). Yet, A_2BX_6 double perovskites generally have small bandgaps and mobile carriers, which are surprising features for isolated BX_6 structures that should behave like isolated molecules. The coexistence of structural disconnection and disperse bands suggest that certain A_2BX_6 double perovskites exist on the conceptual border between a 3D semiconductor with delocalized bands and a 0D molecular salt with localized orbitals. Indeed, our studies on the orbital interactions that dictate the band structure of halide double perovskites show that interactions between halides bordering a vacancy, which are positioned 90° from each other, play a dominant role in determining band dispersion. Importantly, vacancies are much more compressible than metal-halide octahedra. Thus the A_2BX_6 perovskites show a more facile pressure response than typical perovskites. We plan to investigate how to control the extent of electronic delocalization in A_2BX_6 double perovskites by studying expanded and compressed analogs.

Manipulating trap states with pressure: We recently discovered that halide perovskites can spontaneously lose halogen gas. Importantly, the conversion of halides (X^-) in the lattice to neutral X_2 gas dopes the lattice with electrons. These electrons thermally trap and detrap from sub-bandgap states formed by halide vacancies. This equilibrium is highly sensitive to lattice compression and we plan to investigate how pressure dictates the energy and ionization of these trapped electrons. Standard high-pressure transport studies relate conductivity to changes in the bandgap. In contrast, here we can access free carriers at much lower pressures (when the bandgap is still large) by changing the position of donor defects. We are developing a carrier freeze-out model to understand shifts in the energy difference between the trap states and the conduction band as a function of pressure. We will model the pressure dependence of the halide vacancy energy by evaluating high-pressure optical and transport data complemented by high-pressure carrier effective masses obtained through DFT calculations performed on structures determined through high-pressure powder XRD. We predict that this halogen degassing reaction is common to all halide perovskites and we seek to control the structure and concentration of halide vacancies in these lattices in order to: 1) dope halide perovskites to access metallic transport or 2) prevent the self-doping reaction to obtain stable optoelectronic properties, which is crucial for any technological application.

Creating emergent electronic states

The structural similarity between halide and oxide perovskites motivates our search for greater electronic diversity in halide perovskites. One of our long term efforts it to manipulate the inorganic network that is primarily responsible for the electronic structure through lattice compression and synthetic design to access diverse electronic states. We will focus on using pressure to create emergent electronic states in the form of superconductors, topological insulators, and strange metals.

Our discovery of a superconducting-like state with a transition temperature of ~4 K in compressed $(MA)PbI_3$ motivates us to continue the search for emergent electronic states in halide perovskites. This electronic behavior could not be consistently observed across various $(MA)PbI_3$ samples, which makes us speculate on the effects of defects/dopants on the occurrence of superconductivity. The electronic doping levels of $(MA)PbI_3$ vary with synthetic conditions. We plan to develop reliable syntheses of intrinsic, *n*-type, and *p*-type $(MA)PbI_3$ for systematic high-pressure low-temperature conductivity measurements in anticipation of accessing emergent electronic states. We will also investigate the high-pressure low-temperature electrical transport in analogous $(FA)PbI_3$ (recently reported to enter a metal-like state at high pressure), $CsPbI_3$, and $CsSnI_3$ to replicate and study the possible superconducting state. Moreover, theory predicts that cubic halide perovskites such as $CsPbI_3$ and $CsSnI_3$ can evolve into 3D topological insulators under hydrostatic compression, motivating attempts for its experimental realization. High-pressure optical absorption/reflectivity data can provide indirect evidence along with electrical transport measurements. We will also probe if topological insulating states can be accessed in 3D halide perovskites using optical and electrical transport measurements.

Our recent low-temperature electrical transport studies also suggest strange metal behavior in the yellow $CsPbI_3$. The initially non-perovskite structure undergoes a semiconducting-to-metallic transition above 80 GPa where a non-Fermi liquid below 120 K was observed. This state persists over a large pressure range until above 185 GPa, where the *T* exponent approaches 2 indicating the transition into a Fermi liquid. Previous studies on other systems indicate that factors such as lattice deformation, disordered Anderson lattices, and quantum criticality can result in this anomaly. We plan to conduct structural characterization from high-pressure low-temperature XRD, and collaborate on first-principles DFT calculations to provide insight into understanding the underlying mechanism that drives semiconducting $CsPbI_3$ into a strange metal. More importantly, as observed in cuprate and iron-based high-temperature superconductors, a non-Fermi liquid state usually coexists with a superconducting state in the electronic structure phase diagram. We have not yet observed a superconducting signature from measurements down to 2 K, and suspect that a superconducting transition may occur below 2 K so we plan to conduct ultralow-temperature (down to 50 mK) electrical transport measurements at high pressure. We plan to also perform similar measurements and

analysis on $(FA)PbI_3$ and $CsSnI_3$ and look for the signature of strange metal behavior. The results can guide our search for halide perovskite-based superconductors.

Accessing metastability and beyond equilibrium matter

Building on the use of pressure to stabilize a desirable $CsPbI_3$ perovskite phase, we will work on obtaining a full structural solution of the preserved γ-$CsPbI_3$ phase to elucidate what are the structural parameters or chemical potential that contribute to the improved moisture stability of the preserved perovskite phase. Larger-scale synthesis using a multi-anvil apparatus will be attempted. The same strategy will be applied to analogous systems $(FA)PbI_3$ and $CsSnI_3$, with precautions to prevent oxidation of Sn^{2+}. In addition, we propose to use the XPP instrument at LCLS-II for a detailed study on the structural dynamics and intermediate phases as $CsPbI_3$ undergoes a series of phase transitions with and without an intermediate melt state. Femtosecond XRD will allow us to determine the highly pressure- and temperature-dependent transition kinetics throughout the solid-to-solid or melt-quenching and recrystallization processes.

Advancing X-ray characterization at high pressure

Our current and future work requires in-depth, systematic high-pressure studies that rely in particular on the development of X-ray techniques and facilities and the ability to combine them with a DAC. Within this large portfolio of high-pressure X-ray tools at synchrotron and XFEL facilities, there is a wide range in terms of the state of their development. Techniques like synchrotron powder XRD are more mature, and complex samples can be studied to ultrahigh pressures and varying temperatures. Other techniques are still at their initial stages of development like at LCLS-II where our goal we must first demonstrate the feasibility of DAC studies on model systems to moderate pressures. We are particularly motivated to couple the DAC with other external stimuli especially photoexcitation which requires dedicated efforts in order to enable the capability for many of the X-ray techniques we will employ.

Publications FY19-20

Type I

Expanded analogs of three-dimensional lead-halide hybrid perovskites D. Umeyama, L. Leppert, B. A. Connor, M. A. Manumpil, J. B. Neaton, and H. I. Karunadasa, *Angew. Chem. Int. Ed.* DOI:10.1002/anie.202005012, 2020.

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Presentation File Order:

1) Mao_Talk1

2) Karunadasa_Talk2

3) Lin_Talk3

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

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October, 2020

(i) Program Scope

Ultrafast lasers can drive the fastest magnetic switching and phase changes in magnetic materials, on sub-femtosecond to picosecond timescales. However, fully exploiting these capabilities for more energy-efficient nanotechnologies requires a detailed understanding of the physics underlying nanoscale dynamic spin manipulation. At present, our understanding of spin systems is 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 Å to nanometers (exchange length) and femtoseconds (exchange splitting), tools for accurately probing these dynamics 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. In particular, tabletop, laser-based, high harmonic (HHG) sources *are unique as a probe of magnetic dynamics* since they can capture the fastest femtosecond and even attosecond spin dynamics in multiple elements (sites or layers) simultaneously. By combining HHG sources with new spectroscopic techniques, we have made a series of new discoveries about the fastest spin dynamics in materials (Fig. 1).[1-22] We also developed several rigorously-tested new magnetic measurement techniques enabled by correlative spectroscopies. Finally, we were invited to submit three review articles on ultrafast quantum materials science this year.[3,4,12]

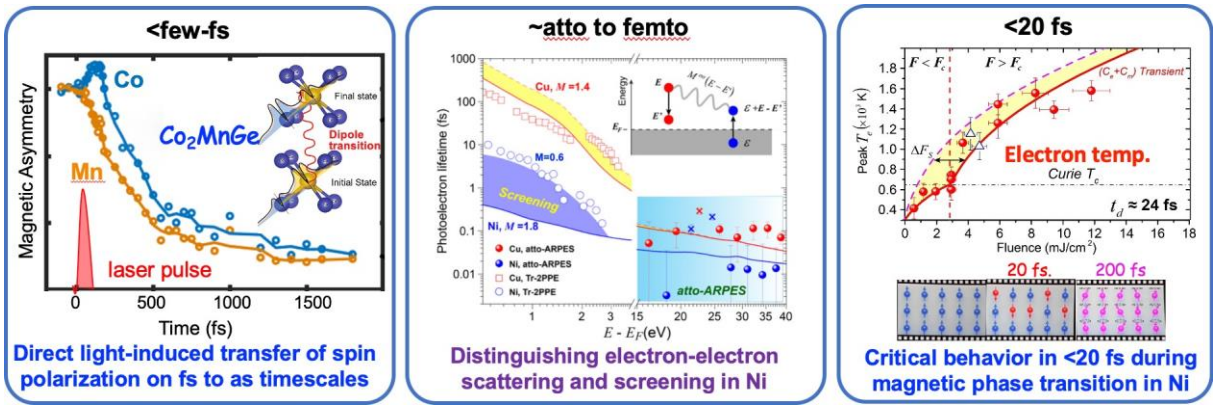

Fig. 1. New timescales for spin manipulation observed experimentally by our group. (left) Light can transfer spin transfer spin polarization between two elements in a Heusler alloy, on few-fs timescales. (center) Distinguishing electron-electron scattering and screening in Ni. (right) The energy required to drive a true magnetic phase transition in Ni is absorbed by the spin system within ~20 fs, clearly observable as an inflection point in the measured electron temperature at the Curie temperature.

(ii) Recent Progress

In a series of exciting discoveries supported by this grant, we showed that light-induced manipulation of spins can be much faster than previously realized (see Fig. 1). We demonstrated that light can transfer spin transfer spin polarization between two elements in a Heusler and FeNi alloys, on few-fs timescales.[1,2] We also showed that the ultrafast quenching of magnetization in

Ni is a true magnetic phase transition, that is launched within ~20 fs.[6,7] At DOE facilities, we developed new approaches for imaging 3D spin textures without any assumptions about the sample, and for capturing domain dynamics.[11, 13,14]

Direct near-instantaneous light-induced spin transfer in Heusler and other alloys [1,2]: We made an unexpected discovery that light can excite spins in many materials on timescales much faster than previously thought – near-instantaneously, on few femtoseconds, and likely even attosecond timescales. Heusler compounds are interesting candidates for efficiently generating pure spin currents for spintronics devices. This is due to their unique band structure, where one spin-channel (the majority band) is metallic in nature, but the other spin-channel (minority) is insulating, with a band-gap at the Fermi energy. It was speculated that the band gap in Heusler materials might lead to a slower magnetic quenching after excition with a femtosecond laser, due to the presence of fewer states to scatter into. *In a very surprising result, we found quite the opposite.* In recent research published in Science Advances, we found that a femtosecond light pulse can directly transfer spin polarization from one element to another in a half-metallic Heusler material, Co_2MnGe, fabricated by NIST. *This spin transfer initiates as soon as light is incident on the material, showing that we can spatially transfer angular momentum between neighboring atomic sites on timescales <10 fs.* Using ultrafast extreme UV (EUV) high harmonic pulses to simultaneously and independently probe the magnetic state of two elements during laser excitation, we found that the magnetization of Co is enhanced, while that of Mn rapidly quenches. By comparing our measurements to density functional theory from the Eriksson group in Uppsala, we showed that *the optical excitation directly transfers spin from one magnetic sub-lattice to another, via preferred spin-polarized excitation pathways*. The enhancement of ferromagnetic ordering demonstrates direct manipulation of spins via light, thus providing a path towards spintronic logic devices such as switches that can operate on few femtosecond or even faster attosecond timescales. These results show that by tuning the band structure, we can control the ultrafast magnetic response in a quantum material.

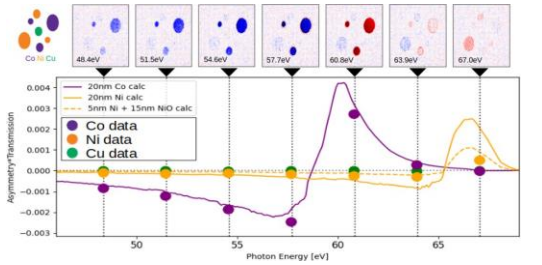

Fig. 2. Hyperspectral Interferometric EUV Magnetic Imaging. The inhomogeneous sample contains magnetic (Ni, Co) and nonmagnetic (Cu) features. By simultaneously measuring the spatially varying XMCD at harmonic wavelengths spanning the M-edges of both magnetic elements, we distinguish the magnetic elements present in the sample, and identify which features also have oxide layers.

Hyperspectral Interferometric EUV Magnetic Imaging [17, 18]: We made significant advances in learning how to sculpt soft X-ray high harmonic beams for enhanced magnetic spectroscopies. We also developed a new technique for spatially-resolved hyperspectral magnetic imaging. To date, HHG studies of magnetic materials have generally been restricted to either monochromatic imaging or spatially averaged spectroscopic measurements. In principle, however, the exceptional coherence and polychromatic nature of HHG should enable hyperspectral imaging of magnetic systems — imaging simultaneously at multiple wavelengths. We demonstrate how orthogonally polarized and phase-locked harmonic sources can enable hyperspectral magnetic imaging. In combination with lensless imaging and pump-probe schemes, this hyperspectral imaging technique can usher in a new class of robust characterization methods for magnetic materials.

Static vector 3D imaging of magnetic textures [14]: Our group was part of a very large team that participated in 4 beamtimes at the DOE LBNL COSMIC facility (ALS). In an exciting series of experiments, the three trainees supported by this grant joined with a team led by STROBE to help

commission the new COSMIC imaging beamline at the ALS for tomographic imaging of a topologically-constrained 3D magnetic field. This required a large team to run 24-7 to take hundreds of scans for the vector tomography imaging (5-11 TB of data on two different beam times). Our group suggested this experiment, UCLA contributed advanced algorithms (Miao and Osher groups), Berkeley hosts the facility (Falcone and Shapiro), while Penn State (Badding group) provided samples. This allowed us to image nanostructured, topologically distinct, magnetic metalattice materials using a new and general vector ptycho-tomography method to image spin textures in 3D, with the highest ~10 nm spatial resolution to date, and without the need for any prior knowledge or assumptions about the sample. As a result, trainees supported by this grant were able to do science at both facility-scale synchrotrons, as well as tabletop-scale high harmonic sources.

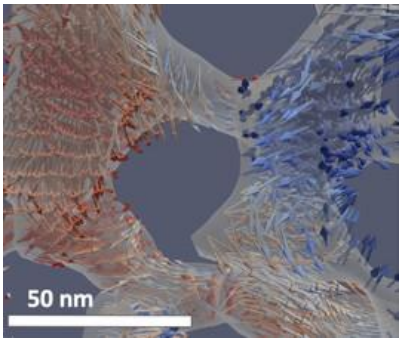

Fig. 3. First general vector ptycho-tomography method to image spin textures in 3D. 3D spin texture in spin-engineered, topologically distinct, magnetic metalattices. The spatial resolution is ~10 nm.

Participation in experiments at LCLS and other DOE-related collaborations [11,13]: Our group is part of a large team led by Tom Silva (NIST), Erik Fullerton (UCSD) and others that used the LCLS XFEL to show that spin transport leads to non-uniform magnetization dynamics of domains. We also discovered a sub-ps excitation mechanism for surface acoustic waves in thin films.

(iii) Future Plans

We will explore exciting new directions, taking advantage of both tabletop HHG sources as well as DOE facilities. First, we will explore the fundamental mechanisms underlying the fastest light-induced spin manipulation in materials, from single element, to alloys, to 2D materials with charge density wave order. We already have samples from several groups. Second, will expand our studies from ferromagnetic to other magnetically ordered systems, to develop new characterization techniques. Third, we will complement our nanoscale static 3D imaging of spin textures at the ALS, by using HHG to capture spin dynamics using EUV and SXR scatterometry. We can also harness our ability to create polarization and phase structured HHG beams (SAM and OAM) to enhance contrast and implement unique excitations and probes of chiral texture. Finally, we will collaborate to combine a new VUV MHz ultrafast light source with an advanced ARPES spin-resolved system to provide complementary insight into the materials described above.

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11. *Ultrafast domain rearrangement induced by optical pumping in ferromagnetic CoFe/Ni multilayers*, D. Zusin et al., submitted (2020). arXiv:2001.11719 (used DOE LCLS facility)
12. *Manipulating and Imaging Spin Dynamics and Textures using coherent EUV and soft X-ray beams*, M. Murnane et al., invited review paper, Nature Reviews Materials (2020).
13. *Sub-ps generation of surface acoustic waves in corrugated thin films*, P. Tengdin et al., in preparation (2020).
14. *General 3D imaging of spin textures in nanostructured magnetic metalattices using vector ptycho-tomoghraphy*, A. Rana et al., in preparation (2020).
15. *Mapping and Controlling the Phonon Excitation Spectrum and Electron-Phonon Coupling during Phase Transitions in Charge Density Wave Materials*, C. Gentry et al., in preparation (2020).
16. *Circularly polarized soft X-ray high harmonic generation and limits using collinear two-color counter-rotating circularly polarized beams*, Q. Nguyen et al., in preparation (2020).
17. *Sculpting circularly polarized soft X-ray high harmonic generation for magnetic spectroscopy and imaging at the L edges*, N. Brooks et al., in preparation (2020).
18. *Hyperspectral Interferometry EUV Magnetic Imaging*, N. Brooks et al., in preparation (2020).

Example Peer-Reviewed Conferences Proceedings since 2018

19. *Direct Time-domain Observation of Attosecond Electron Dynamics in Solids using Attosecond Pulse Sequences*, C. Chen et al., Frontiers in Optics + Laser Science APS/DLS, paper LM1E.3 (2019).
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DOE Basic Energy Sciences
X-ray Scattering PI Meeting

Extended Abstract

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

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Riccardo Comin, Department of Physics, Massachusetts Institute of Technology

James Freericks, Department of Physics, Georgetown University

Rohit Prasankumar, Center for Integrated Nanotechnologies, Los Alamos National Laboratory

David Reis, Department of Applied Physics and Photon Science, Stanford University
PULSE Institute, SLAC National Accelerator Laboratory

Mariano Trigo, PULSE Institute, SLAC National Accelerator Laboratory

Program Scope

The project is aimed at study and discovery of quantum phases that can be induced or significantly perturbed by terahertz (THz) light fields and whose THz-driven responses can be studied by time-resolved x-ray measurements that have become possible since the development of x-ray free-electron laser (XFEL) sources. The samples of interest include perovskites with quantum paraelectric and incipient ferroelectric phases; multiferroics; topological materials; and correlated electron materials including cuprates and nickelates. Coupling among some or all of lattice, electron, and spin degrees of freedom play key roles in determining the ground state phases and the multi-phase landscapes. THz excitation can drive modes corresponding to any of these degrees of freedom, and x-ray probing can enable incisive measurement of the coupled dynamical responses. Allied to the experimental work are theoretical efforts aimed at describing the material behavior and the x-ray spectroscopic probes that can measure it.

Only a handful of THz-induced phase transitions have been demonstrated to date. The multi-phase landscapes of most quantum materials have been elucidated only partially, and in many cases hardly at all. The use of x-ray diffraction, scattering, spectroscopy, and imaging methods for time-resolved measurement of quantum phase dynamics is still under development in many respects, and theoretical treatment of the spectroscopic observables is needed to extract the full information content that they offer. Our challenges are heightened by the limited capabilities of the XFEL facilities that are currently in operation for THz excitation of samples under suitable environmental control (e.g. low-temperature conditions) and for some x-ray measurements of interest including resonant soft x-ray scattering (RSXS). In addition to our experimental and theoretical work described below, we have worked collaboratively with scientific and technical staff at XFEL facilities to enable THz-pump/X-ray-probe measurements.

As we enable and anticipate THz measurements at XFELs, we work in parallel to learn as much as we can about the quantum phases and phase transitions of interest, using optical as well as THz excitation pulses and using tabletop (THz through optical spectral range) as well as XFEL probes. This allows us to gain new information and insights of value in their own right and to bring deeper understanding of the materials to the planning, execution, and analysis of THz XFEL experiments as they become possible. Separate measurements of material responses to THz pumping (probed on tabletops) and measurements of x-ray diffraction, scattering, imaging, and spectroscopic signatures of quantum phase transitions (measured at XFELs using optical pumping) provide us with experience that can closely guide our XFEL experiments in which THz pumping and x-ray probing are combined. The x-ray spectroscopy and imaging measurements may also be compared to the results of our theoretical work on those measurements to clarify the interpretations of the experimental data.

Recent progress and future plans

The five topics discussed below are the subjects of five video presentations submitted with this abstract.

Quantum phases: Structural responses

The Nelson group worked with theorist and team collaborator Andrew Rappe (U Penn) to complete work on the first demonstration of *collective coherent control* in which THz fields were used to drive ions from their initial locations directly into their locations in a new crystalline phase [Li 2019]. The soft modes of the low-temperature quantum paraelectric (QPE) phase of strontium titanate, $SrTiO_3$ (STO), were driven with strong single-cycle THz fields to induce a transient ferroelectric (FE) phase.

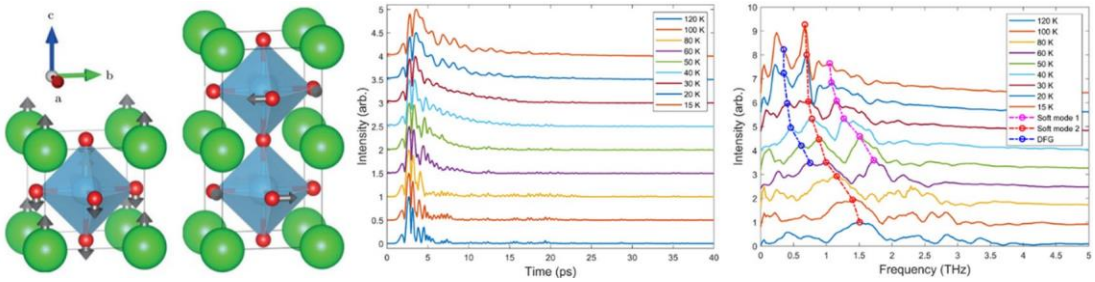

Figure 1. (a) Soft mode (left, shown in the high-*T* cubic phase for simplicity) and antiferrodistortive (AFD) mode along which a cell-doubling transition into the low-T tetragonal phase occurs at 105 K. (b) THz-induced lattice responses probed through optical second harmonic generation. (c) FT of data in (b) showing the two inequivalent soft modes and a difference-frequency feature which may be due to nonlinearly coupled AFD mode displacements.

In very recent results, THz fields polarized in between crystallographic axes induced responses of both inequivalent soft modes. At high field levels (up to 650 kV/cm used for Fig. 1b,c), lattice responses at the differences between soft mode frequencies were observed at temperatures approaching and below the QPE transition temperature of 32 K. These nonlinear responses may be due to collective motion of an antiferrodistortive (AFD) mode that is coupled nonlinearly to the soft modes. In LCLS beamtime scheduled for April 2021, XRD measurements will yield the FE phase structure including soft mode and AFD mode displacements from the initial QPE structure. In subsequent beamtime at SwissFEL, pairs of THz pump pulses will be used for more extensive control over structure and dynamics. Starting from the FE phase structure, a second THz pulse will initiate new coherent motion that will reveal the lattice potential around that strong. A second pulse that arrives during the excursion induced by the first pulse toward the FE structure may separate the multiple THz field interactions leading to the transient phase, indicating the roles played by THz-excited lattice vibrational coherences and populations. This is a first step toward *two-dimensional THz/X-ray spectroscopy* in which the time interval between THz pulses will be varied continuously and XRD data will be recorded as a function of time after both pulses. The resulting FT 2D spectrum will reveal correlations between lattice motions reflected in the behavior of multiple XRD peaks. 2D THz/XAS spectroscopy will also be possible, enabling correlations among THz-induced electronic, spin, and structural responses to all be explored. These experiments will require high repetition rates soon to be available at the LCLS and strong THz fields generated at those rates, recently made possible by team collaborator Matthias Hoffmann (SLAC) [Kramer2020].

Just before the LCLS shut down for the LCLS-II upgrade, our team performed an experiment led by PIs Trigo and Reis to study electron-phonon coupling effects in the lattice of $KTaO_3$. This material is an example of a quantum paraelectric and shares many of the peculiarities of $SrTiO_3$. The experimental work exploits ultraviolet (UV) excitation across the band-gap and diffuse x-ray scattering (static scattering pattern shown in Fig. 2a) to probe structural dynamics to investigate the effect of photoinduced charges on the lattice stability at ultrafast timescales. UV excitation across the band-gap alters the delicate interplay between the electrons and the crystal structure, a key element of the correlated-electron ground states of many perovskite quantum materials. In $KTaO_3$ we found that photoexcitation leads to a strengthening of the forces that stabilize the paraelectric cubic lattice. Fig. 2b shows the dynamics of the

relative intensity at selected reciprocal space points (X and M in the cubic Brillouin zone). A fit to the differential intensity pattern with a real-space model for the interatomic forces (Fig. 2c) shows how the forces are modified by photoexcitation. In the simplest model, the results of this fit indicate that the force between the nearest Tantalum atoms changes more strongly than the rest of the atom pairs, and gives rise primarily to a stiffening of the soft transverse acoustic branch near the M point of the Brillouin zone, as seen in (c). Independently, DFT calculations of $KTaO_3$ phonons treating the photo-excited carrier distribution as a high electronic temperature Fermi-Dirac distribution suggest similar changes in the phonon bands. These calculations predict that photoexcitation induces charge transfer between O and Ta that screens the Ta-Ta force, as shown in the inset of (b). We note that this soft transverse acoustic (TA) branch is strongly coupled to the transverse optical (TO) modes responsible for the incipient ferroelectricity of $KTaO_3$. The TA modes are associated with rotations of the oxygen octahedra (antiferrodistortive, AFD) that yield the numerous phases in materials with perovskite structure. Coupling of THz pulses to these modes through anharmonic interactions via the TO modes, as illustrated in STO discussed above, is a potential avenue for quantum phase control in many materials.

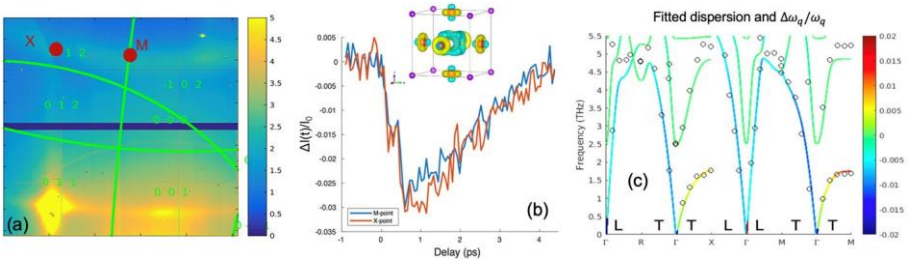

Figure 2. (a) Static x-ray diffuse scattering pattern of $KTaO_3$. The cubic Brillouin zones are indicated by green lines. (b) Time-dependent scattering intensities at X and M points in the cubic BZ. Inset: Changes in charge distribution based on DFT calculations. (c) Phonon dispersion including fits (solid curves) based on force constants computed from the fitted scattering intensity pattern. The color scale indicates the relative change of the frequency with respect to the *ab-initio* computed ground state dispersion.

Topological phases

PI Prasankumar led the TR-XRD experiments on the Weyl semimetal TaAs [Armitage2018, Sirica2019,2020], conducted at LCLS [Lee2020]. The unusual (112) surface orientation of the crystal enabled us to observe and also trace the dispersion of coherent quasi-longitudinal (QL) and quasi-shear (QS) acoustic phonon modes (Fig. 3). The QL mode displays an asymmetric lineshape (Fig. 3(j-l)) that is likely due to a thermal gradient introduced by the pump pulses. This has not been observed previously in any material, to our knowledge, and may offer a facile method for estimation of temperature-dependent lattice softening.

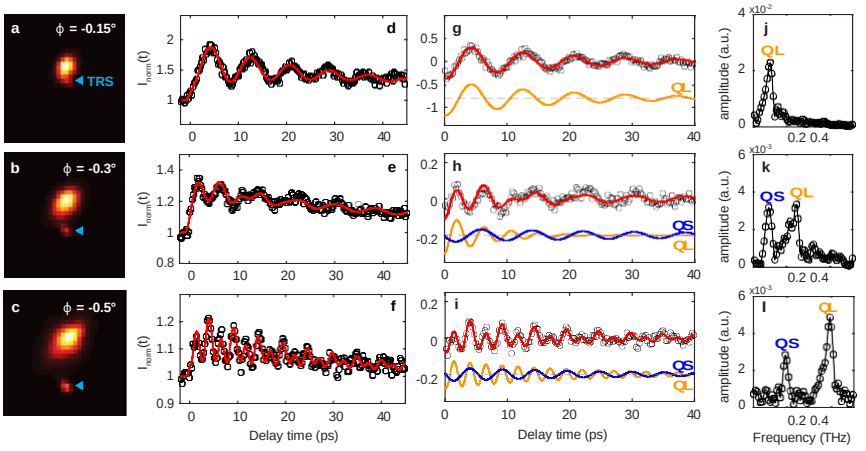

Figure 3. Truncation rod scattering (TRS) from (112) cut TaAs for incident angles of $\Delta\phi$ = (a) -0.15, (b) -0.3, and (c) -0.5 degrees. The resulting transients shown in (d-f) and (g-i) show the extracted QL and QS oscillations in the time domain, followed by frequency domain spectra in (j-l).

The Nelson group led a collaborative study of single-layer and multilayer $MoTe_2$ in which the first *irreversible THz-induced phase transition* was demonstrated [Shi2019]. The initial 2H phase disappeared after a single shot and was transformed into the 1T′ topological insulator phase after the first pulse or after additional pulses, depending on the THz field strength and the sample morphology.

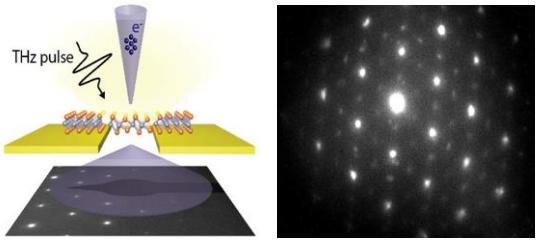

Figure 4. (a) Schematic illustration showing THz irradiation of a single-layer $MoTe_2$ sample that spans a 1-micron insulating gap between parallel gold lines of a THz field enhancement structure. Transmissive electron diffraction is then conducted on the sample. (b) Diffraction pattern from a multilayer sample reveals additional (dimmer) spots induced by a single THz shot, indicating the cell-doubling transition from the initial 2H phase to the 1T′ topological insulator phase.

The disappearance of the initial phase was revealed by the disappearance of optical second harmonic generation (SHG) and of the characteristic 2H Raman spectrum. Measurements of SHG at various delay times following THz excitation showed that the transition occurred on picosecond-nanosecond time scales. Theoretical modeling (by the Kaxiris group, Harvard) indicated that the transition was induced by carriers that were liberated by the THz field and that altered the free energy to favor the 1T′ phase. An application for MeV-UED beamtime at the LCLS is being prepared to permit determination of the structural dynamics intermediate between initial and final phases.

Quantum phases: Electronic responses

In the area of photoinduced electronic phase transitions, ideal candidates for new studies are electronic systems which support multiple symmetry-broken phases energetically close to each other and whose stability or metastability is determined by physical parameters which can be strongly modified by photoexcitation. Tetragonal strontium chromite (α-Sr_2CrO_4) is an exciting compound in this context. Its unusual reversed crystal field and d^2 electronic configuration (at the Cr site, Fig. 5a) create a twofold-degeneracy in both the orbital (d_{xz} / d_{yz}) and spin (+1 / -1) degrees of freedom, setting the stage for the emergence of multiple electronic orders.

The Comin group has synthesized strontium chromite in thin film form and performed resonant hard X-ray scattering studies at the Cr K-edge (~ 6 keV). We discovered two electronic phase transitions: (i) a high-temperature one (~ 110 K) to a spin-ordered Neel state with ordering vector Q_N = (1/2,1/2,4.84) (Fig. 5b A,B); and (ii) a low-temperature one (~ 50 K) to a low-temperature stripe phase with ordering vector Q_s = (1/2,0,4.84) (Fig. 5b C,D), coexisting with Neel order. This stripe phase appears to involve ordering of both the spin and orbital degrees of freedom [Zhu2019].

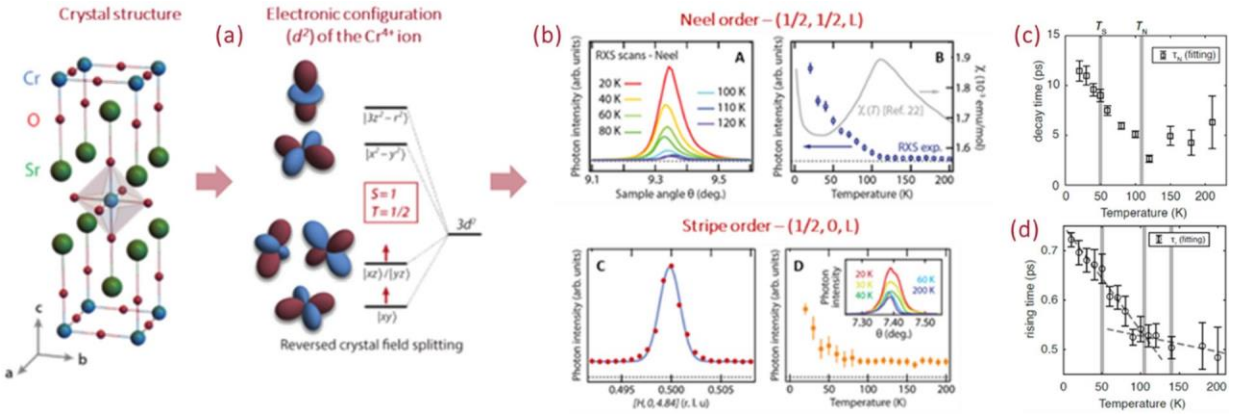

Figure 5. Electronic phase transitions in α-Sr_2CrO_4. (a) Crystal structure and local electronic configuration of α-Sr_2CrO_4. (b) of α-Sr_2CrO_4 ordering. A: Neel order at Q_N = (1/2, 1/2, L) and B: Temperature dependence. C: Stripe order at Q_S = (1/2, 0, L) and D: Temperature dependence. (c) 1.5 eV reflectivity decay time after 1 eV photoexcitation and (d) rise time after 3.1 eV photoexcitation.

These initial studies seeded a collaboration with the Prasankumar group, where the first optical pump-probe experiments were performed on thin films of Sr_2CrO_4 across both the Neel and stripe ordering transitions. Our goal was to understand the dynamic response of the separated spin and orbital orders in Sr_2CrO_4, in preparation for future time-resolved XRD studies at an XFEL. Fig. 5 depicts the temperature-dependent reflectivity dynamics observed with a probe energy of 1.5 eV after femtosecond excitation at (c) 1 eV and (d) 3.1 eV, revealing clear changes across T_N which show that AFM order recovers within ~10 picoseconds (ps). On longer timescales, we also observe signatures of stripe order at T_S after both 1 and 3.1 eV photoexcitation. We are currently preparing a manuscript describing these results. Building on these observations, we plan to measure the dynamical evolution of Neel and stripe order directly in reciprocal space using resonant (hard) X-ray scattering probe at the LCLS (proposal submitted to XPP beamline) after beamtime at SACLA failed due to multiple technical issues at the beamline. We plan to subsequently use a THz pump to drive lattice modes that directly manipulate the local crystal field and the balance between the spin and orbital degrees of freedom.

Our upcoming beamtime at SACLA in January 2021 focuses on using optically induced strain waves to modulate superconductivity (SC) in the YBCO layer of a $SrRuO_3$/$YBa_2Cu_3O_7$/MgO heterostructure (Fig. 6). We will optically drive a strain wave in SRO, modulating the crystal structure of YBCO to induce novel transient states. We will directly observe the associated lattice dynamics in YBCO using TR-XRD, and we are now conducting complementary optical-pump, THz-probe (OPTP) measurements that will enable us to correlate strain and conductivity.

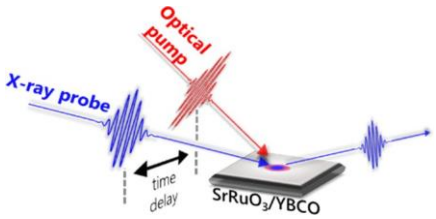

Figure 6. Schematic illustration of optical-pump, XRD-probe experiments on SRO/YBCO.

In addition, recent work [Liu2020, Zhang2020] has shown that near-IR pulses can induce a transient SC-like state in underdoped YBCO, an unexpected discovery since previous work [Mankowsky2014] had indicated that mid-IR pulses resonant with an optical phonon mode were necessary. In the latter case, TR-XRD experiments revealed specific lattice motions that accompanied the transient SC-like state, but this has not yet been done under near-IR excitation. We submitted a proposal to PAL-XFEL to address this issue by performing TR-XRD experiments with near-IR excitation on underdoped YBCO. In preparation, we are performing OPTP experiments on underdoped YBCO films; to the best of our knowledge, transient SC-like states have only been observed in bulk single crystals, so this in itself will provide important information.

Finally, we have recently performed time-resolved magneto-optical Kerr effect (TR-MOKE) measurements on the van der Waals (vdW) magnet CrI_3, which revealed that the amplitude of a specific coherently driven A_{1g} phonon mode strongly depended on the helicity of the pump pulse below the ferromagnetic critical temperature, T_c = 61 K [Padmanabhan2020]. This suggests strong spin-lattice coupling for this mode, and we have submitted a proposal to LCLS to unravel the details of this coupling using TR-XRD experiments with circularly polarized optical pumping. Furthermore, strong THz fields can directly drive magnetization changes by exciting nearby magnon modes; this should also drive changes in the coupled A_{1g} phonon mode that can be observed through 2D THz/THz spectroscopy and ultimately (and most incisively) through 2D THz/X-ray measurements in which correlated responses of core-transition XAS (sensitive to the magnetization) and XRD (sensitive to phonon displacements) could be observed.

Related theoretical efforts are under way in the Freericks group. The first is development of a full quantum theory in the strong-coupling limit for electron-phonon coupled systems, which is able to incorporate anharmonic effects. This approach was applied to cold atoms systems [Dirks 2015] (which, similar to strongly pumped systems, have average energies far from the ground state energy) and has now been generalized from a Coulomb system to an electron-phonon coupled system. We are in the process of completing the code development for incorporation into a complete theory, and we anticipate results soon.

The second effort utilizes a recently developed Monte Carlo approach that allows us to examine nonequilibrium dynamics in one and two dimensions for static phonons. This approach is motivated by the fact that in many interesting materials studied with pump/probe and quantum control experiments, the system has a soft phonon mode (typically CDW systems and ferroelectrics/multiferroics), so when the electronic energy is much higher than the phonon frequency, the approximation of zero phonon frequency is reasonable. We developed the Monte Carlo code in a separate research project and are now moving to applying it to XFEL-related experiments as part of this project. The major drawback of this approach is that the static phonons do not allow for an energy exchange between electrons and phonons. We plan to extend the approach via the Born-Oppenheimer methodology to allow for electron-phonon energy exchange which otherwise is not accounted for.

X-ray pump measurements

We conducted experiments in which the LCLS split-and-delay apparatus was used for x-ray pump, x-ray scattering probe measurements of $KTaO_3$ and $SrTiO_3$ (KTO, STO). The results were striking: pump-induced coherent acoustic phonon modulations were seen in the time-resolved diffuse scattering across wide region of the Brillouin zone. Even though the detector records the diffuse scattering from both the pump and probe, the signals were so strong that they could be observed from raw images, unlike previous experiments in which the dynamical responses could only be discerned after careful subtraction of the background thermal diffuse scattering signals. X-ray pumping, which acts through core electronic absorption, appears to generate intense, tens of nanometer scale point-like sources of localized stress that could be interpreted as a unique type of electron-phonon coupling. The result is an important step toward hard x-ray transient gratings with periods approaching the atomic scale. It also suggests novel prospects for control over lattice dynamics which in other materials may yield correspondingly striking effects on electronic or magnetic degrees of freedom. Further experimentation on other material classes is planned.

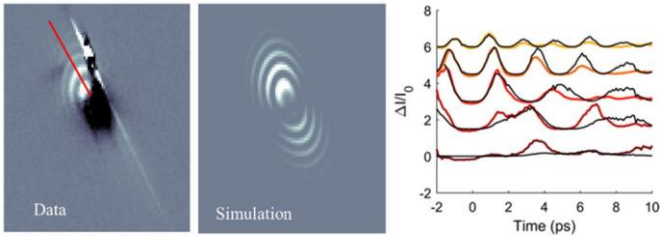

Figure 7. Diffuse x-ray scattering image (experiment and simulation) from STO following x-ray pumping, and time-dependent responses at selected phonon wavevectors. Shown are the difference between unpumped and pumped images, but the signals were so strong that the modulations were visible in the raw images. Representative traces on the right are in absolute units, offset for clarity.

The Nelson group has been involved in the development and use of extreme UV transient grating (TG) measurements in collaboration with scientists at the FERMI EUV beamline, in which crossed pump pulses generate an interference pattern that results in spatially periodic excitation of the sample with a specified spatial period L (or wavevector magnitude q) which can reach unprecedented ranges enabled by the short pump wavelength. The first nanometer-scale TG measurements were reported last year, with EUV pump and probe wavelengths used for measurements of silicon and silicon nitride [Bencivenga2019]. Coherent acoustic waves with frequencies of several hundred GHz and nanoscale thermal transport that was highly non-diffusive were measured with TG spatial periods as short as 28 nm (thermal transport distance < 10 nm). See Fig. 8a. Further measurements were conducted on vitreous silica to gain insight into the nanoscale effects of structural disorder on acoustic attenuation and thermal transport. More recent reflection-mode EUV TG measurements represent a major advance since they enable many bulk materials to be studied with EUV TG measurements, circumventing the need for extremely thin and fragile transmission-mode samples that are compatible with short EUV penetration depths. In July 2020 beamtime (led remotely) we followed up the first EUV TG measurements of magnetic dynamics that we conducted last year [Ksenzov2020] using a Co M_3-edge (3p → 3d) resonant probe beam for diffraction from a TG in Co/Pt in which the pump pulses partially melted magnetic ordering. See Fig. 8b. This project is opening a new avenue for study of ultrafast spin dynamics and nanoscale transport. In additional recent work led by the Comin group, we have studied low-energy

collective electronic modes in strongly correlated materials. We studied two cuprate samples in the antiferromagnetic phase (La_2CuO_4 and Nd_2CuO_4) and one in the charge-density-wave (CDW) phase ($YBa_2Cu_3O_{6.51}$), aiming to detect the emergent collective modes – magnons and amplitudon, respectively – using a Cu M_3-edge probe to maximize our sensitivity to the electronic degrees of freedom. At a TG period of 71 nm ($q \sim 0.1$ nm^{-1}), we observed thermoelastic responses and, in the charge ordered phase of YBCO6.51, a coherent, long-lived oscillatory signal with a frequency of ~2 THz (Fig. 8c). This frequency does not match any known optical phonon mode in this compound but is remarkably close to that of a CDW-induced mode previously measured in YBCO using optical TG measurements [Hinton2013]. This excitation is a likely candidate for the amplitudon mode at the EUV TG wavevector (Fig. 8c, inset). We plan further measurements as a function of temperature, to establish the correlation with the onset of charge order, and as a function of momentum, to map out the momentum-energy dispersion of this collective mode. We anticipate still shorter TG spatial periods becoming available at FERMI, reaching CDW, SDW, striped phase, and other modulation length scales. We ultimately wish to follow EUV TG excitation with THz pumping that may enable resonant excitation of high-q magnons, amplitudons, and other low-frequency, high-q modes. These modes could become accessible because the TG modulation may result in a high-q response to the THz field even though the field itself has no high-wavevector components.

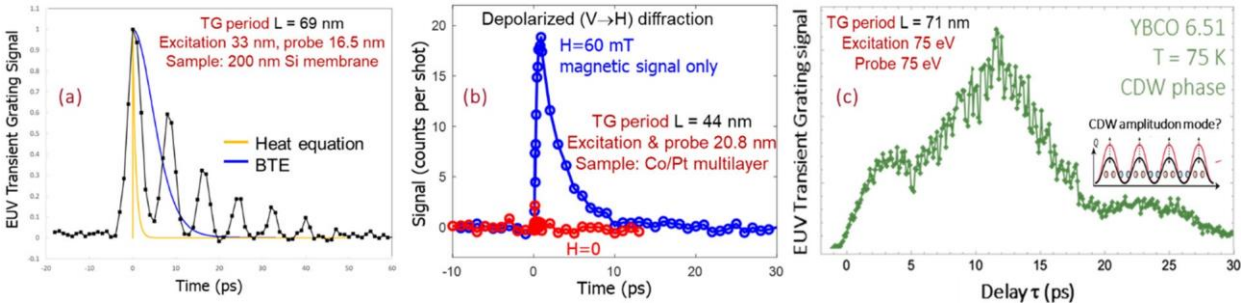

Figure 8. EUV transient grating results. (a) Thermoelastic response in Si showing highly nondiffusional nanoscale thermal transport kinetics. (b) Transient magnetization grating data from Co/Pt multilayer sample with external magnetic field to induce perpendicular magnetic anisotropy. (c) TG data from YBCO6.51 showing 2-THz oscillations that may reveal the CDW amplitude mode at the TG wavevector.

In a step toward achieving the highest TG wavevectors, we conducted the first TG measurements with hard x-ray (7.1 keV) excitation pulses last year in collaboration with scientists at SwissFEL. In this first demonstration, optical rather than x-ray time-delayed probe pulses were used, so the TG spatial period was 770 nm, sufficiently long that the probe light could be diffracted. Strong signals were recorded from many solid samples and liquid water. We are about to submit results for publication showing optical phonon oscillations in bismuth germanate, $Bi_4Ge_3O_{12}$ (BGO). The TG pattern was generated through Talbot imaging of a phase mask pattern, an approach that could produce spatial periods of ~50 nm but could not reach the <1 nm range that should ultimately become accessible with hard x-ray wavelengths. Several of the project team members are working toward other hard x-ray TG methods that would provide access to the full wavevector range. However, many x-ray four-wave mixing measurements such as those on molecular electronic excitations will provide important new information through the use of resonant x-ray wavelengths [Tanaka2002, Healion2014], without a need for high q. An LCLS beamtime proposal will be submitted shortly for all-x-ray TG experiments using Talbot imaging.

New methods

We are developing several new methods that will substantially advance the capabilities for quantum material measurement and control. The Freericks group is developing the theoretical basis for a generalized ultrafast thermometry. This is a nondestructive *in situ* way to measure the population distribution and effective temperature of electrons on an ultrafast time scale. It is well known that the core-hole satellite features in x-ray photoemission spectroscopy (XPS) and the edge features in x-ray absorption spectroscopy are quite sensitive to both electron correlations and temperature. We use this

sensitivity to develop a procedure to correlate their features with the nonequilibrium electron distribution. In Figure 9, we show these features for a system at the critical interaction for the Mott transition. The shape of the satellite peak near zero frequency changes dramatically following pulsed photoexcitation (the features are broadened due to the simulated probe-pulse widths) and one can correlate the changes in amplitude, width, and total weight with the energy gained. Even more interesting is how the equivalent equilibrium result at high temperature (blue dashed curve) looks quite different from the final-time nonequilibrium result. This suggests that one can use these measurements as a test for nonequilibrium populations of electrons. These results should be submitted for publication before the end of the year.

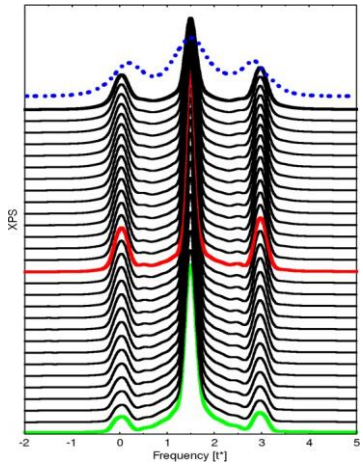

Figure 9. Time traces of a core-hole XPS signal for a material near the Mott transition. The green curve is the initial equilibrium result before the pump is applied (broadened by the probe pulses of finite width), the red highlight is at the pump maximum amplitude and the blue curve is a high temperature response from an equilibrium calculation. One can see the satellite peak change shape, amplitude and width during the nonequilibrium pumping. It never looks similar to the equilibrium result, showing how the measurement can reveal a nonequilibrium distribution of electrons for the duration that it persists.

We have advanced two distinct methods for application of strain to samples in a manner that is compatible with XFEL measurements. Strain is an extremely important degree of freedom in the multiphase landscapes of many quantum materials, and the use of both strain and THz fields offers exciting new prospects for quantum phase control. Trigo has obtained an apparatus for application of static compressional or dilatational strain whose small size is amenable for inclusion along with the clamped sample inside a sample chamber or cryostat. Nelson has demonstrated an optical method for excitation of single-cycle surface or bulk acoustic waves that propagate to the sample of interest which is never irradiated by the acoustic pump light. The acoustic strain lasts for nanoseconds, which is long enough compared to most of our measurements to be quasi-static. Both methods can reach strain levels exceeding 1% in many samples. In parallel work, Nelson has developed methods for optical generation of strong THz fields in extremely compact media that themselves could be incorporated into sample chambers and cryostats, in some cases obviating the need for THz access from outside which requires suitable window materials, accommodation of large THz optics, and engineering of sufficiently short distances from outside to the sample.

We have developed a single-frame diffractive imaging method called Randomized Probe Imaging (RPI), to leverage new opportunities to perform single-shot spatiotemporal imaging at XFELs [4]. In RPI, a sample is illuminated by a structured probe field containing speckles smaller than the sample's typical feature size (Fig. 10B). Quantitative amplitude and phase images are then reconstructed from the resulting far-field diffraction pattern, without requirements for multiple exposure (unlike ptychographic), special finite support constraints (unlike CDI), or prepatterned masks (unlike holography). Therefore, RPI is applicable to extended samples like most bulk or thin film materials and can be performed both in forward scattering (Q~0) and in a Bragg geometry (finite Q). RPI therefore offers an attractive modality for quantitative x-ray phase imaging when temporal resolution and reliability are critical but spatial resolution of tens of nanometers is sufficient. We have demonstrated RPI using soft X-rays (at beamline UE46, BESSY) on Siemens star test patterns as well as magnetic thin films (FeGd) with lateral domains. We could obtain single-frame reconstructions with a penalty in spatial resolution of only a factor two (85 vs. 40 nm) when compared to a ptychography scan acquired under the same conditions (Fig. 10C,D).

We are currently planning an experiment to demonstrate the application of RPI using an XFEL source. The major challenge to be overcome will be to ensure that the method is robust to shot-to-shot fluctuations in the probe function. We will collaborate with the scientists at DIPROI beamline (FERMI, Elettra) in the coming year to test this method at EUV wavelengths and in single-shot mode. In addition to conventional test patterns, we will study magnetic thin films in transmission and at the *M* resonances of transition metals where we can achieve magnetic phase contrast and perform spatiotemporal imaging of magnetic domains.

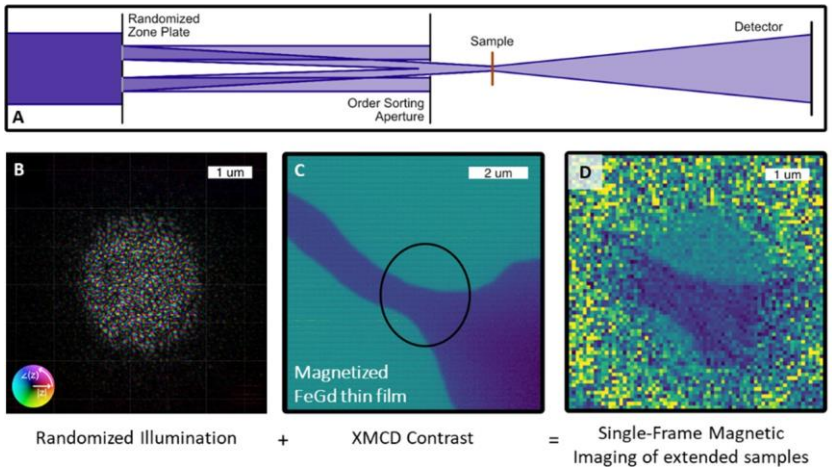

Figure 10. Randomized Probe Imaging. (A) Experimental setup. (B) Randomized illumination function. (C) Ptychographic reconstruction of magnetic domains in a FeGd film. (D) Single-frame reconstruction from the same sample (black circle in C).

Finally, the Nelson group has begun preparations for 2D THz/x-ray spectroscopy which as mentioned above will become possible when the LCLS-II high repetition rate system is operational. We are conducting tabletop 2D THz/THz and THz/optical measurements [Lu2018] on the $SrTiO_3$ quantum paraelectric phase. These will help elucidate the multiple THz light-matter interaction pathways through which the FE phase is induced and will reveal which lattice degrees of freedom are coupled to the THz-driven soft modes. They will set the stage for 2D THz/x-ray measurements which will provide detailed additional information about the ferroelectric structure and the nonlinear phonon-phonon interactions that lead to it and mediate its metastability. 2D THz/THz measurements already have been conducted on canted antiferromagnetic materials in which the light-matter interactions involve the THz magnetic field components [Lu2017]. 2D tabletop THz/THz measurements will be conducted on multiferroics, in which the light-matter interaction pathways can involve THz electric and magnetic fields and whose correlated polarization and magnetization responses could be probed in 2D THz/x-ray measurements that include resonant XAS as well as XRD.

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Structural Signatures of Hidden Order in Spin-Orbit Coupled Systems

Principal Investigator: Raymond Osborn, Argonne National Laboratory

Quantum materials are solids, whose strongly interacting electrons display novel properties that could impact technological fields as diverse as quantum computing, smart sensors and actuators, and low-power electronics. In many quantum materials, the relativistic interactions that couple the electrons' spins to their orbital momenta are particularly strong, and this spin-orbit coupling has been predicted to generate exotic forms of cooperative electron ordering that have not been seen before. Since these emergent electron states have lower symmetry than the materials' atomic lattice, it is anticipated that the crystal structure should also be modified below the ordering temperature. However, there are many examples of materials where, in spite of evidence of electronic order by, for example, optical spectroscopy, no compatible structural changes have been observed by x-ray or neutron diffraction. This may be due to limitations in conventional methods of measuring diffraction, especially when the structural modifications are extremely subtle or only short-range. The objective of this research is to reveal this "hidden order" in quantum materials and thereby elucidate the underlying interactions that would allow them to be harnessed in future applications.

Recent improvements in the brightness of x-ray synchrotron sources, such as the Advanced Photon Source, combined with technological advances in fast area detectors and computational analysis, have greatly enhanced the speed and sensitivity of x-ray diffraction. It is now possible to measure large volumes of scattering data with excellent signal-to-noise in under 20 minutes, allowing the detection of both extremely weak Bragg peaks from modulations in the long-range crystal structure and broad diffuse scattering from short-range fluctuations in the atomic order. Changes in the scattering with temperature can be tracked in a few hours. Such comprehensive measurements enable two novel ways of interrogating the data to ensure that the structural response to electronic order is reliably identified.

First, since these methods generate several terabytes a day, manual inspection of the data is time-consuming and unreliable. This project will develop machine learning tools that will automatically identify multiple components in the scattering, whether weak or broad, by monitoring their variation as a function of temperature. The goal is to perform this analysis fast enough that the measurements of ordering phenomena can be refined during the experiment.

Second, such large volumes of scattering can be transformed using a recently developed method that generates three-dimensional "difference" pair-distribution-functions (3D-ΔPDF), a powerful way of eliminating the average crystal structure to visualize small structural modifications and determine the length scale of atomic fluctuations. This project will develop the field of multidimensional spectral analysis to ensure that the 3D-ΔPDFs are statistically robust, with dramatically reduced artifacts and minimized estimation bias.

By combining high-energy x-ray scattering, machine learning, and spectral analysis to address the problem of "hidden order," this research will also lead to a suite of innovative tools that will impact future investigations of crystalline materials whose properties depend on structural correlations that are short-ranged or too weak to be measurable by conventional diffraction.

Presentation

1. Osborn-Structural-Signatures.pptx

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

DOE-BES Award: DE-SC0006877
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Program Scope

This project is relevant to the mission of the Office of Basic Energy Sciences to achieve an understanding of the atomic structure and structure-dependent properties of materials related to new energy technologies through the application and advancement of cutting-edge x-ray scattering techniques. In particular, our research activities include i) synthesis of metallic nanocatalysts, ii) *ex-situ* high-energy x-ray diffraction (HE-XRD) and atomic pair distribution function (PDF) studies on as prepared nanocatalysts, iii) element-specific structure studies on metallic nanosized catalysts by resonant HE-XRD and iv) *in situ* PDF studies on metallic nanocatalysts.

Recent Progress

We conducted a planned *in situ* PDF study on Pt-transition metal nanocatalysts inside an operating fuel cell and a complementary *ex situ* resonant HE-XRD experiment (Pt K edge) on the same catalysts in their pristine state. Due to their specific nanoalloy structure and dendritic morphology, the catalysts were found to exhibit a greatly enhanced activity for the oxygen reduction reaction taking place at the cell's cathode [see ref. 8]. Results from an earlier *in situ* fuel cell experiment were also summarized and published (see ref. [11]). In the study, we provided strong evidence for the limited applicability of the so-called Vegard's law in the case of metallic nanoparticles. We also published results from i) an earlier resonant HE-XRD experiment (K edge of Pt) on Mn core-Pt shell nanocatalysts (see ref. [7]), ii) *ex situ* PDF studies on nanocatalysts (see ref. [12]), iii) *in situ* study on the nucleation and growth of Au nanocatalysts in solution (see ref. [3]) and iv) *in situ* combined PDF and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study where we provide strong evidence for the oscillatory behavior of gas-phase reactions over metallic nanocatalysts (see Fig.1).

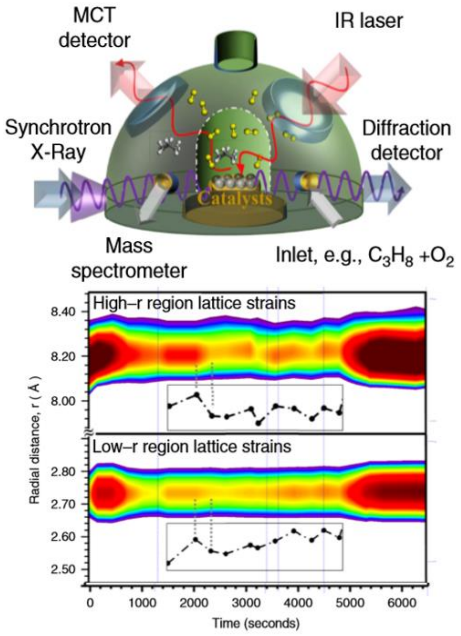

Fig. 1 (first row) Set-up for combined *in situ* PDF and DRIFTS studies. (second row). Oscillatory behavior of bonding (2.75 Å) and higher-r distances in nanocatalysts during oxidation of propane [1].

Our major effort, however, was in the area of atomic structure **studies on lattice instabilities and emergent electronic phases and behavior rooted in the quantum world.** Our studies are relevant to the mission of BES to advance the understanding of the physical world, including quantum materials. Also, they directly respond to the grand challenge before BES to determine how remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents using advanced x-ray scattering techniques. In particular, we initiated studies on interactions between lattice instabilities, electric and magnetic degrees of freedom in i) perovskite multiferroics (MFs) and ii) charge density wave (CDW) systems from the transition metal dichalcogenide (TMD) family. We

conducted a resonant HE-XRD experiment on (K,Na)NbO_3 perovskites (K edge of Nb) and determined the structural origin of the enhanced ferroelectricity observed when the K to Na ratio is close to one [9]. We also conducted a resonant HE-XRD experiment on $Ta(Se,Te)_2$ TMDs (K edge of Ta) and a complementary low-temperature PDF experiment on the same system. Results from the studies are published in two papers [2, 5]. The work on $TaSe_2$ was selected as one of the Advanced Photon Source's science highlights. It clearly reveals the presence of a CDW state at low temperature (see Fig. 2) and that the transition between the normal and CDW state of 2*H*-$TaSe_2$ is gradual, where locally correlated displacements of Ta atoms above the transition temperature T_{CDW} serve as a precursor of the periodic lattice distortions (hexagons of Ta atoms in Fig. 2) observed below T_{CDW}. This result explains the emergence of a "precursor" CDW pseudogap in the normal state of 2*H*-$TaSe_2$ already near room temperature and its smooth evolution into a band gap below T_{CDW}. Specifically, the pseudogap may be attributed to the locally correlated Ta displacements, and the band gap may be understood as being a consequence of the complete alignment of these displacements into a periodic superstructure. Currently we are analyzing low temperature PDF data for the Weyl semimetal candidate $MoTe_2$, concentrating on understanding the structural origin of the extreme magnetoresistance observed at low temperature (< 200 K). We are also conducting PDF guided, large scale modeling on nanosized $BiFeO_3$, aiming at revealing the relationship between lattice distortions and emergent magnetoelectric coupling as a function of the system size, from bulk down to 10 nm.

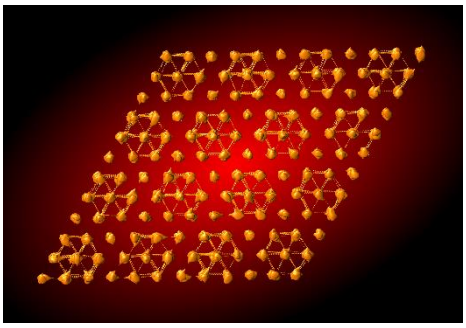

Fig. 2 Top view of a "bulk-averaged" Ta plane in the first CDW phase (about 100 K) of 2H-$TaSe_2$ obtained by mapping a 150 Å x 150 Å x 90 Å model comprising 80,500 atoms onto a single Ta plane. Lines highlight the presence of hexagon-shaped clusters of Ta atoms organized in a superstructure [5].

Future Plans

We plan to undertake systematic studies on the relationship between the lattice distortions and magnetoelectric coupling in substituted $BiFeO_3$ (ABO_3-type) perovskites, where Bi is partially replaced by non-ferroelectric Ba or non-ferroelectric but magnetic Gd, and magnetic Fe is partially replaced by non-magnetic Ti. The studies will allow us to evaluate the combined effect of entangled lattice instabilities, such as octahedral tilts, off-centering of metal ions and local strain, on the emergent magnetoelectric coupling in $BiFeO_3$, where the instabilities are induced by i) A-site structural distortions alone, case of (Bi,Ba)FeO_3 MFs, ii) A-site structural distortions and frustration of Dzyaloshinskii-Moriya (DM) type interactions between Fe atoms due to the presence of a second magnetic species on the A site, case of (Gd,Ba)FeO_3 MFs, and iii) distinct A- and B-site structural distortions and dilution of the network of Fe^{3+}-O^2-Fe^3 bonds & DM interactions due to the presence of a second non-magnetic B-site species, case of (Bi, Ba)(Fe,Ti)O_3 MFs. For the purpose, we will carry out resonant HE-XRD experiments at the K edge of Ba and Gd, and L edge of Bi. We also plan to continue our studies on the relationship between lattice instabilities, CDW and superconducting orders in TMDs, where TM is Ta, Nb and Mo and chalcogenide is Se, S, or Te. Here we will carry out resonant HE-XRD experiments at the K edge of Ta, Nb and Mo. The resonant HE-XRD experiments will be complemented with low temperature ordinary HE-XRD/PDF experiments. Furthermore, we will conduct grazing incidence resonant HE-XRD studies (K edge of Hf) on the emergent ferroelectricity in thin HfO_2 layers. The experimental PDF data will guide large-scale modeling of the studied systems.

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2. **V. Petkov**, K. Chapagain , J. Yang, S. Shastri, and Y. Ren "*Exotic bonding interactions and coexistence of chemically distinct periodic lattice distortions in the charge density wave compound* $TaTe_2$" **Phys. Rev. B**. 102, 024111 (2020).
3. R. K. Ramamoorthy, E. Yildirim, E. Barba, P. Roblin, J. A. Vargas, L.-M. Lacroix, I. Rodriguez-Ruiz, P. Decorse, **V. Petkov**, S. Teychené and G. Viau *"The role of pre-nucleation clusters in the crystallization of gold nanoparticles"* **Nanoscale** 12, 16173 (2020).
4. Ch. Kokkinos, A. Economou, A. Pournara, M. Manos, I. Spanopoulos, M. Kanatzidis, Th. Tziotzi, **V. Petkov**, A. Margariti, P. Oikonomopoulos, G. S. Papaefstathiou "*3D-printed lab-in-a-syringe voltammetric cell based on a working electrode modified with a highly efficient Ca-MOF sorbent for the determination of Hg (II)*" **Sensors and Actuators B: Chemical** 321, 128508 (2020).
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6. S. Chanakian, D. Uhl, D. Neff, F. Drymiotis, J. Park, **V. Petkov**, A. Zevalkink and S. Bux "*Exceptionally high electronic mobility in defect-rich* $Eu_2ZnSb_{2-x}Bi_x$ *alloys*" **J. Chem. Mat. A** 8, 6004 (2020).
7. M. A. Matin, J. Lee, G. W. Kim, Hyun-Uk Park, B. Jun Cha, S. Shastri, G. Kim, Y.-Dok Kim, Young-Uk Kwon, **V. Petkov** "*Morphing Mncore@Ptshell nanoparticles: Effects of core structure on the ORR performance of Pt shell*" **Appl. Cat. B.: Environmental** 267**,** 118727 (2020).
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9. **V. Petkov**, J.-W. Kim, S. Shastri, Sh. Gupta and Sh. Priya "*Geometrical frustration and piezoelectric response in oxide ferroics"* **Phys. Rev. Mat**. 4, 014405 (2020).
10. A. D. Pournara, A. Margariti, G. D. Tarlas, A. Kourtelaris, **V. Petkov,** Ch. Kokkinos, A. Economou, G. S. Papaefstathiou and M. J. Manos "*A Ca2+ MOF combining highly efficient sorption and capability for voltammetric determination of heavy metal ions in aqueous media*" **J. Mat. Chem. A** 7, 15432 (2019).
11. **V. Petkov**, Y. Maswadeh, J. A. Vargas, S. Shan, H. Kareem, Z.-P. Wu, J. Luo, Ch.-J. Zhong, S. Shastri and P. Kenesei "*Deviations from Vegard's law and evolution of the electrocatalytic activity and stability of Pt-based nanoalloys inside fuel cells by in operando X-ray spectroscopy and total scattering*" **Nanoscale** 11 (2019) 5512.
12. Z.-P. Wu, S. Shan, Z.-H. Xie, N. Kang, K. Park, E. Hopkins, S. Yan, A. Sharma, J. Luo, J. Wang, **V. Petkov**, L. Wang, and Ch.-J. Zhong "*Revealing the Role of Phase Structures of Bimetallic Nanocatalysts in the Oxygen Reduction Reaction"* **ACS Catalysis** 8 (2018) 11302.

Coherent x-ray scattering investigations of nanoscale magnetic fluctuations in frustrated magnets

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Program Scope: In frustrated magnets, competing magnetic interactions prevent the formation of semi-classical magnetically ordered ground states and can give rise to phases of matter exhibiting non-trivial entanglement. However, frustrated magnets are also sensitive to chemical or structural disorder and the physical effects of this very minute disorder can mimic expectations for a quantum state. Distinguishing disorder driven from intrinsic phenomena in quantum magnets is a major experimental challenge. The focus of this program is to utilize coherent x-ray scattering as a probe of spontaneous magnetization fluctuations in model frustrated magnets to elucidate signatures of disorder-induced from those of intrinsic quantum phenomena. There is a particular emphasis on studying materials where we have a degree of control over structure and chemical disorder introduced during synthesis. Through these studies, we aim to achieve a systematic empirical understanding of the roles of disorder in controlling the lowest energy magnetic fluctuations in quantum materials, with an eye towards realizing magnetic materials exhibiting quantum entangled ground states.

Recent Progress. *Molecular orbitals from chemical pressure:* This is a new program, but we have already completed a resonant x-ray investigation of a new honeycomb iridate $Ag_3LiIr_2O_6$. This compound was recently synthesize by our collaborators at Boston College and is derived from α-Li_2IrO_3 but with interlayer Li atoms replaced with Ag in an attempt to bring the material closer to the Kitaev spin liquid limit [1]. There is thermodynamic evidence that magnetic order is destabilized and hints of spin liquid physics in $Ag_3LiIr_2O_6$. However the specific role of Ag and influence of possible chemical disorder was not understood.

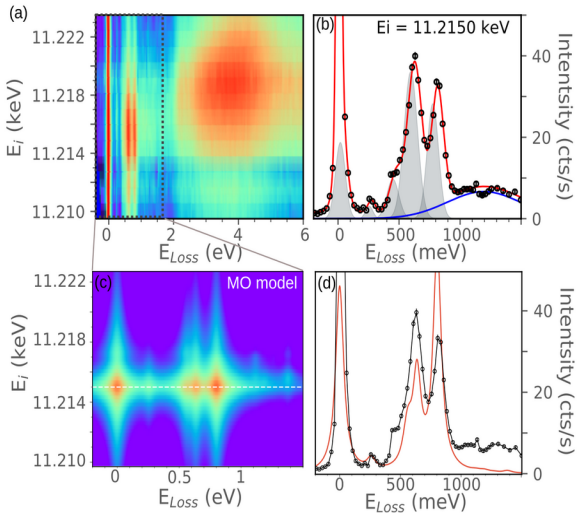

Figure 1. Ir L_3 edge RIXS reveals Molecular orbitals in $Ag_3LiIr_2O_6$. (a) - (b) RIXS spectra. (c) - (d) Molecular orbital model data comparison.

We have carried our a series of x-ray spectroscopy investigations of the Ir local environment and electronic structure. We find deviations from cubic symmetry in the Ir local environment that diffraction measurements could not detect. By comparing ab-initio electronic structure calculations with our data, we have found that the replacement of Li with Ag in $Ag_3Li_2IrO_6$ generates a chemical pressure that drives this compound into the molecular orbital limit, so that the j_{eff} picture does not apply [2]. The low lying molecular orbital states can consistently explain themodynamic data and the molecular orbitals are expected to produce reduced superexchange interactions that result in a reduced Neel temperature than the parent compound. Our results show how chemical pressure can influence the single ion state of transition metal magnets. We are currently preparing a publication describing these results.

Future Plans: We plan to carry out investigations of Ni and Fe based Van der Waals frustrated magnets with an aim to understand the dependence of magnetic correlations on stacking faults and chemical stoichiometry, both of which can be controlled during crystal synthesis and accurately characterized. We have completed preliminary RIXS measurements on bulk samples of one such compound, $NiPS_3$, on the SIX spectrometer at NSLS-II. A series of follow up RIXS measurements is planned and resonant diffraction measurements on samples of varying thickness are planned for the ALS, NSLS-II, and CLS barring travel restrictions.

In collaboration with Mark Dean at Brookhaven National Lab, we plan to carry out resonant diffraction and coherent x-ray scattering experiments on Ni and Fe based frustrated triangular lattice magnets that have been shown to exhibit anomalously slow dynamics. Using resonant scattering, we aim to confirm or rule out proposed spin nematic order parameters and to understand slow glassy dynamics characteristic of these materials.

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4. Yusuke Nambu, Jason S. Gardner, Douglas E. MacLaughlin, Chris Stock, Hitoshi Endo, Seth Jonas, Taku J. Sato, Satoru Nakatsuji, and Collin Broholm. “Spin Fluctuations from Hertz to Terahertz on a Triangular Lattice”. Phys. Rev. Lett. **115**, 127202 (2015)

Publications

This is a new program (September 2020), we have one publication in preparation.

1. A. De La Torre Duran, B. Zager, F. Bahrami, M. Upton, F. Tafti, K.W. Plumb. “Molecular Orbitals From Chemical Pressure In a Honeycomb Iridate”, In Preparation (2020).

Materials Structure Analysis by BCDI and PDF

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

PI meeting Presentations

Ian Robinson "Materials Structure Analysis by BCDI and PDF"
Robinson_PI_meeting_core_2020.pptx

Simon Billinge "Hidden Broken Symmetries: Local structure, dynamics and domains"
PI_meeting_2020-SJB_xray.pptx

Emil Bozin "Pursuit of orbital precursor states in quantum materials"
PI_meeting_2020-ESB.pptx

Abstract

This program brings state-of-the-art x-ray scattering techniques to bear on the structure of materials, especially the strongly correlated electron materials of interest to the Condensed Matter Physics and Materials Science Division (CMPMSD) at Brookhaven National Laboratory. The long-term goal remains to seek structural explanations for the properties of correlated-electron "quantum" materials, including the roles of doping inhomogeneities, as well as magnetic and strained structural domains. Nanoscale fluctuations in strongly correlated systems will be studied to understand their intrinsic properties and thermal excitation. We aim to understand phase transitions of materials through the study of their nanoscale domains. Our experimental approach includes measuring hard and soft X-ray scattering from crystals, nanocrystals, superlattices, powders and thin films, as well as powder diffraction of neutrons. X-ray coherence is critical to some of the methods we are developing, such as Bragg Coherent Diffraction Imaging (BCDI) and X-ray Photon Correlation Spectroscopy (XPCS). Our program is involved in aiding the development of beamlines at the NSLS- II, especially the Coherent Soft X-ray (CSX), Coherent Hard X-ray (CHX), X-ray Powder Diffraction (XPD), Pair Distribution Function (PDF), Hard X-ray Nanoprobe (HXN), In-situ and Resonant Hard X-ray Studies (ISR) and Coherent Diffraction Imaging (CDI) beamlines.

1. Recent Program Achievements

1.1 Orbital Degeneracy Lifting

The local atomic and magnetic structures of the compounds $AMnO_2$ (A = Na, Cu), which realize a geometrically frustrated, spatially anisotropic triangular lattice of Mn spins, have been investigated by atomic and magnetic pair distribution function analysis of neutron total scattering data. Relief of frustration in $CuMnO_2$ is accompanied by a conventional cooperative symmetry-lowering lattice distortion driven by Neel order. In $NaMnO_2$, however, the distortion has a short-range nature. A cooperative interaction between the locally broken symmetry and short-range magnetic correlations lifts the magnetic degeneracy on a nanometer length scale, enabling long-

range magnetic order in the Na-derivative. The degree of frustration, mediated by residual disorder, contributes to the rather differing pathways to a single, stable magnetic ground state in these two related compounds. Our study demonstrates how nanoscale structural distortions can lift the ground state degeneracy and trigger macroscopic magnetic order.

Utilization of complementary neutron and X-ray PDF for mapping temperature evolution of local atomic structures in Ti-based $MgTi_2O_4$ spinel and $NaTiSi_2O_6$ pyroxene, systems featuring spin singlet dimer ground states, the existence of orbital degeneracy lifted (ODL) high temperature precursor states is revealed. Upon heating across their respective orbital selective Peierls transitions, the long range ordered dimer states in these materials evolve into ODL-type states with corresponding local distortions observably smaller than that of the spin singlet dimers. The ODL in weakly correlated Ti-spinel has multi-orbital character, exemplifying diverse flavors of such precursor states. The existence of ODL in strongly correlated Ti-pyroxene demonstrates that formation of such precursors does not require proximity to itinerant-to-localized crossover, and that they can materialize deep in the Mott insulating regime with strong on-site Coulomb interactions, where charge fluctuations are suppressed

1.2 X-ray Imaging

Solution-grown iron-oxide nanocrystals (NCs) of the wüstite system are found to convert into iron-deficient rock-salt and ferro-spinel subdomains but attain a surprising tetragonally distorted local structure. These lattice imperfections are shown to produce local exchange-anisotropy fields that reinforce the nanoparticle magnetization and overcome the influence of finite-size effects. The concept of atomic-scale defect control in subcritical-size NCs could open a pathway to engineer properties with improved performance for hyperthermia heating applications.

We showed that using fly-scan nano X-ray diffraction, we could accomplish a tensile strain sensitivity below 0.001% with a spatial resolution of better than 80 nm over a spatial extent of 100μm on quasi-2D flakes of 1T-TaS_2. Coherent diffraction patterns were collected from a∼100nm thick sheet of 1T-TaS_2 by scanning a 12 keV focused X-ray beam across and rotating the sample. We found that micron- and submicron-sized “bubbles” were formed with clear strain distribution. The experiments use state-of-the-art synchrotron instrumentation and will allow rapid and nonintrusive strain mapping of thin-film samples and electronic devices based on quasi-2D materials

1.3 Laser Melting studies

We used the PAL facility in Korea to observe time-dependent laser-induced melting of polycrystalline gold thin films. We observed the formation of an intermediate new diffraction peak on the low-Q side of each Bragg peak, which we attribute to material trapped at the melting point between the solid and melted states. The peak forms 50ps after laser excitation and persists beyond 500ps. Its width grows rapidly for 50ps, then narrows distinctly at longer timescales. We attribute this to a melting band originating from the grain boundaries of the polycrystalline film and propagating into the grains. Our observation of this intermediate state might have implications for the use of lasers for ablation during pulsed laser deposition.

2. Future Plans

We have started an initiative to use photon correlation spectroscopy (XPCS) to look for critical fluctuations associated with phase transitions. As a second-order transition is approached, it is expected that larger and larger fluctuation will appear on slower and slower time scales. We have developed some potential examples and will continue looking for more crystalline material systems which are potentially slow enough to observe at kHz rates which are possible with Synchrotron sources.

We will develop our understanding of ferroelectric domain formation in Barium and Strontium Titanate using BCDI methods. We will learn how to control the synthesis of nanoparticles to adjust the composition, morphology and crystal structure (tetragonal or cubic). We are targeting the possibility of structural phase core-shell nanoparticles, which have important applications and may show interesting dynamical properties.

Orbital Degeneracy Lifting (ODL) studies will continue with the study by PDF methods of new materials that potentially show ODL. Possible materials include conventional CDW-materials such as $TaCh_2$ (Ch=S,Se), and compositional variations on the $CuIr_2S_4$, $NaTiSi_2O_6$, and FeSe families. Of particular interest is relationship of ODL to the emergent properties and ground states (e.g. pseudogaps, and superconductivity), and the responses of ODL to external stimuli (e.g. pressure, magnetic field,). 3D-ΔPDF experiments will be expanded and the methods developed further to pursue the 3D aspects of the ODL structural responses.

Debye Scattering Equation (DSE) methods will be adapted to look for signs of ferroelectric domain formation in powder diffraction data. Models based on BCDI images will be used to evaluate the sensitivity of the DSE approach.

3. Recent Publications

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[2] “Ultrafast decoupling of atomic sublattices in a charge-density-wave material”, Jun Li, Junjie Li, Kai Sun, Weiguo Yin, Lijun Wu, Renkai Li, Jie Yang, Xiaozhe Shen, Xijie Wang, Huixia Luo, Robert J. Cava, Ian K. Robinson, Yimei Zhu and, Jing Tao, submitted to Nature Materials (2019)

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Electronic and Magnetic Structure of Quantum Materials

Z.-X. Shen, T.P. Devereaux, D.H. Lu, M. Hashimoto, P.S. Kirchmann, J.A. Sobota, and B. Moritz
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Abstract:

To develop a world class experimental and theoretical program in understanding the electronic and magnetic structure of quantum materials, to address BES grand scientific challenges through the utilization of DOE's x-ray user facilities and modern photoelectron spectroscopy with energy, momentum, and/or time and spin resolution. To complement these spectroscopy experiments with in-situ materials synthesis and characterization, and with advanced theoretical simulations. To complement experiments with theoretical investigations on key problems derived from experiments.

Recent Progress

- **A review**

We have finished a comprehensive review of angle-resolved photoemission spectroscopy (ARPES) study of quantum materials for the Review of Modern Physics. [Sobota, He and Shen, *RMP*, commissioned article, arXiv:2008.02378].

- **ARPES study of the high-T_c cuprate superconductors**

In high-Tc cuprate superconductors, by focusing on the doping region around a critical doping at p=0.19, our systematic ARPES studies revealed that we can gain insights into the nature of the strange metal, pseudogap, superconductivity, and also electron-phonon coupling. In particular, we revealed in $Bi_2Sr_2CaCu2O_{8+d}$ the positive effect of the strong electron-phonon coupling for superconductivity [Y. He *et al., Science* **362**, 62-65 (2018)], and a surprisingly temperature independent sharp phase boundary at the critical doping [S. Chen *et al.*, *Science* **366**, 1099 (2019)].

- **ARPES study of iron-based superconductors**

For iron-based superconductor, we performed a systematic study of mechanically detwinned FeSe and detwinned $BaFe_2As_2$ using uniaxial strain device, aiming at understanding the nature of the nematicity. The high resolution data on FeSe allows us to solve the recent controversies regarding the nematic energy scale and the missing electron pocket with dominant d_{xz} character, while a comparative study on $BaFe_2As_2$ reveals a universal momentum dependence of the nematic order parameter with a non-trivial sign change between the zone center and zone corner.

- **Spin structure and dynamics in topological materials**

Spin-resolved ARPES was used to characterize the spin- and orbital- texture of materials with strong spin-orbit coupling, such as the bulk Rashba semiconductor BiTeCl. Theory support allows us to disentangle surface and bulk contributions, and extract information related to Berry curvature. These results are being coupled with time-resolved ARPES measurements on lattice dynamics in topological materials like Bi_2Te_3 and Sb to develop a holistic picture of how phonon modes modify the surface electron and spin structures.

- **ARPES study of quantum thin films**

We further developed our metal and oxide MBE systems, and studied a number of oxide and di-chalcogenide oxide hybrid materials. An example is the dichotomy of 2D electron gas on SrTiO3

termination (PNAS 116, 16687 (2019)). We used 1D cuprate chains as a model system to determine the essential microscopic ingredients in cuprates. In 1D, robust theoretical prediction of a given Hamiltonian provides a special opportunity to test theory. We developed $La_{2-x}Sr_xCuO_{4+y}/La_2CuO_{4+y}$ heterostructures and measured ARPES in-situ to probe the electronic structure of the interface superconductor layer-by-layer Structures.

- **trARPES Studies of Coherent Response**

We study coherent phonon coupling to surfaces states in the topological insulator Bi_2Te_3 and compare our surface-sensitive trARPES measurements to bulk-sensitive time-resolved x-ray diffraction (collaboration Reis group, SLAC) and time-resolved optical reflectivity. We observe different modes at the surface, highlighting the role of local crystal symmetries for driving and coupling to different phonon modes. An analogous set of data was obtained for the sister material Bi_2Se_3, which exhibits an order-of-magnitude smaller response. This points to Bi_2Te_3 as a platform to study topological phase transitions to be studied with LCLS-II experiments.

We performed trARPES to excite coherent phonons in the topological semimetal Sb. We discovered a strong band-dependence of the phonon coupling strength. We have performed frozen-phonon DFT calculations which suggest non-trivial coupling behavior associated with the hybridization between bulk and topological surface states.

- **Theory and Simulation Activities**

We observe a linear temperature dependence of the resistivity in the 2D Hubbard model using determinant quantum Monte Carlo [E. W. Huang et al, Science 366, 987-990 (2019)], providing a foundation for connecting models and simulations for correlated quantum materials to theories for strange metal behavior, especially in transition metal oxides. We also investigate the DC Hall coefficient in terms of thermodynamic susceptibilities using determinant quantum Monte Carlo [W. O. Wang et al, npj Quantum Materials 5, 51 (2020)]. This approximation for the Hall coefficient changes sign as a function of temperature and Hubbard interaction, which we relate to changes in the topology of the apparent Fermi surface, providing further insight into correlated quantum materials that lack well-formed quasiparticles.

We systematically investigate the electronic structure in monovalent, infinite-layer nickelates using density functional theory [E. M. Been et al, arXiv:2002.12300 [cond-mat.supr-con]]. We find systematic electronic structure trends while changing the rare-earth species, and note that compensation from itinerant 5d electrons presents a close analogy to Kondo lattices. The complex interplay between charge transfer, renormalization, and magnetic exchange in these materials provides a new platform for studying competing quantum phases.

Future Plans:

We continue to investigate the cuprate phase diagram, in particular fluctuating superconductivity in the overdoped regime. Further, we plan to study the relationship between superconductivity and antiferromagnetism in electron doped cuprates and multilayer cuprates.

We plan to perform high precision systematic photon energy study of Fe based superconductors for non-trivial physics. In addition, we will further our study on the nematicity in iron based superconductors aiming to understand the nematicity in various Fe based superconductors.

We plan to expand our experimental capabilities to allow simultaneously spin- and time- resolved ARPES measurements with independently tunable pump and probe pulse wavelengths. We are also aiming to develop the capabilities of our spin spectrometer to enhance measurement efficiency. These capabilities will be applied to magnetic topological insulators and topological superconductors.

Using in-situ oxide MBE and ARPES capability, we will continue to refine our study of 1D Model system. We will study the Lifshitz transition in overdoped La2-xSrxCuO4+y thin films. The extensive doping range achievable in this system will also provide a materials platform to understand the pairing mechanism as we indicated in the Bi2212 and Bi2201 systems. We will study oxide heterostructures and oxide metal hybrid structures.

Building on earlier study of two out-of-plane A1g phonon modes in Bi2212 [Yang et al PRL 122 (2019) 176403], we extend this activity to Bi2201 and Bi2223. These measurements highlight that trARPES selectively probes strongly coupled modes at the Fermi surface. This opens demonstrate the unprecedented power of tr-ARPES to gain insight on mode and electronic state specific coupling information.

We will continue to perform quantum Monte Carlo simulations for the single-band Hubbard model, emphasizing coupling to oxygen phonon modes, nematicity, and the impact on photon spectroscopies and other material properties. We also will investigate properties of the 2D Hubbard model in the presence of external fields using quantum Monte Carlo to characterize higher-order electronic and thermal correlation functions in materials that lack well-defined quasiparticles.

We will investigate multi-layer models of strongly correlated quantum matter using Kondo-lattice-like or Anderson-lattice-like models for the infinite-layer nickelates. We will focus on understanding the generic electronic structure and spectra of coupled weakly interacting and correlated layers and the impact on general properties and competing phases.

FY 2020 Journal Publications:

1) publications intellectually led by this FWP

1. S.N. Rebec, T. Jia, H.M. Sohail, M. Hashimoto, D. Lu, Z.-X. Shen, and R.G. Moore, "Dichotomy of the photo-induced 2-dimensional electron gas on $SrTiO_3$ surface terminations", PNAS **116** (Aug. 2019) 16687

2. P.T. Brown, E. Guardado-Sanchez, B.M. Spar, E.W. Huang, T.P. Devereaux, and W.S. Bakr, "Angle-resolved photoemission spectroscopy of a Fermi–Hubbard system" Nature Physics **16** (Oct. 2019) 26

3. S.-D. Chen, M. Hashimoto, Y. He, D. Song, K.-J. Xu, J.-F. He, T.P. Devereaux, H. Eisaki, D.-H. Lu, J. Zaanen, and Z.-X Shen, "Incoherent strange metal sharply bounded by a critical doping in Bi2212" Science **366** (Nov. 2019) 1099

4. E.W. Huang, R. Sheppard, B. Moritz, and T.P. Devereaux, "Strange Metallicity in the Doped Hubbard Model"

Science **366** (Nov. 2019) 987

5. M. Yi, H. Pfau, Y. Zhang, Y. He, H. Wu, T. Chen, Z.R. Ye, M. Hashimoto, R. Yu, Q. Si, D.-H. Lee, P.C. Dai, Z.-X. Shen, D. H. Lu, and R. J. Birgeneau, "Nematic Energy Scale and the Missing Electron Pocket in FeSe"
   Phys. Rev. X **9** (Dec. 2019) 041049

6. K.J. Xu, Su-Di. Chen, Yu He, J.F. He, S.J. Tang, C.J. Jia, E.Y. Ma, S.K. Mo, D.H. Lu, M. Hashimoto, T.P. Devereaux, and Z.-X. Shen, "Metallic Surface States in a Correlated d-electron Topological Kondo Insulator Candidate $FeSb_2$"
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   Phys. Rev. Mat. **4** (March 2020) 034801.

8. W. O. Wang, J. K. Ding, B. Moritz, E. W. Huang, and T. P. Devereaux, "DC Hall coefficient of the strongly correlated Hubbard model,"
   npj Quantum Materials **5** (July 2020) 51.

2) Collaborative publications

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10. Y.-D. Chuang, X. Feng, A. Cruz, K. Hanzel, A. Brown, A. Spucces, A. Frano, W.-S. Lee, J. Kim, Y.-J. Chen, B. Smith, J. S Pepper, Y.-C. Shao, S.-W. Huang, L. A. Wray, E. Gullikson, Z.-X. Shen, T.P Devereaux, A. Tremsin, W. Yang, J. Guo, R. Duarte, and Z. Hussain, "Momentum-resolved resonant inelastic soft X-ray scattering (qRIXS) endstation at the ALS", Journal of Electron Spectroscopy and Related Phenomena (Oct.2019) https://doi.org/10.1016/j.elspec.2019.146897

11. Yi-Fan Jiang, Thomas P. Devereaux, and Hong-Chen Jiang, "Field-induced quantum spin liquid in the Kitaev-Heisenberg model and its relation to α-$RuCl_3$", Phys. Rev. B **100** (Oct. 2019) 165123

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20. J. Wu, Z. Zhuo, X. Rong, K. Dai, Z. Lebens-Higgins, S. Sallis, F. Pan, L.F. J. Piper, G. Liu, Yi-De Chuang, Z. Hussain, Q. Li, R. Zeng, Z-X. Shen, and W.Yang, "Dissociate lattice oxygen redox reactions from capacity and voltage drops of battery electrodes", Science Advances **6** (Feb. 2020) eaaw3871

21. Xuxin Huang, Martin Claassen, Edwin W. Huang, Brian Moritz, and Thomas P. Devereaux, "Biexciton Condensation in Electron-hole Doped Hubbard Bilayers - A Sign-problem-free Quantum Monte Carlo Study", Phys. Rev. Lett. **124** (Feb. 2020) 077601

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Control and Understanding of Matter Using Ultrafast Modalities from LCLS-II

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Abstract

Recent years have witnessed an explosion in material systems which exemplify some of the most profound and challenging concepts in condensed matter physics, including quantum topology, unconventional superconductivity, and novel physics from excitonic and polaronic interactions. Novel x-ray spectroscopy and scattering techniques utilized in ultrafast experiments have all proven to be powerful probes that address these frontier problems in quantum materials. Due to the unique capabilities of LCLS-II, we will have the unprecedented opportunity to integrate these approaches into a unified program that goes well beyond the simple sum of individual components. We will develop and apply the integrated program to a range of quantum materials. This will not only extend our understanding of matter to the intrinsic length- and time-scales of electrons and atoms in quantum materials, but also to exercise control over fundamental processes which give rise to emergent phenomena. These opportunities represent a synthesis of the Grand Challenges for Basic Energy Sciences, and the associated applications have the potential to revolutionize energy science and technology. We are developing a program of time-resolved angle-resolved photoemission experiments and time-resolved x-ray scattering experiments at LCLS-II, complemented by time- and spin- resolved photoemission and optics experiments in the laboratory and at synchrotrons. To achieve these research goals, we are screening suitable target materials, forging collaborations with LCLS staff, and forming an international collaborative consortium. Topological, excitonic and polaronic matters are investigated in this period.

Recent Progress

We have formed an international consortium to develop photoemission experiments at LCLS-II using a new photoemission system known as Momentum Microscope. By measuring electronic valence bands, core levels and their electron diffraction simultaneously, we will spearhead a new experimental paradigm to reveal the correlated dynamics of electronic and atomic structures in a “one-stop” measurement of states of quantum matter with bulk sensitivity and element specificity. This vision requires a high repetition rate FEL and high efficiency photoemission spectrometer. This new Momentum Microscope ARPES spectrometer represents the ultimate limit in electron spectrometer efficiency, ideal for trARPES experiments at LCLS-II due to considerations of space-charge issues. This activity combines our lasers, photoemission and scientific acumen with the extensive momentum microscope instrumentation expertise in Europe for LCLS science. The initial activity is to host and test a new instrument at SLAC, with the design being compatible with experimental hall constraint at LCLS-II.

Regarding trARPES work, we developed a formalism, substantiated by experiments, for determining the experimental parameters for optimizing the partitioning of the time-bandwidth product in trARPES, which is an important step for tailoring trARPES experiments towards specific scientific questions. In preparation for future THz-pump ARPES-probe experiments, we are developing a 3D time-dependent simulation to model streaking effects and action of the ponderomotive force to guide experiment and

analysis, and to delineate intrinsic sample physics from trivial, extrinsic electrodynamics. We are studying the topological Weyl-material WTe_2 in collaboration with UED studies from Aaron Lindenberg's FWP, and comparison of electronic and lattice information shows a rich mode and band dependence of the phonon coupling strength.

Together with Matthias Hoffmann, we are using all-optical methods to investigating how THz pumping can break the inversion symmetry in the 3D Dirac semi-metal Cd_3As_2 with the goal to create ultrafast topological switch from Dirac phase to Weyl phase. Other work includes trying to flip magnetic moments in topological $MnBi_2Te_4$ antiferromagnet.

For x-ray scattering related works, we first highlight our preliminary investigations on the putative excitonic insulator Ta_2NiSe_5. Using RIXS at Ta and Ni L-edges, we observe signatures of the joint-density-of-state between the lowest energy conduction and valence bands. These observations could help us gain further insight into the hybridizations between Ta and Ni states across the transition temperatures. In addition, we also highlight a proof-of-principle experiment in which we used an MCP/timepix fast detector in a time-resolved RIXS measurement at LCLS. Using the detector, we achieved a higher energy resolution for the RIXS measurement and facilitated pulse-by-pulse data acquisition and analysis. This work demonstrates the feasibility of using the MCP/timepix detector at LCLS, as well as the need of LCLS-II for high quality time-resolved RIXS experiments.

In recent experiments, Cuk lab was able to directly measure the spatial extent of a hole-polaron in $SrTiO_3$ (STO) through the strain induced by forming polarons at the interface of a Schottky junction using the phase response of ΔR to coherent oscillations of acoustic waves in transient optical reflectance spectroscopy. The polaron is be formed within 0.5 nm of the interface—a little larger than the Ti-O-Ti lattice constant. We can verify this by different conditions where the strain is generated not by charge-trapping to create surface polarons, but rather by heat from laser absorption; the phase change is 90°. Alongside optical transitions (near-IR, VIS) which report primarily on the charge trapped in the polaron, characteristic vibrational modes (mid-IR) which report on the symmetry of the accompanying lattice distortions, this GHz-THz spectroscopy on the polaron size advances the microscopic view of the polaron using ultrafast spectroscopy.

Future Plans

We expect to commission the Momentum Microscope at SLAC in preparation for trARPES beamtimes at LCLS-II. In parallel, we will develop complementary lab-based trARPES, and spin/time-resolved ARPES, as well as optical experiments to identify most suitable science case and material candidates for such LCLS-II experiments. Part of this development will be toward establishing THz-pump, ARPES-probe capabilities for the study of phonons, CDW amplitude modes, Higgs modes in superconductors, and photocurrents in topological materials.

We plan to continue to explore excitonic physics using RIXS. In addition, we also plan to resume our investigations on polaronic behaviors in quantum materials, taking the bi-layer manganite as our model system. These works will lay foundation for the future time-resolved RIXS experiment at LCLS-II. In addition, we will also join LCLS scientists for both instrument commission and early science programs. In particular, we will collaborate to establish expertise at SLAC that is crucial to implement the polarization analysis capabilities at the RIXS instrument of LCLS-II. This implementation can open up new scientific areas at LCLS-II.

We are planning for THz-pump, optical-probe experiments with our newly built cryostat setup in Matthias Hoffmann's lab. Areas of interest include novel mechanisms for driving coherent phonons in topological materials as well as polaronic liquid like manganites.

We plan to explore the formation of a small polaron using a UV-pump that generates polarons at the interface of a transition metal oxide and time-resolved x-ray diffraction of the atomic positions. The transient optical experiments on STO provide a basis for this, in that they report on the time-dependent strain deformations in the continuum limit; the x-ray probe would provide the needed atomic resolution to understand local bond-reorganization. This could be extended to materials in which the spatial extent and nature of the polaronic distortions are directly relevant to their collective properties, such as manganites.

FY 2020 Journal Publications:

Category 1

1) A. Gauthier, J. A. Sobota, N. Gauthier, K.-J. Xu, H. Pfau, C. R. Rotundu, Z.-X. Shen, and P. S. Kirchmann
Tuning time and energy resolution in time-resolved photoemission spectroscopy with nonlinear crystals
J. Appl. Phys. **128**, 093101 (Sept. 2020)

2) N. Gauthier, J. A. Sobota, M. Hashimoto, H. Pfau, D.-H. Lu, E. D. Bauer, F. Ronning, P S. Kirchmann, and Z.-X. Shen
Quantum-well states in fractured crystals of the heavy-fermion material $CeCoIn_5$
Phys. Rev. B **102**, 125111 (Sept. 2020) [Editor's Suggestion]

Category 2 (collaborative publications)

3) S.N. Rebec, T. Jia, H.M. Sohail, M. Hashimoto, D. Lu, Z.-X. Shen, and R.G. Moore
Dichotomy of the photo-induced 2-dimensional electron gas on $SrTiO_3$ surface terminations
Proceedings of the National Academy of Sciences **116**, 16687 (Aug. 2019)

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Physical Review Letters **123**, 066402 (Aug. 2019)

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Metallic Surface States in a Correlated d-electron Topological Kondo Insulator Candidate $FeSb_2$
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Momentum-resolved resonant inelastic soft X-ray scattering (qRIXS) endstation at the ALS
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Nature Physics **16**, 218 (Jan. 2020)

12) M. Hepting, D. Li, C.J. Jia, H. Lu, E. Paris, Y. Tseng, X. Feng, M. Osada, E. Been, Y. Hikita, Y.-D. Chuang, Z. Hussain, K.J. Zhou, A. Nag, M. Garcia-Fernandez, M. Rossi, H.Y. Huang, D.J. Huang, Z.-X. Shen, T. Schmitt, H.Y. Hwang, B. Moritz, J. Zaanen, T.P. Devereaux, and W.S. Lee
Electronic structure of the parent compound of superconducting infinite-layer nickelates
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Review of Scientific Instruments **91**, 033905 (Mar. 2020)

14) Y. Wang, Y. Chen, C. Jia, B. Moritz, and T. P. Devereaux
Time-Resolved Resonant Inelastic X-Ray Scattering in a Pumped Mott Insulator
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Spectroscopic fingerprint of charge order melting driven by quantum fluctuations in a cuprate
Nat. Phys. (Aug. 2020)

16) Z. Zhang, A. S. Fisher, M. C. Hoffmann, Z. Huang, B. Jacobson, P. S. Kirchmann, W.-S. Lee, A. Lindenberg, A. Marinelli, E. Nanni, R. Schoenlein, M. Qian, S. Sasaki, and J. Xu,
A high-power, high-repetition-rate THz source for pump–probe experiments at Linac Coherent Light Source II
J. Synchrotron Rad. **27**, 890 (June 2020)

FY 2019 Journal Publications:

H. Soifer, A. Gauthier, A. F. Kemper, C. R. Rotundu, S. L. Yang, H. Xiong, D. Lu, M. Hashimoto, P. S. Kirchmann, J. A. Sobota, Z. X. Shen
Band-Resolved Imaging of Photocurrent in a Topological Insulator
Phys. Rev. Lett. **122**, 167401 (2019)

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

Principal Investigator: Prof. Oleg G. Shpyrko, University of California San Diego

1. Program Scope:

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 and XFEL facilities.

Our program has two major topical branches:

(1) Nanoscale Dynamics – including ultrafast, driven dynamics (studied by Ultrafast X-ray scattering at XFELs as well as sometimes synchrotron facilities), as well as slow, glassy dynamics processes (studied by X-ray Photon Correlation Spectroscopy, or XPCS),

and

(2) X-ray Imaging, using either Coherent X-ray Diffractive Imaging (CXDI) or Nano-diffraction/Nano-spectroscopy techniques. A major "holy grail" challenge involves studying evolution of materials and devices properties and functionalities under operating (operando) conditions, and our primary focus was on understanding the role played by defects and their dynamics in defining those functionalities, as seen in real devices, under real operating conditions, in real time.

2. Recent Progress (Selected):

2.1 Nanoscale Dynamics

Studies of Spin-Phonon, and Charge-Phonon interactions via Ultrafast X-ray Scattering

The spin-phonon interaction in spin density wave (SDW) systems often determines the free energy landscape that drives the evolution of the system. [1,2] When a passing energy flux, such as photoexcitation[3], drives a crystalline system far from equilibrium [4,5], the resulting lattice displacement generates transient vibrational states. [P1] We expanded on our previous studies demonstrating transient enhancement of CDW order parameter in Chromium [6] using a traditional pump-probe (single photoexcitation followed by an x-ray probe) with a study that included double photoexcitation [6] with an X-ray Free-Electron Laser (XFEL) probe to control and detect the lifetime and magnitude of the intermediate vibrational state. [P2, P3]

Additionally, we investigated the energy transfer process to the optically pumped phonons in a Cr thin film using ultrashort x-ray pulses from a free-electron laser. [P1] In addition to measuring and confirming the known long-wavelength dispersion relation of Cr along a particular acoustic branch, we are able to determine the relative phase of the phonons as they are generated. The Cr sample exhibits two generation mechanisms for the phonons: the releasing of a preexisting charge density wave at higher frequencies, and the creation of an acoustic strain pulse via laser heating that dominates at lower frequencies. For the latter mechanism, we are able to measure

the frequency dependence of the time required to generate the phonons. The absolute magnitudes of the delay times measured are found to be much shorter than the equilibrium electron-phonon coupling times we compute, indicating that the coupling strength is greatly enhanced when the electronic system is out of equilibrium with the lattice, as has been seen in bismuth and other systems. [P1]

Resonant X-ray Photon Correlation Spectroscopy Studies of Domain Dynamics in Magnetite

Mesoscale phenomena plays an important role in the dynamics of phase transitions in strongly correlated electron systems. In order to fully understand and tailor the mesoscale functionalities in complex oxides, detailed access to nanoscale regime, correlation lengthscales, and temperature evolution of the order parameter is required. We used X-ray Photon Correlation Spectroscopy (XPCS) at National Synchrotron Light Source II (NSLS-II) to investigate collective dynamics and thermal fluctuations in magnetite near the metal-insulator transition. The first regime is characterized by an Arrhenius trend where the fluctuations in orbital order increase as a function of increasing temperature, yet the system remains insulating. In the second regime, the phase separation into the metallic and insulating domain occurs, and the kinetics is governed by the interfacial energy between the insulating and metallic interface. These studies show that the evolution of orbital fluctuations results in a two-step mechanism for thermally driven phase transition in magnetite. [P4, P5]

Methodology of extending XPCS to XFELs
One of the challenges of modern XPCS beamline setups at XFELs is the angular mismatch (and often the positional mismatch) between the split-and-delay x-ray pulses arriving at the sample. We have addressed these challenges in our recent study that demonstrates that even angular spread of the x-ray beams greated than the angular dimensions of the speckle size can be effectively utilized to perform XPCS or speckle visibility (XSV) measurements at ultrafast timescales. [P6]

2.2 Operando Imaging of Defect Dynamics:

Spectro-nanoscopic operando imaging of electric-pulsed driven proton-doping in perovskites. We investigated the microscopic distribution of hydrogen ions in hydrogen-doped nickelates by performing in operando X-ray studies of a representative in-plane nickelate device. For this experiment, a perovskite nickelate $SmNiO_3$ in-plane device is catalytically doped with protons using a Pd electrode on top of the film through annealing in forming gas. We then apply electrical stimuli to the nickelate device and track the changes in the electronic structure by measuring X-ray absorption spectra (XAS) maps. [P7]

Nanoscale Operando Imaging of volatile vs. persistent Mott transition in VO_2.
We performed operando imaging of electrically driven metallic filament formation in VO_2 devices. While under most conditions the resistive switching is volatile (i.e. metallic filament persists only while voltage is applied to the sample), large voltages and/or longer time of applied voltage result in persistent metallic state of the device which remains conducting even once voltage is turned off. Our combined x-ray imaging/fluorescence/diffraction measurements provide a detailed nanoscopic picture of the formation of the filament and indicate that migration

of oxygen vacancies facilitated by large current is likely responsible for persistent metallic state, which can be re-set back to insulating behavior after annealing. [P8] This work builds up on other nanoimaging of VO2. [P9, P10]

We have also carried out several CXDI measurements of magnetic nanocrystals under applied magnetic fields [P11, P12] as well as ultrafast x-ray scattering [P13].

3. Future Plans

Defect Formation and Degradation Mechanisms in Perovskite Solar Cells

The transition towards renewable energy is one of the most profound challenges of today's science and technology and requires the discovery of novel phenomena and materials. Perovskite solar cells are a promising new area of study, with efficiencies reaching over 20% in just 5 years of research. [7-12] A major problem preventing commercial use of this new solar technology is their lack of stability against heat and humidity. [7,10,11]

Solar power has the potential to provide for the energy needs of the entire world. Hybrid perovskite solar cells (PSCs) are a cheap, easy-to-make alternative to more traditional silicon and GaAs-based photovoltaics and have already equaled or surpassed the efficiency of established thin-film technologies such as cadmium telluride, copper indium gallium selenide-based cells (CIGS), organic photovoltaics, and amorphous silicon. Highly-localized defects, such as impurities or single-structural defects, can shunt the diode and cause large recombination currents and losses in efficiency. Synchrotron-based nanoscale characterization of defects in silicon, thin-film, and organic solar cells [13-16] have led to fundamental understanding of the large-area efficiency losses caused by nanoscale defects. Recently, similar insights from synchrotron-based characterization of perovskite solar cell materials have begun to be established. [15,16]

The aim to utilize Coherent X-ray Diffractive imaging to understand the microstructural origins of performance degradation in perovskite solar cell materials.

We aim to study the thermal and moisture stability of mixed-cation formamidinium-cesium (FA/Cs) lead bromide perovskite solar cells [8,11] by CXDI in Bragg geometry. By using Bragg CXDI, we aim to follow the dynamic evolution of the crystal structure as a function of humidity and temperature in a number of hybrid perovskites in order to elucidate their role on the overall stability.

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

PIs: Andrej Singer (Cornell), Darrell Schlom (Cornell), Kyle Shen (Cornell), Nicole Benedek (Cornell), John Harter (UCSB)

Program scope

This research aims 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

Controlling phonon lifetime and electronic instability with light: The spin-phonon interaction in spin density wave (SDW) systems often determines the free energy landscape underpinning the system's evolution. When a passing energy flux, such as photoexcitation, drives a crystalline system far from equilibrium, the resulting lattice displacement generates transient vibrational states [2]. The manipulating intermediate vibrational states in the vicinity of the critical point, where the SDW order parameter changes dramatically, would then allow dynamical control over functional properties. We combined double photoexcitation with an X-ray Free-Electron Laser (XFEL) probe to control and detect the lifetime and magnitude of the intermediate vibrational state near the critical point of the SDW. We applied Landau theory to identify the control mechanism as a repeated partial quench and sub-picosecond recovery of the SDW. Our results showcase the capabilities to influence and monitor quantum states by combining multiple optical photoexcitations with an XFEL probe. They open new avenues for manipulating and researching the photoexcited state's behavior in charge and spin order systems near the critical point (see **Fig. 1**).

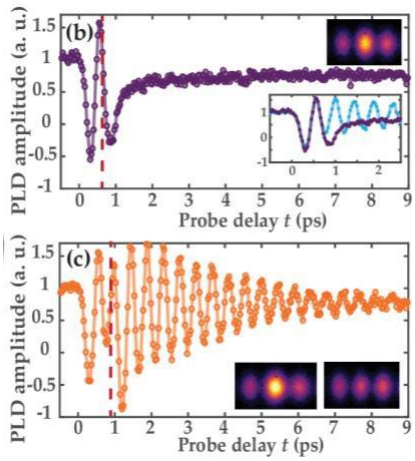

Fig. 1: **Femtosecond control of phonon dynamics near a magnetic order critical point.** Using the critical point of a spin density wave, we can induce a phonon, enhance damp it entirely after an arbitrary number of periods (a) or increase its lifetime (b) (the fist laser pulse arrives at t=0 ps, second pulse arrives at the dashed vertical line). The insets show the x-ray data [Oleg Gorobtsov et al. under review].

Symmetry breaking electronic instabilities drive ordering transitions in condensed matter. Despite many advances in the microscopic understanding of the ordered states, a more nuanced and profound question often remains unanswered: how do the collective excitations influence the electronic order formation? Here, we study the formation of the spin density wave

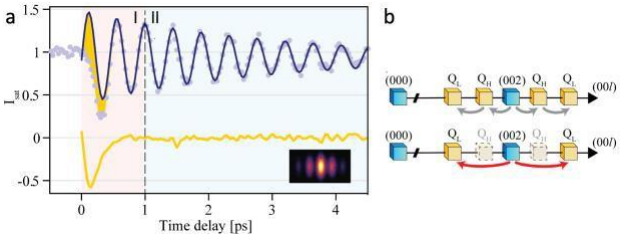

Fig. 2: Phonon-assisted formation of a Spin Density Wave. We use x-ray diffraction for tracking the transient SDW order parameter through its coupling to the lattice (a). We find that after the quench, the order parameter recovers with the low temperature period, thereby directly bypassing a state expected in thermal equilibrium (b). [Jiaruo Li et al., submitted]

(SDW) after its quench by femtosecond laser pulses. By exploiting the persistent spin-lattice coupling, we probe the SDW through the transient lattice distortion, measured by femtosecond X-ray diffraction. In a thin film, the temperature-dependent SDW period is quantized, allowing us to probe the out-of-equilibrium formation path of the SDW precisely. We find that within 500 femtoseconds after a complete quench, the SDW forms with the low-temperature period, directly bypassing a thermal state with the high-temperature period. Our results show how a coherent ionic lattice vibration markedly modifies the pathway and the timescale of an electronic phase transformation, highlighting the opportunity for using collective excitations to guide electronic instabilities. Furthermore, we demonstrate how diffraction at X-ray lasers and persistent spin-lattice coupling enable momentum-resolved interrogation of the transient electronic order in the presence of collective excitations.

Understanding electronic, magnetic, and structural properties of strained Ca_2RuO_4

Tuning magnetism in a strained quantum material: CRO is a strongly correlated material whose antiferromagnetic insulating ground state is susceptible to external stimuli. For example, a CRO film under compressive epitaxial strain becomes a ferromagnetic metal [3,4]. Here, we show that by using epitaxial strains with various strengths and symmetries, we achieve the ferromagnetic CRO films with the highest T_C ever reported and tailor magnetic anisotropies in the ferromagnetic state. We have used oxide MBE to grow CRO films on $SrLaAlO_4$ (SLAO) (001) and $YAlO_3$ (YAO) (110) substrates, whose high crystal quality is characterized by HAADF-STEM images with sharp interfaces and no trace of dislocations, as shown in Figs. 1(a) and (b). SLAO has a tetragonal lattice and imposes isotropic compressive biaxial strain to CRO films up to 3.5%. YAO has an orthorhombic lattice and imposes anisotropic compressive biaxial strain to CRO films with 3.5% and 4.9% along both in-plane directions. As a result,

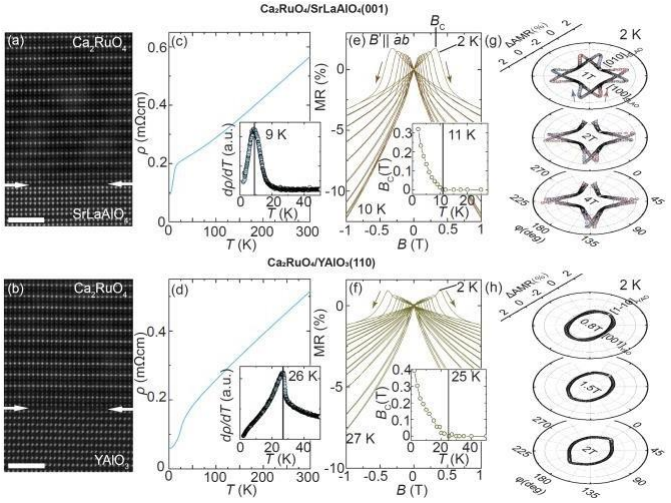

Fig. 3: Controlling ferromagnetic easy axis of CRO/SLAO (001) and CRO/YAO (110) films via epitaxial strain. (a) and (b) HAADF-STEM images with the 3 nm scale bar. (c) and (d) In-plane resistivity ρ as a function of the temperature T. The insets are the temperature derivatives of the resistivities $d\rho/dT$, showing the Curie temperature T_C at the peak. (e) and (f) ρ as a function of the magnetic field B showing ferromagnetic hysteretic behaviors, measured at various temperatures. The field sweeping directions are labeled by the arrows. The insets are the coercive field B_C as a function of T, where B_C is defined as the field value where the magnetoresistance reach the maximum value. (g) and (h) In-plane anisotropic magnetoresistance as a function of magnetic field azimuthal angle φ measured at various field strengths and a temperature of 2K. [Shen, Schlom, unpublished]

both kinds of films are ferromagnetic metal, characterized by a low-temperature resistivity drop, with $T_C \sim 9$ K and 26 K, respectively, as defined by the maximum slope in resistivity temperature curves (see Figs. (c), (d)). The hysteretic behavior in the magnetoresistance further confirms the ferromagnetism (see Figs. (e),(f)). Due to the large strength of the strain, we note that the CRO/YAO film has much higher T_C than that of all previously reported CRO films [3,4].

We probed the magnetic anisotropy in the ferromagnetic states by the anisotropic magnetoresistance (AMR). AMR exhibits minimal value when the applied magnetic field is along the easy axes due to the minimal spin scattering. We found that the easy axes of these films are along the in-plane direction. However, their in-plane magnetic anisotropies are distinct. The CRO/SLAO film displays a 4-fold symmetric magnetic easy axes, along four in-plane Ru-O bond directions, whereas the CRO/YAO film display a 2-fold symmetric magnetic easy axes which are along $[001]_{YAO}$ directions (only two of the in-plane Ru-O bond directions, see Figs. 1(g), (h)). In addition to their distinct symmetries, these magnetic axes are also different from that in an antiferromagnetic CRO bulk, where the spins are 45° tilted from Ru-O bond directions. These results demonstrate a practical approach to tailor the magnetic anisotropy in strongly correlated oxide thin films in general and open new avenues for ultrafast tuning magnetism with light.

Electronic control of magnetism in a strained quantum material: Here, we also show that the ferromagnetism in CRO can be electrically controlled, which is not only extremely critical in device applications but also shed new light in understanding the emergent ferromagnetic phase itself. To apply the electric field control, we use a 150-nm thick amorphous SiO_2 as the gate dielectric in a top-gated field-effect transistor (FET) device (see Fig. 2(a)). Fig. 2(b) shows the resistivity-temperature curve under various gate voltages applied from room temperature, which exhibits a metal-to-insulator transition as well as the complete suppression of the ferromagnetism. A close examination of the T_C as defined by maximum resistivity slope shows a non-monotonic dome-like behavior, as shown in the inset of Fig. 2(b). The dome-like behavior is much more apparent in the gating dependence of the ground state coercive fields, as shown in Fig. 2(c). In Fig. 2(d) we summarize the gate-temperature phase diagram of the CRO/SLAO. Below V_G = 20V the device has a ferromagnetic ground state with a weak-dome-like T_C reaching maximum at V_G = 15V. Beyond V_G = 20V the device has a metal-to-insulator cross over at low temperatures. To understand the physical origins, we looked into the tight-binding calculated band structure of a similar nearly ferromagnetic $Ca_{0.8}Sr_{0.2}RuO_4$ bulk, which was directly confirmed by

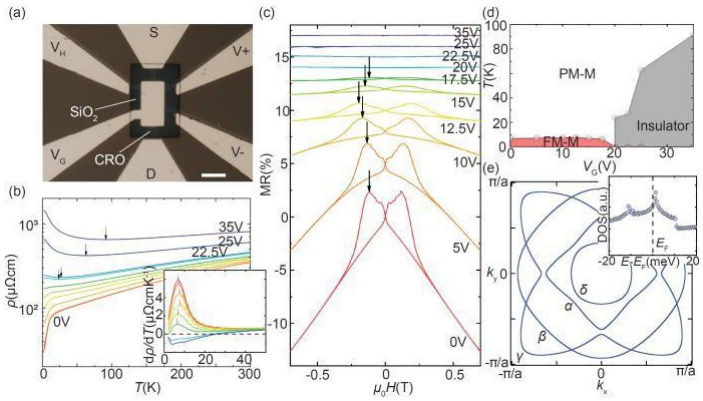

Fig. 4: Electrical control of ferromagnetism in CRO/SLAO (001) films. (a) Optical microscopic image of a CRO field effect transistor device, with a 20 μm scale bar. (b) In-plane resistivity ρ as a function of T under various gate voltage V_G, showing a metal-to-insulator transition. The inset is dρ/dT as a function of T, showing the Curie temperature T_C at the peaks.(c) In-plane magnetoresistance MR as a function of applied field H, measured under various V_G, at 2 K. The data is shifted vertically for clear comparison. (d) A summary of the temperature-gate phase diagram, where FM-M stands for ferromagnetic metal and PM-M stands for paramagnetic metal. (e) Speculated Fermi surface of CRO/SLAO films, based on the tight binding model calculation in ref. [1], for a similar compound of metallic $Ca_{0.8}Sr_{0.2}RuO_4$. The inset is the density of state (DOS) as a function of binding energy E-E_F. [Shen, Schlom, unpublished]

ARPES band measurements [1], and assume that this band structure carries the major characteristics of the ferromagnetic CRO/SLAO films. The Fermi surface is characterized by four bands, namely α-δ bands, as shown in Fig. 2(e). At 2 meV above Fermi level, α and δ touch and undergo a Liftshitz transition, leading to a sharp peak in the density of states, known as the van Hove singularity (vHs), as shown in the inset of Fig. 2(e). Here, we tentatively explain the above results using this vHs: the large density of states in the very close vicinity (order of 2 meV) of the vHs favors Stoner criteria and leads to itinerant ferromagnetism in CRO/SLAO thin films even with zero gate bias. At V_G = 15 V (electron doping), the Fermi level is tuned at the vHs point, leading to the maximum T_C and coercive field strength.

X-ray nano-diffraction in a strained quantum material: The origins of a Mott metal-insulator transition (MIT) lie in an interplay of structural, electrical, and magnetic effects. The multitude of degrees of freedom opens a wide variety of control possibilities, including pressure, current, and - in thin coherent films – strain engineering. Such a flexibility makes Mott insulators attractive for technological applications in memory elements, optical switches, and brain emulation, but also makes understanding them challenging. In materials where the MIT is structurally driven, such as the layered perovskites $Ca_{2-x}Sr_xRuO_4$, strain engineering provides a particularly powerful tool to alter the transition properties, specific to thin coherent films and unavailable in a bulk material. Therefore, understanding the strain engineered MIT transition in coherent films is crucial for their application in electronics. We have performed x-ray nanoprobe measurements on a thin film Ca_2RuO_4 with a strain-engineered prolonged metal-insulator transition. We mapped the structural changes in the film at different points during the transition, tracking the distribution of structural phases between room temperature and 60 K. We applied principal component analysis to the results of nanoprobe measurements to gain further insight into the structure. We observe domains of the low-temperature phase of a 100-300 nm width growing and orienting along a single direction at lower temperatures. The domains are extrinsic and not pinned by defects, growing differently at repeated heating and cooling the film.

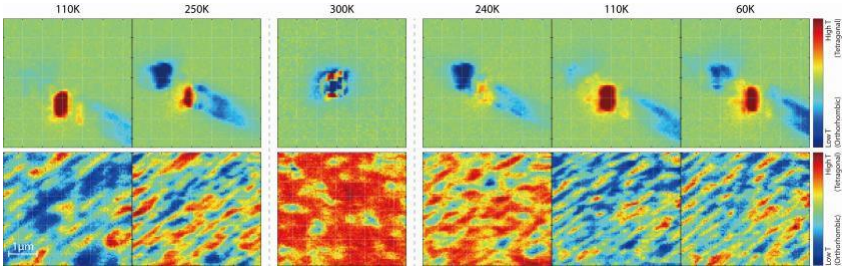

Fig. 5: Intrinsic heterogeneity of a Mott insulator revealed by X-ray nanoimaging. In a thin Ca_2RuO_4 film we use x-ray nanobeams for imaging the phase distribution of the high temperature and low temperature domain. Top row: distribution of the diffraction signal in the reciprocal space, bottom row: the distribution of phases determined in nanoimaging (image 4 μm **x** 4 μm). [Singer, Schlom, Shen unpublished].

Light induced phase transformation in a strained quantum material: On the same strained Ca_2RuO_4 thin films investigated in static conditions, we have performed pump-probe x-ray measurements at SACLA: we induced a structural phase transition with laser pulses and interrogated the response with diffraction experiments (reciprocal space mapping) with a sub-picosecond resolution. Starting from the low temperature phase, high fluence laser pulses

transform the system into the high temperature phase including a volume change within 1 ps, showing unique dynamics inaccessible in bulk (see **Fig. 6**).

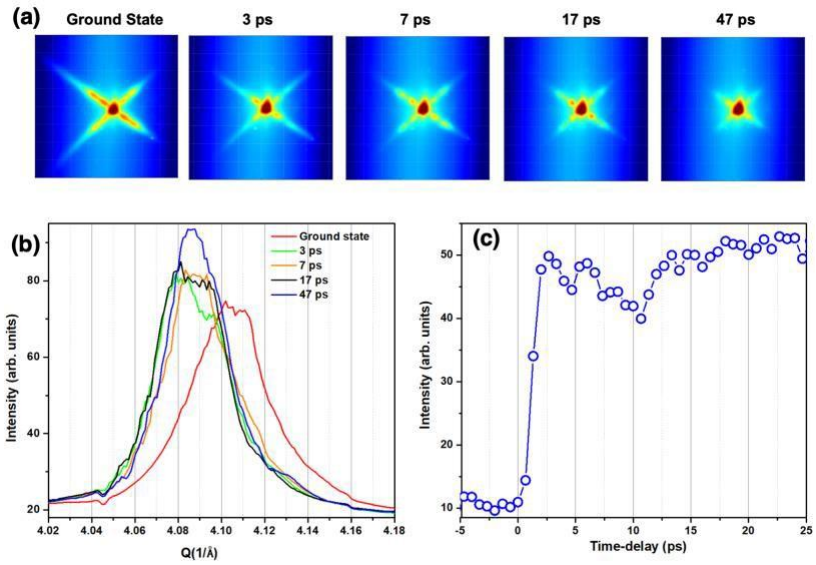

Fig. 6: Light induced phase transformation in a strained quantum material. (a) Slices through the reciprocal space perpendicular to the scattering vector (008). The image spans 1 nm^{-1}. (b) The transient position of the Bragg peak. (c) The intensity of the HT peak as a function of the time delay at a fixed position of the Ewald sphere. [Singer, Schlom, Shen unpublished].

Nematic type of symmetry in Sr_2RuO_4 thin films: One of the principal goals of this project is to explore mechanisms by which ultrafast optical pulses can be used to guide materials into novel ground states. Recently, electronic nematicity or a large nematic susceptibility was uncovered in high-quality Sr_2RuO_4 thin films using angle-resolved transverse resistivity measurements[5]. Motivated by this work, we have started to investigate ultrafast control of this nematic state using optical pump-probe experiments, and preliminary results are promising. Figure 7 (a) shows the change in probe reflectivity (800 nm) induced by a pump pulse (1515 nm) as a function of time delay between pump and probe. While the long-timescale differential reflectivity is independent of scattering plane angle, the short-timescale behavior shows a marked dependence on angle. This can be more clearly seen in Figure 7 (b), which shows the rotational anisotropy of the differential reflectivity (integrated within the region indicated in Figure 7 (a)). The transient response shows a striking C_2 symmetry, in stark contrast to the static reflectivity, which shows isotropic behavior. Remarkably, the data suggests that while the electronic nematicity does not manifest in the static reflectivity itself, it couples strongly to the ultrafast transient electronic response. We anticipate this preliminary work will motivate future XFEL experiments exploring the ultrafast control of electronic nematic order in Sr_2RuO_4 thin films.

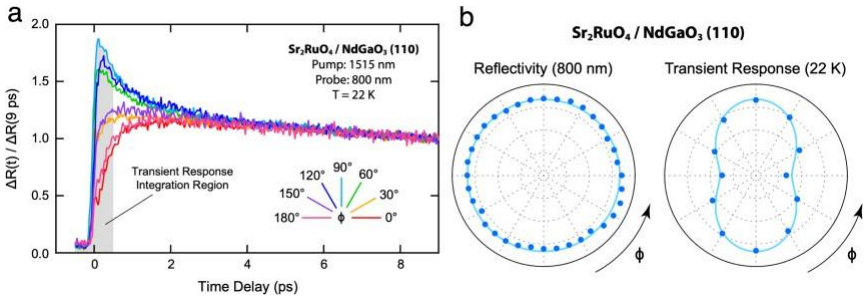

Fig. 7: Rotational anisotropy in the transient reflectivity in Sr2RuO4. (a) change in probe reflectivity (800 nm) induced by a pump pulse (1515 nm) as a function of time delay between pump and probe. (b) Angular dependent reflectivity. [Harter, Schlom, Shen, unpublished].

Future work

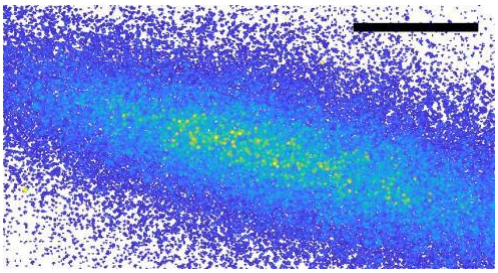

Fig. 8: X-ray speckle recorded 1 ps after photoexcitation at LCLS. The horizontal direction is approximately along the scattering vector, normal to the thin film surface. The scale bar is 0.1 nm^{-1}.

Femtosecond x-ray speckle metrology: To investigate how the induced phases emerge in space and time we will use speckle interferometry. In conventional x-ray diffraction, interference between neighboring atoms produces Bragg peaks. Coherent x-rays at novel synchrotron sources and XFELs allow recording interference from extended objects, for instance, multiple nucleation centers during a phase transition. Intensity correlations in momentum space are directly related to order parameter fluctuations in real space. During each realization of the phase transition (after each photoexcitation) the non-thermal phase nucleates and forms domains. The coherent speckle measured at a fixed time delay will reflect the exact domain configuration. Different domain configurations will generate different speckle patterns, enabling categorizing transition pathways. Figure 7 shows a speckle pattern recorded at LCLS in a recent experiment (Run 18, LV77).

ARPES on strained ruthenates: We have obtained some preliminary ARPES data on CRO/SLAO films and discovered that their band structures are indeed very similar to those of nearly ferromagnetic $Ca_{0.8}Sr_{0.2}RuO_4$ bulk. However, the data quality is limited due to the ex-situ MBE-ARPES transferring process, which compromises the film's surface quality and thus affects the surface-sensitive ARPES measurements. Now, in order to decisively understand the ferromagnetism in CRO films as well as its electrical control, we are building an in-situ MBE-APRES system for our dedicated ruthenate MBE chamber and will perform in-situ MBE-ARPES experiments to obtain high-quality band structure data on ferromagnetic metallic CRO films such as CRO/SLAO and CRO/YAO. We will also carry out ARPES measurements on more insulating films such as CRO/$LaAlO_3$ and CRO/$NdGaO_3$ to shed light on the strain-induced metal-to-insulator transition physics, as well as ultrafast time-resolved physics, which is also related to the CRO lattice deformation. These future experiments should be a critical piece in the jigsaw puzzle for understanding the fundamental mechanisms in CRO and serve as a strategy to guide the ultrafast control of CRO out of equilibrium.

Deterministic structural switching through giant nonlinear phononics: Extensive first-principles density functional theory studies by our team have identified various switching pathways and barriers. The most promising of these involves applying a modest amount of tensile epitaxial strain such that the symmetry is lowered from the equilibrium R-3c (#167) space group to orthorhombic Imma (#74). Excitation of an IR-active phonon in this orthorhombic phase results in transient ferroelastic switching via a phase with Fmmm symmetry. Since the Imma and Fmmm phases are crystallographically distinct, the switching process should be observable in an ultrafast X-ray experiment. Indeed, we will be testing this prediction on thin-films of $LaAlO_3$ grown on NSAT by Schlom at LCLS (Run 18, March 2021, LV79).

We have also recently initiated new theoretical work aimed at elucidating the chemical underpinnings of the anharmonic lattice coupling pathways that drive ultrafast optical processes, such as that described above for LaAlO3. Although prior theoretical work has provided some insights into the physical mechanisms of ultrafast structural switching, none of this work has addressed the chemical underpinnings of the mechanism, a critically needed advance to

systematically identify materials that may exhibit particularly large or unusual responses. We have recently developed a new theoretical and computational framework that allows us to precisely and systematically decompose the anharmonic coupling constants that control structural switching into contributions from different atoms and electronic states. As a first step, we are using this technique to understand the effects of epitaxial strain and hydrostatic pressure on ultrafast structural switching in $LaAlO_3$ and $SrTiO_3$.

Remote epitaxy of free-standing single crystals: We will use "remote epitaxy" to make freestanding single crystals of $LaAlO_3$ and RuO_2 that are a few nanometers thick. Remote epitaxy is a technique utilizing graphene to enable the epitaxial growth of thin layers that once grown can be peeled off from the substrate.[6-10] This liberating technique makes it possible to integrate single-crystal stacks of structurally and chemically incompatible materials. It was pioneered by Jeehwan Kim from MIT over the last few years starting with semiconductors, but our recent joint work shows that it also works spectacularly for oxides.[11] Once freed from the underlying substrate we will impose uniaxial and biaxial strain on these ultrathin single crystals. Having ultrathin free-standing films makes it possible to impose huge strains on oxides before they break. For example, uniaxial tensile strains as high as +8.2% and biaxial tensile strains as large as +5% were recently imposed on $La_{0.7}Ca_{0.3}MnO_3$ membranes.[12] In addition to using the imposed strain to alter the ground state of these ultrathin $LaAlO_3$ and RuO_2 single crystals, we will use strain to position the ground state in a desired initial position from which it will be photoexcited to access other metastable states.

Presentation layout:

Our work is put together in a single presentation with narration in PowerPoint. Playing the slides will play the narration. One can also play a specific slide separately. The presenters (slide numbers) are:

Past work: Singer (1-4), Shen (5-9), Harter (10-12), Singer (13)

Future work: Singer (14), Shen (15-16), Benedek (17-18), Schlom (19-20)

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J. P. Ruf, H. Paik, N. J. Schreiber, H. P. Nair, L. Miao,1 J. K. Kawasaki, J. N. Nelson, B. D. Faeth, Y. Lee, B. H. Goodge, B. Pamuk, C. J. Fennie, L. F. Kourkoutis, D. G. Schlom, and K. M. Shen, "Strain-stabilized superconductivity", in review, preprint at: arXiv:2005.06543

Oleg Gorobtsov, Louis Ponet, Sheena Patel, Nelson Hua, Anatoly Shabalin, Stjepan Hrkac, James Wingert, Devin Cela, James Glownia, Diling Zhu, Rajasekhar Medapalli, Matthieu Chollet, E.E. Fullerton, Sergey Artyukhin, Oleg Shpyrko, Andrej Singer, "Femtosecond control of phonon dynamics near a magnetic order critical point", in review, preprint https://doi.org/10.21203/rs.3.rs-40430/v1

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

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DESC0019096

This project aims to develop methods for multiscale x-ray measurements for probing microstructural responses in polycrystals under a wide range of loading conditions. The aim is to combine existing methods such as High Energy Diffraction Microscopy (HEDM) that probes on the micron to millimeter length scales with Bragg Coherent Diffractive Imaging (BCDI) that is sensitive to individual crystalline defects and their motions. The motivation is that this range of length scales includes the fundamental units of deformation (dislocations, their motions and interactions with each other and other types of defects) and the length scales over which macroscopic emergent behavior is seen. Combining information in related samples and measurements will provide unique and critical input for model development.

While both HEDM and BCDI are existing measurement methods, there are shortcomings in both that currently prevent necessary physics from being extracted. This following gives a brief list of our (and our collaborators') progress toward bringing these methods together.

HEDM

- Robust and scalable reconstructions of near-field HEDM maps of grain structures from collected diffraction images. We have implemented Python – PyCUDA based GPU codes (referred to as HEXOMAP for High Energy X-ray Orientation Mapping) that can run on machines from workstations to GPU loaded supercomputers. Output formats are a simple square lattice of points in two dimensions that can be stacked to form 3D structures. A variety of optimizations are available such as checking for twin-related neighboring grains. This code has been applied to simple and to multi-phase material states.
- Also in near-field HEDM, we have developed to ability to extract spatially resolved intra-granular variations in deformation (strain tensor) states from optimized data sets. Deformation tensor optimization can be performed directly on the voxelized lattice output by HEXOMAP. The complete tensor maps are in contrast to the one dimensional projection information obtained in currently standard Dark Field Microscopy or BCDI measurements focused on single Bragg peaks.
- Near-field and far-field HEDM measurement determine unit cell orientations of large ensembles of grains in polycrystals. We have been able to apply FF-HEDM to grains with sizes that are compatible with BCDI measurements at both 34-ID-C and, high energy BCDI at 1-ID-E. These orientations allow selection of nano-sized grains whose full orientation and all relevant Bragg peak positions are known. This capability allows the BCDI measurements to study multiple peaks from a selected grain and thus allows the 3D strain field to be obtained. Further, we expect to be able to obtain sub-micron resolution center-

of-mass positions of these grain through NF-HEDM methods applied to center of mass peak positions.

BCDI and HE-BCDI

- As above, we have worked with both Siddarth Maddali and Stephan Hruszkewycz (Advanced Photon Source) to combine HEDM with HE-BCDI measurements at 1-ID to study fully oriented grains. hopeful current measurements. In the most recent beam time, 10/21-10/27, a new sample design was used with platinum deposited into a trench cut (with a focused ion beam) in a silicon wafer. The sample was annealed at 650 °C to allow the Pt to recrystallize into strain-free grains. The aim of the "trench sample" is to confine the high-Z polycrystalline sample in a narrow line so that determining neighbor relationships is simplified (compared to a polycrystalline thin film). Tomography mapped the location of the line of Pt and far-field HEDM was performed to determine grain orientations. A strongly diffracting grain was identified and BCDI was performed on select reflections. This success opens the way to performing an experiment in which the sample is (gently) heated to obtain thermally-induced stress with the aim of measuring changes in BCDI reflective of changes in defect structures.
- In addition, we are working with Richard Sandberg (BYU), Reeju Pokharel (LANL), Saryu Fensin (LANL), Ross Harder (APS) and Anastasios Pateras (ex-LANL) at 34-ID-C in a related effort to gain full orientation information from grain arrays. The LANL group installed a new monochromator that allows pink beam Laue based orientation maps to be collected and then the double bounce silicon monochromator is put in place to obtain a coherent beam for BCDI. Doctoral student Yueheng Zhang is verifying a code to index orientations in polycrystalline samples so that determining neighbor relationships is made routine. As in the 1-ID effort, the aim is to identify sets of neighboring grains and obtain BCDI data from the set so that interactions between them during loading can be characterized.
- Doctoral student Matthew Wilkin is first author on a manuscript entitled "Multi-Reflection Phase Retrieval with Convergent Support Evolution for Multi-Reflection Bragg Coherent Diffraction Imaging" that describes a new approach to reconstructing strain fields in individual grains. The new approach allows peaks of varying quality to be included in the reconstruction while at the same time refining the support (grain size & shape). This represents a close collaboration with Siddarth Maddali (APS) to advance the state of the art.

Early Career: Fluctuations in Quantum Materials

PI: Joshua J. Turner

SLAC National Accelerator Laboratory

Program Scope: The purpose of this project is to advance the frontier in quantum materials through the measurement of fast, spontaneous fluctuations while in equilibrium. These are at the heart of the fundamental physics in these types of solids, but have never been directly measured. The key component will be the application of a newly developed coherent scattering method which can access these fluctuations on relevant energy scales, referred to as X-ray Quanta Fluctuation Scattering (XQFS). This new tool has been demonstrated on a topological magnetic material [1], and early results point to the tremendous potential for this approach to provide important new insight into fundamental open questions in condensed matter. It 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 [2]. By analyzing X-ray quanta variations as a result of scattering from a solid sample using short X-ray pulses [3], statistics are used to extract the stochastic fluctuation information of the system. This offers the ability to address a range of important current problems in materials physics.

The specific focus will be on the cuprates, the quantum materials known for exhibiting high- temperature superconductivity [4]. These studies will answer a key question which has been the subject of numerous experimental and theoretical investigations: do density wave fluctuations in copper oxides induce high-temperature superconductivity? Answers to this, and related questions, will provide answers to one of the predominant intellectual challenges in the field of condensed matter.

This project will open the door to study how properties of matter emerge from complex correlations of the atomic and electronic constituents and how they can be controlled: one of the grand challenges of the U. S. Department of Energy. Furthermore, the development of XQFS experiments at nanosecond, picosecond, and femtosecond timescales [5] will enable a revolutionary new method to measure equilibrium properties of materials at the nanoscale and over a critical range of time scales that will allow for both a direct comparison to theoretical models and provide necessary information to develop novel materials systems. This project will bring a fresh perspective to understanding quantum materials and has the further potential to go well beyond condensed matter. This research program will connect equilibrium measurements of fluctuations with ultrafast dynamics in a quantum material, a connection with much potential to be explored.

Recent progress

- The dedicated instrument at LCLS-II for condensed matter is called *q-RIXS* and is an instrument currently estimated for delivery on the order of ~ 1 year from now, and will be dedicated to RIXS. This is an ideal place to perform XQFS and therefore we have been working closely with the LCLS-II and the *q-RIXS* design team to ensure the instrument will be able to perform measurements important for work in XQFS and we expect to drive the early science effort at this instrument in this field.
- We published *Phys. Rev. B* **101**, 201103 (2020) led by our Research Associate Lingja Shen on robust orbital density waves in a strongly correlated electron system. This work was highlighted by SLAC in a press release here, and was also chosen by *PRB* as an Editor's Choice.
- We published *Appl. Phys. Lett.* **116**, 181901 (2020) led by our Research Associate Vincent Esposito on fluctuations in a skyrimion lattice system. This is an important XQFS development measured near a first

order phase transition boundary which showed a much different dynamics then what we observed previously deep in the skyrmion phase.

- We have also been working closely with our collaborators in Lund (E. Blackburn *et al*.) and have made some key XPCS measurements at DESY on a high-temperature superconductor at even slower scales, since this was performed at a synchtrotron. These results seem to indicate a very valuable finding in terms of unraveling physics of the pseudo-gap (PG) phase. This will also contribute to future work we will propose at the LCLS-II, as it not only contains valuable information on the PG transition, but indicates the need for faster time studies, especially with application to the CDW phase.
- We are currently establishing a new mode with the team at SSRL to perform resonant soft x-ray scattering remotely of cuprates and other exotic materials that we need to fully characterize before XQFS measurements can take place.
- We have been invited to submit a review article on our new developments in the area of ultra-fast quantum materials by Editors from Modern Physics Letters B. This will be submitted later this year.
- We are currently conducting an international search for the fifth team member to complete the team built around this ECA. This will be a neutron or x-ray person which specializes in fluctuations in quantum materials and will also be shared with Lund University.
- We are working closely with the Integrated Circuits Department Head of the Advanced Instrumentation for Research Division, part of the Technology Innovation Directorate at SLAC, for supporting the research and development of novel ideas for detectors which will be applicable to XQFS. Specifically, new types of detectors, called "Experiment Specific X-ray Cameras", built on the ePix platform, but with a dedicated XQFS-based pixel architecture. Note: for the near future the current detector capabilities will suffice, but for high-repetition rate on the horizon, we need to acquire single-photon counting detectors that run at high repetition rate.
- We have authored a SLAC technical note on the needs for X-ray Quanta Fluctuation Scattering (XQFS) for LCLS-II. This goes into the detail about instrumentation as well as detector needs, and documents how to ensure we will have the capabilities we need to carry out our research program

Future Plans

- The LCLS-II decided to initiate its first soft x-ray experiments in AMO and in liquid phase chemistry experiments. We together with colleagues submitted 4 hard condensed matter proposals that our team is a part of. All four proposals were ranked highly and hence instigated a restructuring of first soft x-ray experiments at LCLS-II. One of the two first soft x-ray beamlines will now lead with the hard condensed matter proposals, originally not part of the program which was intended to focus on chemistry. We are currently designing some modifications to the *chemRIXS* instrument to be able to accommodate the condensed matter experiments, and will now execute this set of experiments in a one-time program dedicated to solids at the start of the run for this LCLS-II instrument.
- The main goal for the next year is to focus on successful XQFS experiments in the soft x-ray range using the new instruments being constructed currently at LCLS-II. Our team is already involved in all of the currently planned condensed matter experiments, half of which are XQFS, which will set the stage for future work we plan to carry out at the *q-RIXS* station, especially when the high-repetition rate option becomes available.
- We will in parallel plan to measure in the hard x-ray range as well at LCLS, but the largest impact in this area is estimated to come from the soft x-ray, with direct sensitivity to electronic order.
- We are continuing to pursue measurements at other X-FEL facilities to supplement these developments.

- We have been awarded beamtime at the European XFEL to try XQFS-type measurements at a slower time-scale based on the repetition rate of that facility. We have chosen appropriate high-temperature superconductors for this study to try to understand how magnetic and charge order fluctuations develop on slower time scales.

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4. S. Droste, S. Zohar, L. Shen, V. E. White, E. Diaz-Jacobo, R. N. Coffee, A. H. Reid, F. Tavella, M. P. Minitti, J. J. Turner, J. S. Robinson, A. R. Fry and G. Coslovich, "High-sensitivity x-ray/optical cross-correlator for next generation free-electron lasers", *Opt. Express* **28**, 23545 (2020) doi: 10.1364/OE.398048

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Correlating tomographic chemical inhomogeneity and low energy electronic structure in layered quantum materials (DE-SC0014697)

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This research aims to develop high-resolution lab-based microARPES and use it in conjunction with standing wave x-ray photoemission spectroscopy (SW-XPS) to close the feedback loop between chemical/structural disorder and emergent low-energy electronic properties in layered quantum materials. Doped topological insulators and intercalated transition metal dichalcogenides will be the initial pilot systems. One aspect of this research will be the development of a lab-based laser microARPES experimental system, crucial for accurate angular information from cleaved 2D materials with curved surfaces, specimens with mesoscale inhomogeneity, and access to specimens with small dimensions. Concurrently, SW-XPS will be pursued both at conventional and microfocused photoemission beamlines, with the goal of applying this photoemission technique as a component of controlling band structure and interactions in quantum materials and also push SW techniques into the realm of microscopy.

In the past year, we have made progress in wrapping up a project on SW-XPS studies on a synthetic multilayer of BFO ($BiFeO_3$,Ferroelectric+AFM) /LSMO ($La_{0.7}Sr_{0.3}MnO_3$, Ferromagnet), where the interface shows combined ferroelectric and ferromagnetic behavior. We have found that depending whether the BFO is on top of LSMO or vis vera, the interface is either really sharp or very diffuse, suggesting that the aforementioned hybrid interface behavior is not strongly dependent on the morphology of the interface. A manuscript is in preparation, and will be posted to ArXiv soon. We have also performed the first SW-XPS measurements on (nominally) Cu-intercalated Bi2Se3 to search for evidence of Cu outside of the van der waals gap. Preliminary data observes Cu in the crystal, and also observes a SW signal for the rest of the elements, indicating that the added copper does not strongly degrade the crystallinity. However, the signal to noise ratio of the copper SW signal is not high enough yet for quantitative conclusions. We have developed a code to simulate the SW experiments on single crystals, intended to be used during experiments to optimize conditions. After additional testing it will be publicly available. We have also implemented a 6eV lightsource and focused it onto the sample position in our ARPES chamber. Estimated spot size is presently several tens of microns.

In the near future, we plan on measuring $Cu_xBi_2Se_3$ at a different lightsource with higher photon flux (remote beamtime), to ascertain the distribution of these nominal intercalants. Additionally, we are very close to achieving an ARPES spectrum from our new lightsource. Once this lightsource is validated, we will move onto the next phase, in which the final focusing lens is placed inside the ARPES chamber, allowing for a beam spot of <10 microns. Going forward, this lightsource can also be applied to spatially resolved pump-probe experiments, in which a spatially-separated (optical) pump pulse is used to either locally heat the lattice near the microfocused UV spot, or more interestingly, is used to initiate a strain wave to provide local dynamic strain whose effects on electronic structure can be measured by the microfocused probe.

Publications resulting from work supported by this DOE grant only over the previous two years:

1. Journal Article: Unexpected termination switching and polarity compensation in $LaAlO_3/SrTiO_3$ heterostructures	
Journal: Physical Review Materials	
Publication Status: Published	**Publication Date:** Nov 2018
Volume: 2	**First Page Number or eLocation ID:** 112001(R)
Issue: 11	**Publication Location:** https://link.aps.org/doi/10.1103/PhysRevMaterials.2.112001
Author(s): G. Singh-Bhalla, P. B. Rossen, G. K. Pálsson, M. Mecklenburg, T. Orvis, S. Das, Y.-L. Tang, J. S. Suresha, D. Yi, A. Dasgupta, D. Doenning, V. G. Ruiz, A. K. Yadav, M. Trassin, J. T. Heron, C. S. Fadley, R. Pentcheva, J. Ravichandran, R. Ramesh	
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2. Journal Article: Depth-resolved resonant inelastic x-ray scattering at a superconductor/half-metallic-ferromagnet interface through standing wave excitation	
Journal: Physical Review B	
Publication Status: Published	**Publication Date:** Dec 2018
Volume: 98	**First Page Number or eLocation ID:** 235146
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Author(s): C.-T. Kuo, S.-C. Lin, G. Ghiringhelli, Y. Peng, G. M. De Luca, D. Di Castro, D. Betto, M. Gehlmann, T. Wijnands, M. Huijben, J. Meyer-Ilse, E. Gullikson, J. B. Kortright, A. Vailionis, N. Gauquelin, J. Verbeeck, T. Gerber, G. Balestrino, N. B. Brookes, L. Braicovich, C. S. Fadley	
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3. Journal Article: An Efficient Algorithm for Automatic Structure Optimization in X-ray Standing-Wave Experiments	
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Volume: 230	**First Page Number or eLocation ID:** 10-20
Issue: -	**Publication Location:** http://dx.doi.org/10.1016/j.elspec.2018.10.006
Author(s): O. Karslıoğlu, M. Gehlmann, J. Müller, S. Nemšák, J. A. Sethian, A. Kaduwela, H. Bluhm, C.S. Fadley	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1016/j.elspec.2018.10.006
Acknowledgment of DOE support: Yes	**Peer Reviewed:** Yes

4. Journal Article: Hard x-ray standing-wave photoemission insights into the structure of an epitaxial Fe/MgO multilayer magnetic tunnel junction	
Journal: Journal of Applied Physics	
Publication Status: Published	**Publication Date:** Aug 2019
Volume: 126	**First Page Number or eLocation ID:** 075305
Issue: 7	**Publication Location:** http://dx.doi.org/10.1063/1.5089556
Author(s): C. S. Conlon, G. Conti, S. Nemšák, G. Palsson, R. Moubah, C.-T. Kuo, M. Gehlmann, J. Ciston, J. Rault, J.-P. Rueff, F. Salmassi, W. Stolte, A. Rattanachata, S.-C. Lin, A. Keqi, A. Saw, B. Hjörvarsson, C. S. Fadley	
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Acknowledgment of DOE support: Yes	**Peer Reviewed:** Yes

Preprint:

1. Preprint: Two-dimensional electron systems in perovskite oxide heterostructures: Role of the polarity-induced substitutional defects	
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Publication Status: Under review	**Publication Date:** Dec 2019
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Understanding Mesoscale Nonequilibrium Heterogeneity by Multimodal X-ray Imaging

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Program Scope

This program is targeted at probing and understanding mesoscale nonequilibrium heterogeneities to help bridge the knowledge gap from atomistic to macroscopic length scales. Snapshots of localized material properties with distinct structural, electronic, and optical characteristics will be captured simultaneously and correlated unambiguously using suitable ultrafast THz, optical or x-ray radiation. The 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.

Recent Progress

Sub-terahertz collective dynamics of polar vortices [1]. Topological structures constructed from electrical polarization rather than spin have recently been realized in ferroelectric superlattices[1,2], promising for ultrafast electric-field control of topological orders. However, little is known about the dynamics of such complex extended polar structures which in turn underlies their functionalities. Using terahertz-field excitation and femtosecond x-ray diffraction measurements (Fig. 1A), we observe ultrafast collective polarization dynamics that are unique to polar vortices, with orders of magnitude higher frequencies and smaller lateral size than experimentally realized magnetic vortices[3]. These collective excitations arise from the unique connectivity of electric polarization ($\boldsymbol{P}$) that continuously rotates around a core with non-zero $\nabla \times \boldsymbol{P}$ in each polar vortex supercell (magenta circles, Fig.1B). The microscopic picture of vortexon mode was obtained by first-principles-based atomistic calculation. In this mode, a transient order of collective atomic motion (purple circles) emerges and interweaves with the static polar vortices (magenta circles). Its time-dependent vorticity $(\nabla \times \boldsymbol{u})$ of atomic displacements ($\boldsymbol{u}$) oscillates on a few picosecond time scales (Fig. 1B). Zoom-in snapshot shows the nanoscale circular patterns of lead ion atomic displacements spanning many unit cells**.** The experimental observations of these modes were made by monitoring the diffraction intensity changes of selected Bragg peaks upon THz-field excitation, in agreement with dynamic phase-field simulation (Fig. 1C). The vortexon mode is sensitively dependent on the in-plane strain, as predicted by the theory (Fig. 1D). The discovery of collective modes of polar vortices is the key to exploring novel

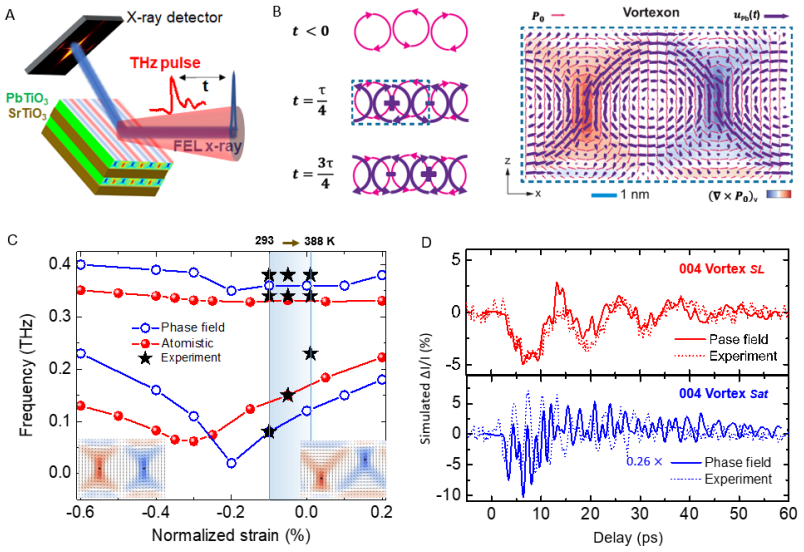

Fig. 1 (A) THz-pump, x-ray diffraction probe of $(PbTiO_3)_{16}/(SrTiO_3)_{16}$ superlattice film using LCLS. (B) The schematics of vortexon (purple circle) emerges and evolves during its oscillation period of T, overlaying with the static polar vortices (magenta circle). "+" and "-" label the signs of its vorticity. The zoom-in view of the dotted box shown on the right is the snapshot of the calculated transient lead-cation displacement (purple) in each unit cell, overlaying the polarization (magenta arrows) and its curl (color) at the ground state. (C) Simulated (solid) and measured (dotted) diffraction intensity of the 004 vortex peaks and satellites as a function of time at 293 K. (D) The calculated frequencies of the collective modes as a function of normalized strain in comparison with experimental data. The vertical blue lines indicate the strain at 293 K and 388 K. The vortex pairs on the bottom shows the calculated ground state for -0.4 and 0.2% strain, respectively.

material properties of polar topological defects and opening opportunities such as in electric-field-driven data processing and storage with ultrahigh speed and density.

XSNOM: a multimodal imaging instrument that integrates scanning near-field optical microscopy with x-ray diffraction microscopy [2]. This new instrument termed "XSNOM" allows simultaneous nanoscale characterization of electronic/near-field optical properties of materials together with their crystallographic structure (Fig. 2A), facilitating the investigation of local structure-property relationships. It also enables AFM-tip-bias control of ferroelectric materials with *in-situ* x-ray microdiffraciton [3]. We anticipate that the APS upgrade to a low-emittance storage ring will further benefit the X-ray diffraction imaging capabilities to improve the XDM spatial resolution to tens of nm.

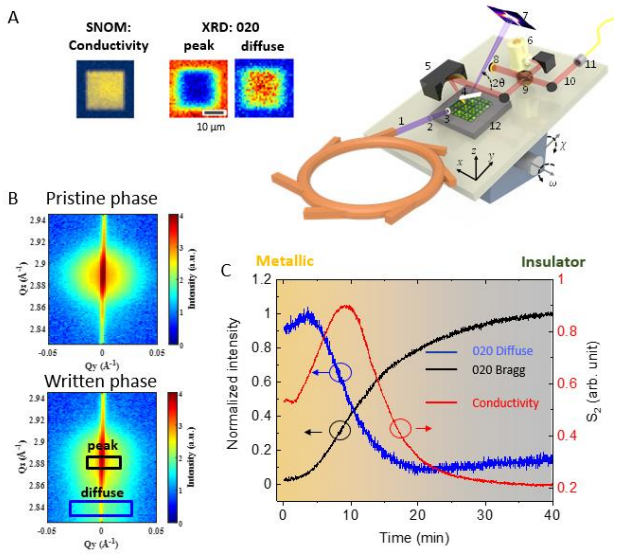

Fig 2. (A) Schematic of XSNOM, which shows the synchrotron x-ray is focused by zone plate to the AFM-tip for SNOM measurements. Left: real-space images of the biased-tip written metallic domains by scanning near-field optical microscopy and x-ray diffraction microscopy. Right: XSOM setup from Ref.[2]; (B) Q_y-Q_z cuts of reciprocal space maps of pristine and written phases. (C) The evolution of diffraction intensity (blue and black) and near-field optical reflectivity (red) as a function of time after written at time zero and under x-ray illumination.

Using this newly developed instrument, we studied nanoscale defect-driven phase transition in VO_2. We first report the insulator to metal phase transition can be realized on nanoscales using a local electric field via sharp metallic tips, in collaboration with Prof. Cen at West Virginia University [4]. Using XNSOM (Fig. 2A), as led by this program, we went beyond the *ex-situ* studies to simultaneously record the structural electronic processes during the defect-driven phase transitions in VO_2. The reciprocal space maps (Fig. 2B) revealed that the written phase exhibited an emergence of diffuse diffraction intensity at the lower Q_z of the 020 Bragg peak. The disordered lattice structure with oxygen vacancy enhanced the metallicity as simultaneously measured by the increase of near-field optical reflectivity (Fig. 2C). Interestingly, we found the written metallic phases were not stable under x-ray illumination. The time-dependent signal changes in the structural and electronic probing channels depicted the evolution of the written phase. The initial increase of near-field optical reflectivity (S_2) peaked at 10 minutes (red curve, Fig. 2C) is due to the-ray-induced carriers diffusion in VO_2. The subsequency decay of S_2 was related to the transformation of the disordered lattice structure to the ordered monoclinic lattice as shown by the change in the x-ray diffraction signal. We are working with our theory collaborators to provide a precise picture of the structural underpinnings and evolution of defect-driven phase transitions.

Future Plans

At the end of this program next FY, the research activity will be integrated into the SRS group at the Materials Science Division (MSD) as part of the x-ray scattering FWP at ANL. The planned activity next year thus will focus on the following tasks to ensure a smooth transition.

(1) Completing the VO_2 studies, which are in synergy with the proposed research activities of coherent diffraction imaging of VO_2 nanoparticles by Hoydoo You in the SRS group.
(2) Developing nanoscale magnetic imaging modality based on NV quantum sensors for XNOM. This task is particularly aligned with SRS group engagement with ANL QIS efforts.
(3) Studying dynamics of polar skyrmions by THz-pump, x-ray probe measurements at LCLSII.

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Table of Content:

Quantum Engineering Exciton Dynamics in 2D-Heterostructures

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Program Scope

The recent emergence of two-dimensional (2D) quantum materials, such as 2D semiconductors and magnetic insulators, have provided new platforms for studying light matter interactions with external controls.[1,2] Access to high quality heterostructures formed by different 2D materials further enabled the exploration of emergent phenomena which were not otherwise. The objective of this program is to investigate and understand these phenomena associated with excitons via advanced heterostructure engineering. During the last couple years, we have realized visualization of band structures with in-situ electrostatic gating[3] and moire excitons[4] in 2D heterobilayer; revealed intrinsic valley pseudospin lifetime[5], spontaneous valley exciton polarization due to interacting carriers[6], and zone-edge phonon replicas of valley excitons[7] in hBN sandwiched monolayers; and explored exchange field control of exciton dynamics[8] in magnetic heterostructures. Selected progress is described below.

Visualizing electrostatic gating effects in two-dimensional heterostructures: As powerful as angle-resolved photoemission spectroscopy (ARPES) has proven to be for studying quantum materials, in-situ electrostatic gating of any kind remains a challenge. Such capability is indispensable for investigating numerous phenomena, from basic to exotic, where reversible tuning of the carrier doping or electric field is required. In this project, using carefully designed 2D heterostructure devices combined with a micron-scale beam spot, we realized micro-ARPES on electrostatically gated samples.[3] In 2D semiconductors (MoS_2, $MoSe_2$, WS_2 and WSe_2) we see the conduction band when we dope with electrons using the gate (Fig. 1a). This overcomes a fundamental limitation of ARPES that it probes only occupied states, allowing us to resolve controversies about the location of the conduction band edge in these materials and to measure the single-particle band gap. We find that the band edge is always at the K-point in monolayers and measure the band gap in each case. In atomically thin WSe_2, we find that the Q point is about 30 meV higher than K in monolayer WSe_2 but becomes lower than K (making the band gap indirect) in 2+ layers (Fig. 1a). We also observe that the band structure changes on gating, with the band gap decreasing substantially at moderate electron doping levels – such a direct visualization and measurement of band gap renormalization has not been possible before (Fig. 1b). Our work opens the

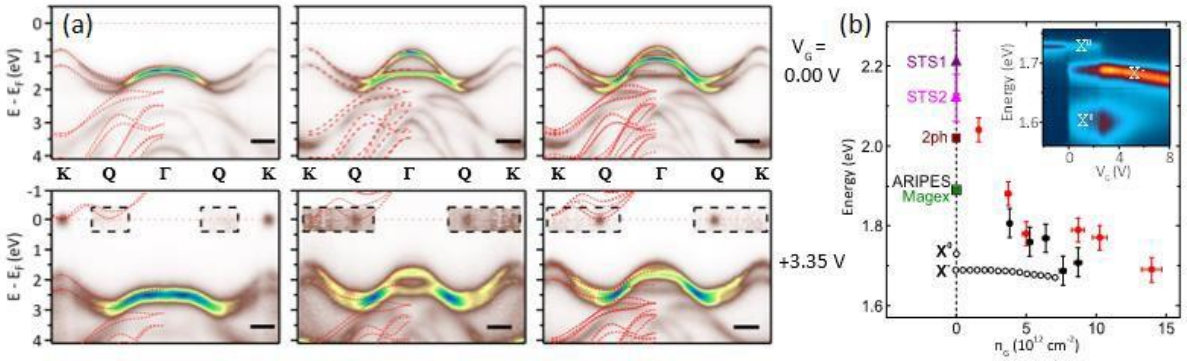

Fig. 1. μ-APRES results of atomically thin WSe_2 with in-situ electrostatic gating. **a**, Energy-momentum slices along $\boldsymbol{\Gamma - K}$ for 1L, 2L, and 3L WSe_2. In each case the upper panel is at $V_G = 0$ and the lower at $V_G = +3.35\ V$. Scale bars are 0.3 Å^{-1}. Red dashed lines are DFT calculations. The intensity in the dashed boxes is multiplied by 20 to enhance the weak $\boldsymbol{Q}$ -point features. **b**, Carrier-density dependent band gap measurements on monolayer WSe_2. Solid circles: ARPES measurements of the band gap E_g at 100 K in Device 1 (red) and Device 2 (black). Open circles: photoluminescence peak positions for the neutral exciton (X^0) and negative trion (X^-) in Device 2, also at 100 K. The inset shows the raw photoluminescence data.

possibility of observing electric field-controlled phenomena such as topological phase transitions and the opening of correlated gaps in superconductors, Mott insulators, twisted bilayers, and other systems.

Observation of moiré exciton: Heterostructures of monolayer semiconductors host moiré superlattice structure with periodic potentials, which can trap excitons to form an excitonic lattice. In this project, we realized moiré excitons in $MoSe_2/WSe_2$ heterobilayers with twist angle control[4] (Fig. 2). Our main experimental findings include: (1) Observation of photoluminescence peaks near the free interlayer exciton energy but with over 100 times narrower linewidths (~100 μeV) than that of free excitons, demonstrating the quantum-dot-like trapping potential of interlayer excitons. (2) Observation of strong circular polarized photoluminescence (over 60%) of trapped interlayer excitons, showing that all trapping sites maintain three-fold rotational symmetry. Importantly, the polarization is determined by the twist angle, which is co-circularly polarized for near 60° and 20° degree twisted sample and cross circularly polarized for zero twisted sample. This is a fingerprint of moiré traps not possible in randomly formed

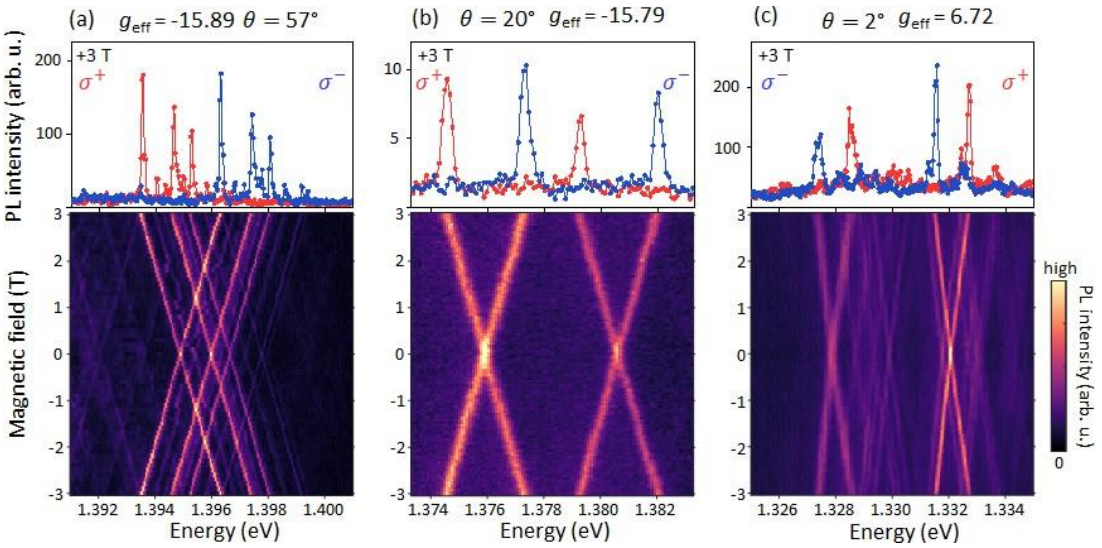

Fig. 2 | Observation of moiré exciton in MoSe2/WSe2 heterobilayer. Top row: polarization resolved photoluminescence spectra at 3T. Bottom row: photoluminescence intensity plots as a function of magnetic field and photon energy. **a, b, c** corresponds to samples with twist angles of 57, 20, and 2 degree, respectively.

potential traps. (3) Demonstration twist angle dependent *g*-factors, which take two distinct values, -15.9 and 6.7, in samples with twisting angles near 60° and 0°, respectively. The *g*-factors are homogenous not only across the same sample, but also across different samples with similar twist angles. For 20° twisted heterobilayers, the emitters become two orders of magnitude dimmer but they remarkably possess the same *g*-factor as the 60° heterobilayer. This is consistent with the Umklapp recombination of interlayer excitons near the commensurate 21.8° twist angle, which has opposite valley index pairing at the second Brillouin zone. Our observation of moiré excitons provides a promising starting point to explore exciton many-body effects.

Valley phonon replica in monolayer WSe_2: The coupling between spin, charge, and lattice degrees of freedom plays an important role in a wide range of fundamental phenomena. In recently emerged monolayer semiconductors, while carriers feature a valley pseudospin associated with the well-known valley optics, the crystal structure also endows phonons a valley degree of freedom corresponding to the modes with momentum vectors pointing to the high symmetry corners of the hexagonal Brillouin zone (±K points). Direct manifestations of such zone edge phonons in optical spectroscopy are rarely observed due to the large phonon momenta that need to be compensated during the quasiparticle relaxations in order to conserve momentum. In this work, using monolayer semiconductor WSe_2 as a model system, we identified three valley phonons and their strong interactions with quasiparticles, resulting in a remarkably

rich spectrum of sharp resonances corresponding to various exciton complexes and their emission channels through valley phonon emissions (Fig. 3).[7] Our key results include identification of efficient spin-conserving intervalley scattering of quasiparticles assisted by valley phonons during dark exciton and trion relaxation processes; uncovering the intervalley exciton I^o, where the electron and hole are localized in opposite valleys; revealing the dominance of the spin-conserving intervalley scattering of electrons assisted by valley phonons over spin-flip intravalley scattering by zone-center phonons during the exciton formation process. Our work uncovered previously inaccessible valley phonons and their critical role in spin and pseudospin scattering and relaxation process in monolayer semiconductors and resolved almost all spectral features in the complicated photoluminescence spectrum of monolayer WSe_2.

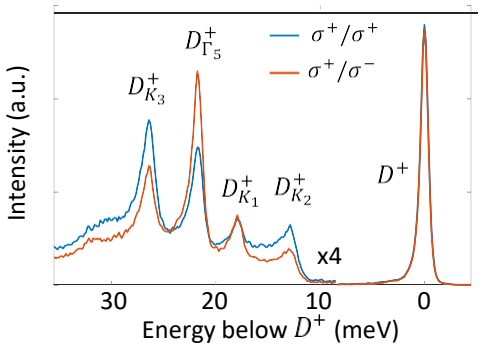

Fig. 3. Polarization resolved PL spectra of monolayer WSe2, which reveals positively charged dark trions (D^+) and K_2, K_1, Γ_5, and K_3 phonon replicas.

Layered resolved magnetic proximity effect in CrI3/WSe2 heterostructure: At the interface formed by nonmagnetic and magnetic materials, the properties of the former can be drastically influenced by the adjacent magnetic order. Such an effect is usually short range due to the finite coherence length of the overlapping electronic wavefunction at the interface. In this project, we demonstrated proximity-induced ferromagnetism in monolayer WSe_2 while interfacing with thin flake CrI_3.[8,9] For instance, spontaneous

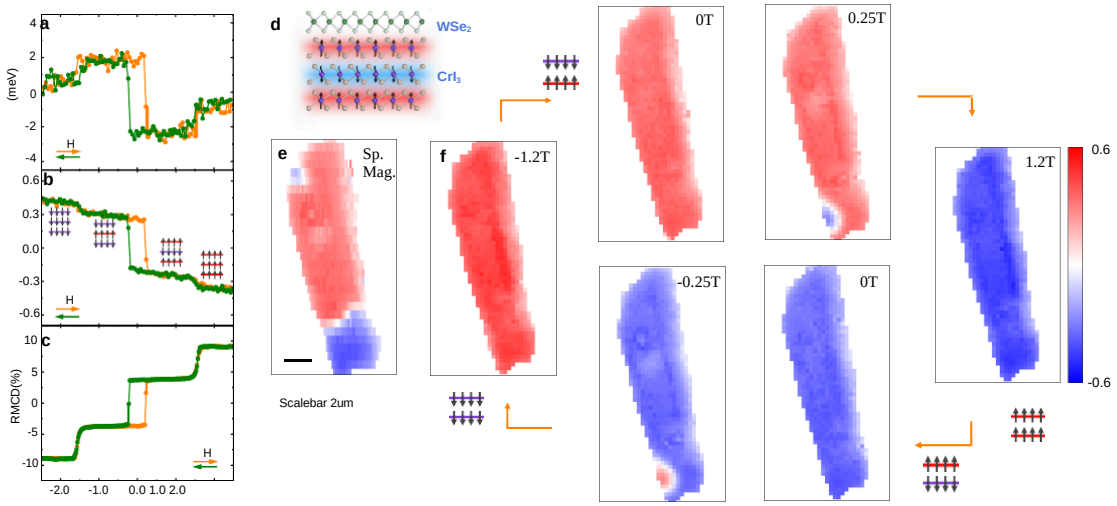

Fig. 4. Layered Resolved Magnetic Proximity Effect in CrI3/WSe2 heterostructure. a, Valley Zeeman splitting, **b**, degree of circular polarization in photoluminescence, **c**, and reflective magneto-circular dichroism of WSe_2/trilayer CrI_3 heterostructure as a function of magnetic field. **d**, schematic of the heterostructure. Orange and green curves represent magnetic field sweeping up (increase) and down (decrease), respectively. **e-f,** imaging layered antiferromagnetic-ferromagnetic domains in bilayer CrI_3 by monolayer WSe_2. **e**, Spatial map of ρ of spontaneously circularly polarized WSe_2 photoluminescence as the heterostructure cools down to 1.6K without applying magnetic field. **f**, Spatial map of ρ at selected magnetic fields. Layered antiferromagnetic and ferromagnetic domains at ±0.25T maps are indicated. Insets depict the magnetic states. Scale bar: 3 μm.

valley excitonic Zeeman splitting, which is equivalent to large exchange field (~13T), is demonstrated in the absence of an applied magnetic field.[9] In addition, we uncovered layer resolved magnetic proximity effects (Fig. 4).[8] We employ polarization-resolved magneto photoluminescence to measure of the

proximity effect of CrI_3 substrate on the valley dynamics of WSe_2. Combined with the magnetic order of CrI_3 determined by reflective magnetic circular dichroism (RMCD), we show that spin-dependent charge transfer between WSe_2 and CrI_3 is dominated by interfacial CrI_3 layer, while the exchange field has a strong dependence on the magnetization in the next nearest neighbor layer. Built on this layer resolved effect, we implement monolayer WSe_2 as a magnetic sensor to probe the domain effects in bilayer CrI_3, which is otherwise challenging by conventional techniques due to the vanishing magnetism in the antiferromagnetic order. At zero magnetic field, we uncovered both reconfigurable and pined layered AFM domains. Near the metamagnetic transitions, we observe the evolution of AFM/fully spin-polarized domains as a function of magnetic field. These domain patterns are likely due to the inhomogeneous distribution of strains introduced by heterostructure fabrication. Our work provides new means to control proximity effects as well as probe magnetic order via van der Waals engineering.

Future Plans

We will continue to investigate the exciton effects in moiré superlattice structures and magnetic heterostructures with external control, including twist angle, electrical field, doping, strain, hydrostatic pressure, and exchange field effects.

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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, Boston, MA
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

Table of contents for the presentation: Our team presentation has two PPT files, named "Xiaodong Xu Team Presentation-Part 1" and "Xiaodong Xu Team Presentation-Part 2". The presentation contains three main parts: (1) Spin Lattice Coupling in van der Waals magnets. This part is presented by Xiaodong Xu to cover recent progress in 2D magnets CrI_3, including giant nonreciprocal second harmonic generation, magnetoelectric control of inelastic light scattering, and 2D magnons and optical selection rules. (2) Charge and lattice coupling effects. This part is presented by Nuh Gedik, and will cover optical detection and manipulation of spontaneous gyrotropic electronic order in a transition metal dichalcogenides semimetal. Items (1) and (2) are in "Xiaodong Xu Team Presentation-Part 1". (3) On-going and future direction in "Xiaodong Xu Team Presentation-Part 2". This part is presented by Haidan Wen, who will discuss time resolved X-ray probe of critical behavior in zigzag antiferromagnets.

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

Giant nonreciprocal second harmonic generation from layered antiferromagnetism in bilayer (Xu, Xiao): Second harmonic generation (SHG) is a ubiquitous nonlinear optical process, which is indispensable for investigating symmetry-related fundamental phenomena that are otherwise challenging to probe. To date, SHG phenomena is usually dominated by systems with broken lattice inversion symmetry. In crystals with a centrosymmetric lattice structure, SHG can exist too, for example, due to underlying magnetic order, but is generally believed to be a very weak effect. In this work, we uncovered a giant and nonreciprocal SHG in the newly discovered, magnetic CrI_3 bilayers, which possess a centrosymmetric lattice structure (Fig. 1).[1] We demonstrated that the SHG is solely originated from the layered antiferromagnetism of CrI_3 bilayer, where individual monolayers are ferromagnetic and their interlayer magnetic coupling is antiferromagnetic.[2] Such a magnetic structure breaks both spatial inversion and time reversal symmetries, necessary for electric dipole allowed nonreciprocal SHG. For a direct comparison, the value of $|\chi^{(2)}|$, a measure of the strength of SHG, is 2-3 orders of magnitude stronger than that in Cr_2O_3 bulk (a model

material for studying antiferromagnetism-induced SHG),[3] and ~10 orders of magnitude stronger than SHG induced by surface ferromagnetism in transition metal thin films (the first material

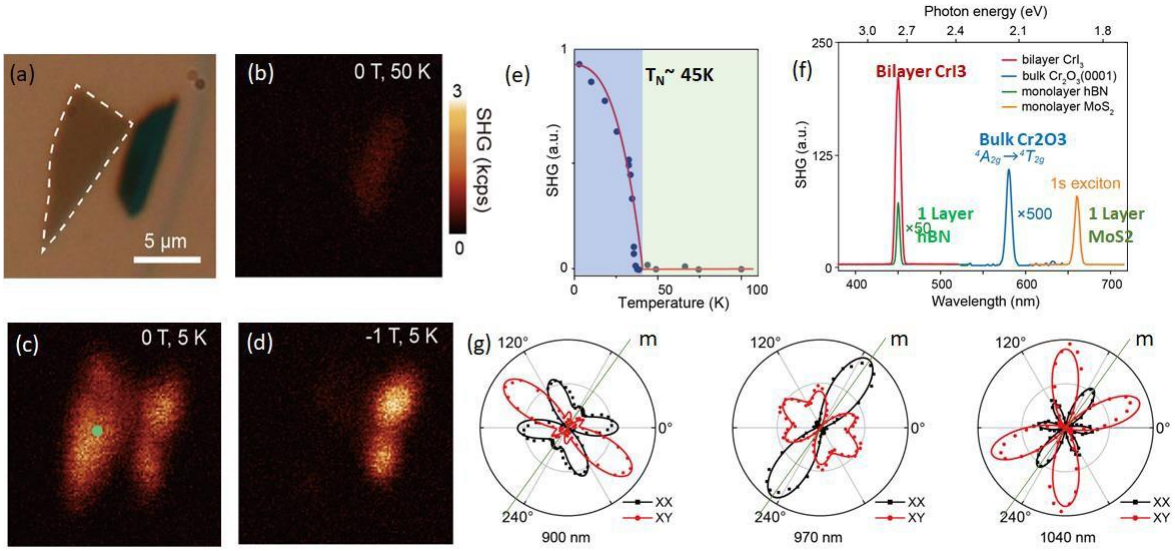

Fig. 1. **Giant nonreciprocal SHG from layered antiferromagnetic bilayer CrI_3. (a)** Optical microscope image of a CrI_3 bilayer (delineated by the white dotted line) and a thicker flake. Scale bar: 5 μm. **(b-d)** The corresponding SHG intensity images when the bilayer is **b**, nonmagnetic (0 T, 50 K), **c**, antiferromagnetic (0 T, 5 K) and **d**, ferromagnetic (-1 T, 5 K). **(e)**, SHG intensity of the bilayer as a function of temperature. **(f)** Comparison of the SHG response with bulk Cr_2O_3 and other 2D materials. The excitation wavelengths for bulk Cr_2O_3 crystal (1160 nm) and MoS_2 monolayer (1320 nm) were chosen so that their second harmonic photon energies are resonant with their respective electronic transitions ($^4A_{2g}\rightarrow{}^4T_{2g}$ and 1s exciton state). **(g)**, Azimuthal SHG polarization dependence at 0 T with the fundamental wavelength of 900 nm, 970 nm and 1040 nm. Solid lines are fits by the c-type second order nonlinear tensors associated with C_{2h} symmetry (monoclinic stacking structure).

system for observing the magnetization-induced SHG). To compare with the SHG from crystals with non-centrosymmetric lattices, the layered antiferromagnetism induced SHG in bilayer CrI_3 is on the same order of magnitude as the best 2D nonlinear optical materials discovered so far (e.g. MoS_2 and WSe_2).[4,5] The ability to access antiferromagnetic states then enables us to reveal the symmetry of spin-lattice structure by polarization-resolved SHG. Due to the extreme sensitivity of SHG to symmetry, we ruled out the rhombohedral structure by observing broken three-fold rotational symmetry in CrI_3 bilayer below the Neél temperature . Rather, we uncover the C_{2h} symmetry, which establishes that the monoclinic structure is responsible for the layered antiferromagnetic ground states. This understanding is crucial for developing microscopic theory in understanding the magnetic properties of CrI_3.[6]

Tuning Inelastic Light Scattering via Spin-Phonon Coupling in atomically thin CrI_3 (Xu, Xiao): The inelastic light scattering from collective quasiparticle excitations, e.g. Raman scattering, is a powerful probe of fundamental properties in a material. In this project, we systematically study the interplay between magnetism and the vibrational degrees of freedom in layered magnets CrI_3 down to the monolayer limit (Fig. 2).[7] In the monolayer, we found a giant Raman Kerr effect originated from a ferromagnetic order induced Hall component in the A_{1g} Raman tensor. The linearly polarized inelastically scattered light rotates as much as ~40º, about two orders of magnitude larger than that in magneto-optical Kerr effect. For bilayer CrI_3, we show that the Raman optical selection rules can be controlled by the magnetic order. We demonstrated that antiferromagnetic order breaks global inversion symmetry and thus activates the original Raman

silent Davydov-split phonons. The inversion symmetry restores in the fully spin aligned state, which consequently leads to the precise magnetic and electrical switching of this phonon mode. Our work shows that vdW magnets provide a new platform for exploring emerging spin phonon coupled physics.

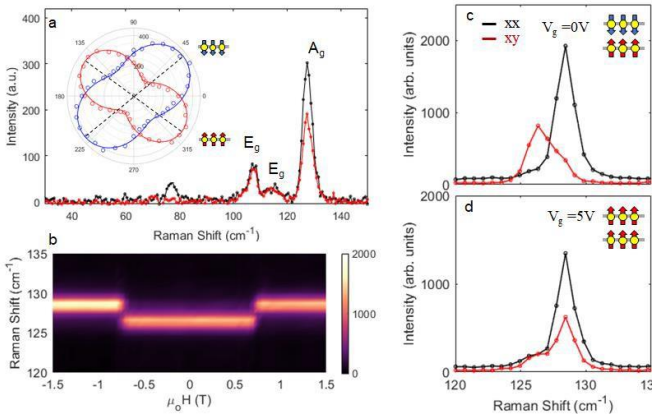

Fig. 2. Tuning inelastic light scattering via spin-phonon coupling in atomically thin CrI_3. (**a**) Raman spectra of monolayer CrI_3 at 15K. Black and red traces are co-linear and cross-linear excitation and detection, respectively. Inset: Polar plots of Ag intensity vs detection polarization with magnetization pointing up (red) and down (blue). (**b**) Cross-linear polarization detection of A_g mode vs magnetic field. (**c-d**) Raman spectra at Vg=0 and 5 V, which switches the magnetic student and thus the Davydov-split phonon mode.

2D magnons and magnetic order dependent optical selections (Xu, Xiao): Quantized collective excitations in magnetic materials, i.e. spin waves or magnons, have been researched for decades due to their fundamental connection to magnetism and their potential for wave-based computing and other spintronic applications. In this work, we discover 2D acoustic and optical magnons with unique optical selection rules strictly governed by crystal symmetry, layer number, and the magnetic configuration in atomically thin CrI_3 (Fig 3).[8] In monolayers, we found that for a given magnetization orientation, 2D magnons can only be excited with one helicity of light. The scattered light is cross-circularly polarized with respect to the excitation polarization, resulting from the conservation of magnon and photon angular momentum in a honeycomb lattice. As the total angular momentum change of the magnon creation and annihilation process is $\pm 3\,\hbar$, the threefold rotational symmetry of the lattice enables this otherwise forbidden cross-circularly polarized optical selection rule in a rotational analogue to the Umklapp scattering. We show that these selection rules are relaxed in bulk single crystals, highlighting the intimate connection between magnetism and symmetry in the 2D limit. In addition to the low-frequency acoustic magnon modes, we reveal a high-frequency optical magnon mode at 140 cm^{-1} (4.2 THz). This mode is Raman-silent in monolayers, but optically active in bilayers and bulk due to a relaxation of the parity criterion resulting from the layer index. This layer-dependent optical selection rule is unique to 2D magnets and has never been reported before. In addition, we are able to directly resolve the two degenerate optical magnon modes in the layered antiferromagnetic states and confirm that they carry opposite angular momentum and satisfy conjugate optical selection rules. Applying a magnetic field to switch between the layered antiferromagnetic and ferromagnetic-like states results in the loss/restoration of inversion symmetry, allowing for the unique symmetry control over the optical magnon selection rules in bilayer CrI_3.

Spin-lattice interaction in two-dimensional materials (Xiao): In addition to the experimental efforts, we investigate the role of magnon-phonon interaction in the thermal Hall effect. In a magnetic insulator, the heat current can be carried by either magnons or phonons. Thus, the thermal Hall effect can be used as an effective probe of these charge-neutral excitation. Using symmetry arguments, we show that the magnon-phonon interaction can induce a thermal Hall effect whenever the mirror symmetry in the direction of the magnetization is broken.[9] In the limit of strong magnetic anisotropy, this effect can be understood as a phonon Hall effect, driven by an

effective magnetic field in the phonon sector introduced by the magnon-phonon interaction. In the more general case where the magnons and phonons are close in energy, we have developed a theory to treat both excitations on an equal footing. Our result sheds new light on the dynamical aspect of the spin-lattice interaction.

2. *Charge dynamics and its coupling to lattice degrees of freedom*

Dynamical slowing down in a photo-induced phase transition [10] (Gedik and Wen): Complex systems, which consist of a large number of interacting constituents, often exhibit universal behavior near a phase transition. A slowdown of certain dynamical observables is one such recurring feature found in a vast array of contexts. This phenomenon, known as critical slowing down, is well studied mostly in thermodynamic phase transitions. However, the dynamics is much less understood in highly nonequilibrium settings, where the time it takes to traverse the phase boundary becomes comparable to the timescale of dynamical fluctuations. In this work, we focus on a paradigmatic CDW system, $LaTe_3$. Like other rare-earth tritellurides, $LaTe_3$ possesses a quasi-2D structure and develops a unidirectional CDW below $T_c \approx 670$ K. Upon the arrival of a strong femtosecond laser pulse, the CDW order is transiently suppressed. We first establish the timescale for this process by performing ultrafast electron diffraction (UED) and transient optical spectroscopy (TOS); previous measurements from time- and angle-resolved photoemission spectroscopy (trARPES) and time-resolved X-ray diffraction (trXRD) are also included to obtain a comprehensive view of the ultrafast melting process. While UED and trXRD track the evolution of CDW satellite peaks at characteristic wavevector $\mathbf{q}_{CDW}$, TOS and trARPES probe the change in the spectroscopic gap. Remarkably, despite the different observables, the initial response that corresponds to CDW suppression proceeds with a similar timescale around 400 fs.

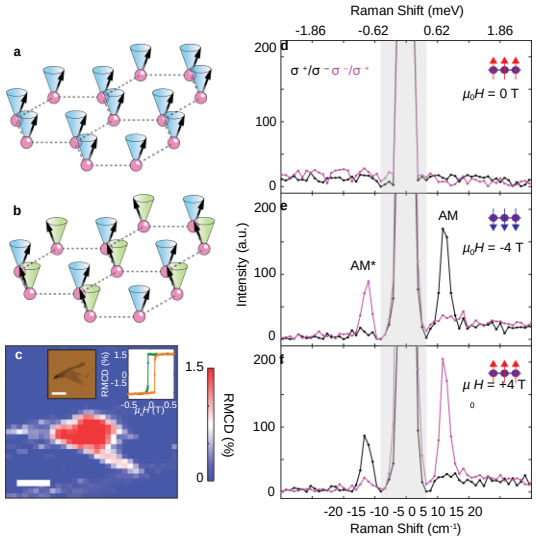

Fig. 3. 2D spin wave. a-b, Depiction of the two types of spin waves in ferromagnetic monolayer CrI_3: **a** in-phase acoustic mode, and **b** out-of-phase optical one. **c,** Zero-field reflective magnetic circular dichroism (RMCD) map of an encapsulated monolayer CrI_3 flake. Scale bar: 4 μm. The right inset shows an RMCD sweep while the left is an optical micrograph of the sample. **d-f,** Low-frequency cross-polarized Raman spectra taken at **d,** zero-field **e,** -4 T, and **f,** 4 T. The grey box indicates the spectral range of our optical filter below which the magnon is unresolvable.

Among the four techniques discussed, TOS possesses the best temporal resolution and signal-to-noise ratio, enabling us to more quantitatively investigate the timescale of CDW suppression, denoted by τ, as we vary the laser excitation density, F, quoted in terms of absorbed photon number per unit volume. Fig. 4 shows the timescale of the initial CDW suppression for different excitation densities. A salient feature is that the time τ displays a non-monotonic trend as a function of excitation density (orange circles), with a maximum at $\sim 2\times10^{20}$ cm^{-3} (black arrow), where the CDW satellite peaks seen in UED first vanishes completely. To confirm this non-monotonic trend, we similarly track the suppression of superlattice peaks using UED at various excitation densities (blue diamonds). Despite significantly larger errors due to lower signal-to-noise ratio and poorer temporal resolution compared to the TOS measurements, the initial timescale in the UED

experiments suggests the same non-monotonic behavior in τ. We further note a recent measurement on $SmTe_3$, a CDW compound in the same family as $LaTe_3$, which demonstrates a similar trend in the initial system response.

To interpret this maximum CDW suppression time at the threshold excitation density, we draw some parallels between the present nonequilibrium study and its equilibrium counterparts. In equilibrium, when the temperature is close to T_c, time-domain measurements of the order parameter indicate a reduced rate of change, which signifies critical slowing down. Here, we use photoexcitation density in lieu of temperature as the tuning parameter, and we extend the timescale to the femtosecond regime. Similarly, we interpret the maximum value of τ at exactly the threshold excitation density as a signature of dynamical slowing down in this ultrafast phase transition.

More quantitatively, this maximum value of τ exhibited at the threshold excitation density can be reproduced by solving the time-dependent Ginzburg-Landau equations, which describe the dynamics of the CDW order parameter in response to a sudden change in the free energy potential instigated by the femtosecond light pulse. In our calculation, two separate order parameters were considered, one for the electronic part and the other for the lattice part of the CDW. The pair captures the distinct timescales involved in the faster electronic response compared to the slower ionic movements.

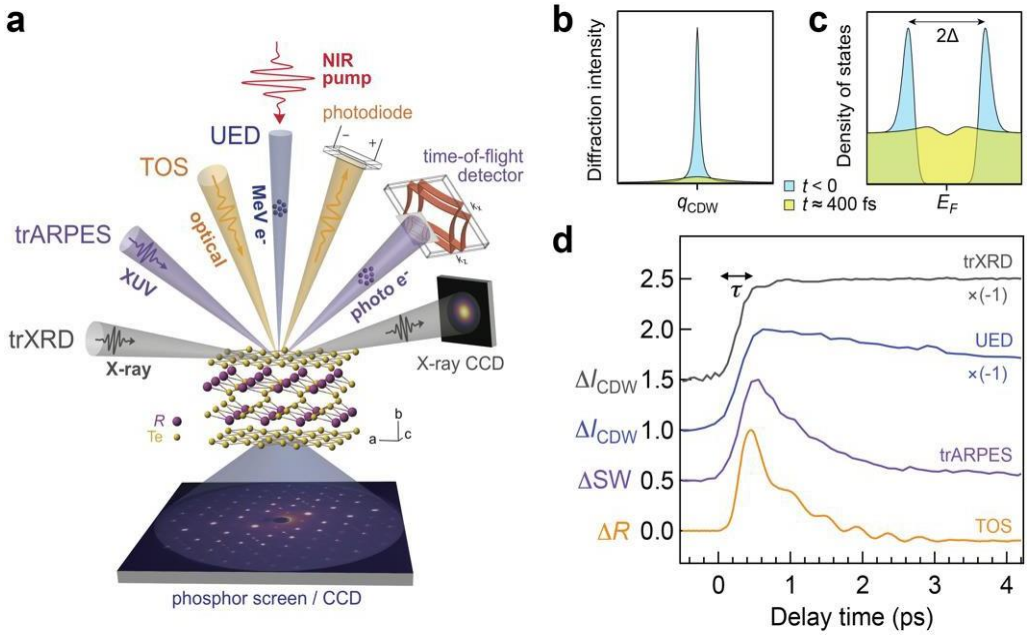

Figure 4. a, Schematics of different time-resolved probes, including UED, TOS, trARPES, and time-resolved X-ray diffraction (trXRD). **b**, **c**, Schematics of the superlattice peak and density of states before (blue) and after (yellow) photoexcitation. **d**, Normalized transient response of superlattice 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. The initial rise time, τ, is ~400 fs in all setups after the temporal resolution of individual setups is taken into consideration. trXRD data is adapted from Moore *et al.*, *PRB* **93**, 024304 (2016).

Spontaneous gyrotropic electronic order in a transition-metal dichalcogenide (Gedik and Xiao)[11]: The observation of chirality is ubiquitous in nature. Contrary to intuition, the population of opposite chiralities is surprisingly asymmetric at fundamental levels. Examples range from parity violation in the subatomic weak force to the homochirality in essential biomolecules. The ability

to achieve chirality-selective synthesis (chiral induction) is of great importance in stereochemistry, molecular biology and pharmacology. In condensed matter physics, a crystalline electronic system is geometrically chiral when it lacks any mirror plane, space inversion center or roto-inversion axis. Typically, the geometrical chirality is predefined by a material's chiral lattice structure, which is fixed upon the formation of the crystal. By contrast, a particularly unconventional scenario is the gyrotropic order, where the electrons spontaneously organize themselves to exhibit macroscopic chirality in an originally achiral lattice. Such a gyrotropic order, proposed as the quantum analogue of the cholesteric liquid crystals, has attracted significant interest. However, to date, a clear observation and manipulation of the gyrotropic order remains lacking. We realized optical chiral induction and observed a gyrotropically ordered phase in the transition-metal dichalcogenide semimetal 1*T*-$TiSe_2$. We show that shining mid-infrared circularly polarized light while cooling through the critical temperature leads to the preferential formation of one chiral domain. The chirality of this state is demonstrated by measuring an out-of-plane circular photogalvanic current, whose direction depends on the optical induction. While the role of the domain walls deserves further investigation with local probes, the methodology demonstrated here can be applied to discover and control chiral electronic phases in other quantum materials.

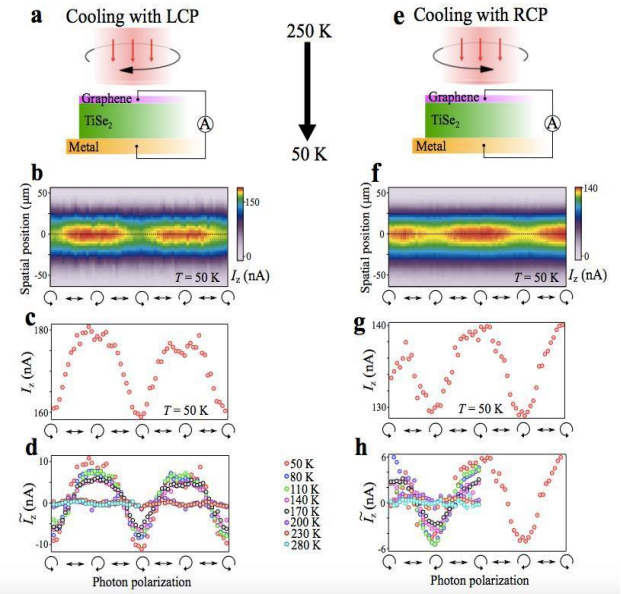

Fig. 5. a, We shine left circularly polarized (LCP) light on the sample while lowering its temperature from T = 250 K to 50 K. **b,** The out-of-plane photocurrent I_z at $T = 50$ K as a function of the light polarization (horizontal axis) and the beam spot location (vertical axis). **c,** I_z at $T = 50$ K as a function of polarization. A clear out-of-plane CPGE is observed. d, $\tilde{I}$ at different temperatures as we warm sample up from 50 K toward room temperature. Here $\tilde{I}$ means the polarization-dependent part (the CPGE) of I_z. We observe that the CPGE persists up to 170 K and then vanishes rather abruptly. **e-h,** Same as panels (a-d), except that we shine right circularly polarized (RCP) light on the sample while lowering its temperature from T = 250 K to 50 K. The emergent CPGE is found to be reversed.

In order to determine whether the sample is chiral or not we measure the difference in photocurrent along the wavevector of the light when the helicity of the light is changed between right and left circular polarization (circular photogalvanic effect (CPGE)). If the sample is achiral, no difference is expected, if it is chiral this photocurrent becomes allowed by symmetry. Our experimental setup involves a mid-infrared scanning photocurrent microscope equipped with a continuous-wave CO_2 laser ($\lambda = 10.6$ μm, $\omega = 117$ meV), which allows us to measure the mid-infrared photocurrent as a function of beam spot location, light polarization and temperature. In order to probe the out-of-plane photocurrents I_z, we have fabricated vertical photoactive devices consisting of a $TiSe_2$ flake sandwiched by a transparent graphene electrode on the top and a metal electrode on the bottom. The thickness of the $TiSe_2$ flakes is comparable to the laser skin depth (~ 200 nm) calculated from the optical conductivity at $\lambda = 10.6$ μm. This ensures that a significant

vertical fraction of the flake is photoactive. The critical temperature of the 2 × 2 × 2 CDW phase transition of our $TiSe_2$ samples was determined by X-ray diffraction to be around 198 K.

First, we have characterized the basic photoresponse of our devices. We did not observe any polarization dependence at 250 K, above the transition temperature. Lowering the temperature to 50 K (below the Tc) gave similar results with no evidence of chirality. In this case, the sample was cooled down without being illuminated by laser. We then shine circularly polarized light on the sample during the entire cooling process. Surprisingly, a markedly different situation is observed. As shown in Fig. 5a, we shine left circularly polarized (LCP) light on the sample while lowering its temperature from $T = 250$ K. Upon reaching low temperature ($T = 50$ K), we measure I_z as a function of polarization with the beam spot parked at the sample center (Figs. 5b&c). We observe a clear polarization dependence: I_z is maximum for LCP and minimum for right circular polarization (RCP). This pattern clearly demonstrates the emergence of an out-of-plane CPGE photocurrent. By increasing temperature step by step, we observe in Fig. 5d that the CPGE persists up to 170 K and then vanishes rather abruptly. We repeat the measurements described above but change the light polarization during cooling to RCP (Figs. 5e-h). Remarkably, the sign of the out-of-plane CPGE is reversed (Figs. 5f-h). Other behaviors such as the temperature dependence (Fig. 5h) and the spatial distribution (Fig. 5f) are qualitatively similar.

The observation of the out-of-plane CPGE directly demonstrates the existence of the rare gyrotropic order in the 1*T*-$TiSe_2$. The observation of CPGE sign reversal upon shining different circular polarization while cooling reveals a novel chiral induction with light. Gedik and Xiao worked together and developed microscopic theories for both the chiral induction and the gyrotropic order, which can explain our observations.

Anisotropic structural dynamics of monolayer crystals (Wen, Xu)[12]: 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 of Wen and Xu group, 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. 6a). 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 (Fig. 6b). The model-assisted fitting suggests an asymmetric intralayer spacing change upon excitation. These experimental observations are further supported by first-principle calculations. 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.

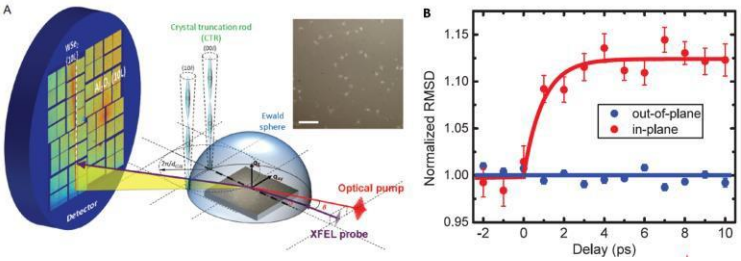

Fig. 6. a) Femtosecond x-ray diffraction setup. Upon optical excitation, a grazing incident x-ray beam scatters at the monolayer flakes of WSe_2, which produces vertical streak diffraction patterns on the detector. b) The extracted atomic vibration amplitude along the in-plane and out-of-plane direction as a function of delay following optical excitation.

Tunable layer circular photogalvanic effect in twisted bilayers (Xiao)[13]: We develop a general theory of the layer circular photogalvanic effect (LCPGE) in quasi-two-dimensional chiral bilayers, which refers to the appearance of a polarization-dependent, out-of-plane static dipole moment induced by circularly polarized light. We elucidate the geometric origin of the LCPGE as two types of interlayer coordinate shift weighted by the quantum metric tensor and the Berry curvature, respectively. As a concrete example, we calculate the LCPGE in twisted bilayer graphene, and find that it exhibits a resonance peak whose frequency can be tuned from visible to infrared as the twisting angle varies (Fig.7). The LCPGE thus provides a promising route toward frequency-sensitive, circularly polarized light detection, particularly in the infrared range.

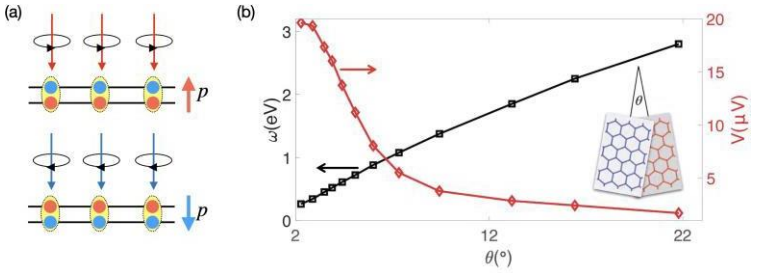

Fig. 7. a. Schematic illustration of the LCPGE. Circularly polarized light induces a static out-of-plane dipole, whose direction flips when the circular polarization of light is reversed. Red and blue disks stand for negative and positive charges, respectively. b) The peak position (black) and the corresponding potential difference (red) generated by the LCPGE at different twisting angles. We have assumed a laser power 1 mW/μm^2.

Future Plans

Our future plan focuses on three directions. The first one is to investigate potential intrinsic collective modes of moiré superlattice and its moirépattern reconstruction under intense ultrafast optical excitation utilizing newly developed, state-of-the-art ultrafast facilities at DOE labs including UED at SLAC and UEM at ANL. The second is to study correlated electronic phenomena in 2D materials using materials' nonlinearities, such as nonlinear photocurrent to uncover topological and correlated physics in twisted bilayer graphene (twBLG), and electrical-current induced insulator-metal transitions (IMTs) in Ca_2RuO_4. Lastly, we will investigate highly nonlinear spin-phonon interaction in Fe_3GeTe2 and CrI_3, probe the origin of critical fluctuations in zigzag antiferromagnets such as $FePS_3$, and realize THz excitation and possible control of 2D magnons. To gain microscopic understanding of magnetic, electric, and structural coupling effects, we will employ magneto-optical spectroscopy and X-ray linear and circular dichroism to directly probe the magnetic order while employing UED and tr-ARPES to resolve the structural and electronic dynamics.

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