Stanford Institute for Materials and Energy Sciences (SIMES)

Field Budget Request for FY2017

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

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Overview:

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

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

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

Progress in FY2016

LCLS-related activities:

- In the first pulsed magnetic experiment at LCLS, we discovered a three dimensionally (3D) ordered charge density wave (CDW) in YBCO. These results have now been published. [Gerber et al]
- We have performed the second pulsed magnetic field experiment at LCLS to further investigate the 3D CDW state in $YaBa_2Cu_3O_{6.67}$. We confirmed that this order also exists at doping level away from the 1/8. Remarkably, we find that the 3D CDW is incommensurate and unidirectional with a well-defined onset at a critical field strength proportional to the H_{C2}. It possesses long correlation length both in- and out-of-the CuO2 planes, yielding a correlation volume of order 10^5 unit cells. This is by far the largest CDW correlation volume ever seen in any cuprate and is representative of the high field ground-state of an “ideal” disorder-free cuprate. This CDW is in start contrast to the coexisting short-range bi-directional CDW that is pinned due to quench disorder, despite of sharing the same origin. We are now preparing a manuscript to publish these results.
- We characterized the ultrafast coherent lattice response in a FeSe film, grown by Dr. Moore/ Z. X. Shen group in another FWP. A complementary time-resolved ARPES measurement to directly reveal the time-evolution of the electronic states is also in progress by Dr. Kirchmann/Z. X. Shen group in another FWP. We are preparing a manuscript to publish this work.
- We completed a MEC, LCLS experiment studying the dynamic strength and texture development in a suite of Fe samples (varying composition, crystallinity, crystal orientations) under shock compression. We are currently

analyzing our MEC results on this and previous measurements on H_2O and summarizing results for shock-released SiO_2.

- We carried out time-resolved measurements at the LCLS at the XPP beamline and at SSRL (beamline 10-2) probing structural dynamics in 2D materials. The experiment was very successful and two papers will be submitted on this work during FY16. We observed two unique and unexpected responses: 1) In multilayer transition metal dichalcogenide (TMDC) films we see that photo-excitation leads to large amplitude unexpected compressive stresses and strains, pushing the 2d layers closer to each other. We have shown that this can be understood in terms of a light-induced Casimir effect, with the effect scaling like the square root of the carrier density. 2) In monolayer TMDC films, large amplitude in-plane strains were observed, developing on picosecond time-scales, as probed by time-dependent measurements of the truncation rod associated with the monolayer film. This work is still under analysis but may allow for dynamic reconstruction of the unit cell changes occurring within the monolayer.
- Time-resolved measurements at SSRL and LCLS have been successful in probing thermal transport and related dynamical processes in a number of materials, including PbTe (paper submitted) and in the 2d TMDC materials. An additional paper, separate from the two described above on TMDC materials, is also in progress.
- Using the above technique at LCLS, we have studied the ultrafast changes in the phonon structure of VO2 as it undergoes the metal-insulator transition triggered by a laser pulse. We observed an sudden (~ 100fs) increase in the diffuse scattering due to the Rutile phonons across the Brillouin zone, even when the initial state is well in the monoclinic phase. This has strong implications on the timescale for structural transformation and the potential role of the phonon entropy in stabilizing the Rutile structure at high temperatures.

RIXS activities:

- We performed an ultrahigh resolution RIXS measurement at ESRF to investigate the phonon excitations in a heavily underdoped Bi2212. We found the phonon intensity increases with increasing momentum, reflecting the momentum dependent electron-phonon coupling. Remarkably, we also found the phonon intensity reaches a maximal at a momentum position higher than that of a CDW, as well as a funnel-like intensity emanating from the CDW is also observation. These anomalies are due to the intersection between the phonon and the particle-hole continuum associated with the CDW, which has not been observed before until our measurements. The data analysis is still in progress. We will prepare a manuscript to publish these results soon.
- We performed high resolution RIXS at SLS to investigate the magnetic excitations in heavily underdoped LSCO. We find that the magnetic excitations exhibit a notable softening and change of dispersion along the (0,0) to (π, π) direction when the doping concentration increases to enter the superconducting phase. We have also observed bi-magnon excitations near the zone center, which has not been observed before. The data analysis is still in progress.
- Two modular X-ray emission spectrographs have been fully assembled and fiducialized for q-RIXS. The commissioning performed at BL6.3.2 of the ALS gives a resolving power of 1,600 at 500 eV with the commercial CCD detector. This resolving power is in agreement with the design specification.
- The q-RIXS endstation assembling is nearly complete, with experimental chamber already installed on the hexapod. The sample cryostat was re-developed and is expected to be completed in fall 2015. The endstation assembly is expected to be completed before the end of 2015.

Theory activities:

- Successfully obtained 2.75M CPU-hours in allocations for computational simulations at NERSC.
- We have developed a detailed analysis of how elementary spin and charge excitations can be measured using RIXS, and how they relate to simple two-particle correlation functions.
- We have formulated a theory for how phonons can be resonantly enhanced using RIXS, and demonstrated how the role of polarization and symmetry can be used to determine the strength and momentum dependence of electron-phonon coupling in a completely different way than neutron, Raman, optics, or non-resonant inelastic x-ray scattering.
- We have carried extensive simulations on the Hubbard-Holstein model to determine the nature of momentum-dependent collective modes across a quantum transition between Mott and Peierls system as a function of Coulomb and electron-phonon interactions.
- We have investigated the nature of single hole doped in two-leg Hubbard and t-J ladders and found strong evidence for the presence of nontrivial mutual statistics between the spin and charge parts of the injected in the isotropic limit. This novel mutual statistics make the injected hole behave qualitatively different with the conventional Bloch-quasiparticle and may give rise to the pairing glue for the two-hole bound state.

Work on high pressures:

- We have been studying the effect of pressure on the structural and electronic properties of transition metal chalcogenides (TMCs). We have recent results on a silver chalcogenide, Ag_2S, which has generated interest as a potential topological insulator by coupling high pressure synchrotron XRD, Raman, and IR spectroscopy. We are working on extending TMC systems to hybrid TMC-intercalated complexes by introducing foreign atoms or molecules between the layers, and understanding the effect of pressure on their electronic and optical properties.
- Organic-inorganic hybrids form the basis for natural and synthetic functional materials because they can combine the mechanical stability and electronic properties of inorganic solids with the tunability and flexibility of organic molecules. We studied the structural, optical, and electronic changes resulting from the application of pressures up to 50 GPa on three-dimensional (3D) Pb-halide hybrid perovskites, through a combination of in situ synchrotron single crystal and powder x-ray diffraction, electronic photoluminescence spectroscopy, dc conductivity measurements, optical observations, and density functional theoretical calculations. We reported the first high-pressure single crystal structures of 3D hybrid perovskites that allow us the rare opportunity of understanding how compression modulates the structures and thereby their optoelectronic properties.
- In addition, we have conducted high pressure experiments on a wide range of energy related materials including anode materials for Li batteries, bulk metallic glasses, and upconverting nanoparticles.

Structural dynamics:

- Measurements using high field THz pulses probing dynamic changes in phase-change materials were completed and this paper is under review. This paper studies electric-field-induced structural and electronic changes in proto-typical phase-change materials, showing that amorphous-to-crystalline phase transitions and ultrafast threshold switching can be driven by THz fields used as an all-optical bias. It shows that the threshold switching process occurs on time-scales orders of magnitude than previously thought to be possible. In FY16 we have also carried out further temperature dependent measurements probing the mechanisms for these ultrafast changes.
- We have also carried out measurements at the SLAC Ultrafast Electron Diffraction facility (UED) probing structural dynamics in both 2d and 3d hybrid perovskites. These measurements are the first to probe the structural dynamics that underlie the opto-electronic functionality of these materials. In the prototypical material methylammonium lead iodide which has set records for PV efficiency but for which the fundamental mechanisms for this functionality are unknown, we directly probe through these measurements the time-scales and mechanisms for hot carriers to couple to the lattice. We also find, through measurements of the pair correlation function, that the dominant change occurs within the iodine octahedron, providing a fundamental new understanding of the dynamical structural changes within these materials and a link to many other strongly correlated oxides.

2D transition metal dichalchogenides (TMDC):

- The two-dimensional transition metal dichalcogenides (TMDCs) present unique opportunities to control the band structure by strong time-varying electric fields produced by sub-gap laser excitation through Floquet states. We have recently demonstrated how the control of the polarization state of intense, pulsed sub-gap radiation can be used to manipulate valley pseudospin. The read-out of valley pseudospin is accomplished using polarization analysis of photoluminescence.
- Multilayer transition metal dichalcogenide materials have weak interlayer interactions that allow for novel methods of ultrafast electronic layer control. We have applied ultrafast x-ray diffraction using the LCLS to monitor interlayer spacing of TMDC materials following electronic excitation. In addition to the expected expansion following femtosecond laser excitation on the ten picosecond time scale associated with the thermal response, our study has revealed a novel *electronic effect* that leads to ultrafast interlayer *contraction*. The effect can be understood in the context of electronic modification of the Casimir force between the TMDC layers.
- In collaboration with LBNL team, we have observed charge density wave order in 1D mirror twin boundaries of single layer MoSe2 – adding a new many body dimension to the rich physics seen 2D TMDC.
- In collaboration with LBNL team, we characterized the collective ground state of single-layer NbSe2, where we illustrate the impact of the dimension on the collective behavior.
- We have performed Floquet analysis of "quantum geometry" effects in monolayer dichalcogenides driven with circularly polarized light. We characterized non-trivial, topological surface states associated with both sub-gap and above gap pumping with potential for both future experimental observation/characterization and applications.

Expected Progress in FY2017

LCLS activities:

- We will continue using the pulsed magnet field setup at LCLS to investigate the doping dependence of the three dimensionally ordered CDW to determine the position of critical points of the three dimensional CDW in the phase diagram.
- Commissioning and early experiments of *q*-RIXS endstation will be conducted at the ALS beamline 8.0.1. Using its unique capability of high data acquisition efficiency and continuously variable spectrometer angle, we plan to perform energy-resolved resonant diffraction and momentum-resolved RIXS measurements on classical correlated materials. We also plan to submit a new proposal for seeking the LCLS beamtime to carry out the first time-resolved *q*-RIXS experiment at LCLS. We had previously submitted a proposal and received an excellent rating of 1.5 with the comment that we get back to LCLS after the *q*-RIXS instrument is operational.
- We will summarize our Fe results from MEC, LCLS.
- We will apply coherent control techniques to demonstrate for the first time selective excitation of high q phonons using optical excitation. If successful this will provide a new mechanism for controlling and probing matter both in and out of equilibrium. We will also study anharmonic decay of coherent zone-center phonons to high wavevector phonons which has been theoretically linked to parametric resonance.
- Over the next period we will use the demonstrated technique of Fourier Transform IXS to probe the ultrafast lattice response of VO_2 upon photoexcitation across the metal-insulator transition.

RIXS activities:

- We will continue to explore the collective excitation in high temperature cuprates. In particular, we have received another beamtime at the ESRF to investigate collective excitations in an electron-doped cuprates, $La_{2-x}Ce_xCuO_4$ to explore the quantum criticality behavior in the phase diagram. In addition, we will further investigate the phonon excitations and the particle-hole continuum of CDW in hole-doped cuprates that are crucially complementary with other existing measurements on cuprates.
- We will also explore to use RIXS for the investigation of the rich physics of oxide heterostructure. In particular, in collaboration with Hwang's FWP, we are now trying to explore RIXS measurement on $LaNiO_2$ films.
- Third modular X-ray emission spectrograph has been fully assembled and fiducialized. q-RIXS endstation will be installed at BL8.0.1 at the ALS by the end of summer 2016. To make the best use of q-RIXS system we decided to develop a separate branchline on BL 8.0.1, which is designed to provide fully optimized beam characteritics suitable for q-RIXS experiments
- SpectroCCD with 5μm spatial resolution has been successfully tested with qRIXS spectrometer at the ALS, and demonstrated a resolving power of ~5000 at C K-edge, which is only limited by the beamline and not the q-RIXS spectrometer. The early results are extremely promising as one could clearly resolve vibronic states in HOPG for the first time. This is leading to new opportunities to utilize study of vibronic state for determining electron-lattice coupling with q-resolution and disect "emergence" arising due to electron-lattice interacting degrees of freedom.
- Commissioning and early experiments of q-RIXS endstation will be conducted at the ALS beamline 8.0.1. Using its unique capability of high data acquisition efficiency and continuously variable spectrometer angle, we plan to perform energy-resolved resonant diffraction and momentum-resolved RIXS measurements on classical correlated materials. We also plan to submit a new proposal for seeking the LCLS beamtime to carry out the first time-resolved q-RIXS experiment at LCLS. We had previously submitted a proposal and received an excellent rating of 1.5 with the comment that we get back to LCLS after the q-RIXS instrument is operational.

Theory activities:

- Secure computational resources at NERSC and other supercomputing centers.
- Continue the development of complete theories for RIXS that take advantage of the new lower energy resolution at ESRF, with a specific focus on electron-phonon interactions and superconducting excitations and collective modes.
- Extending the development of a theory for time-resolved RIXS and conduct simulations of the experiments that will be conducting at LCLS-II once it becomes operational.
- Develop a theory for Floquet excitations of two-particle quantities, determining that not only due replica copies of electronic bands emerge under pump conditions, but fundamental copies of multi-particle excitations can appear as well.
- Continue the development of Floquet codes to investigate "quantum geometry" in transition metal dichalcogenides with potential applications in "valleytronics".

- We will perform a theoretical investigation of the dynamics of kagome antiferromagnet by focusing on the quantum spin liquid phases and the propagation between them, to better understand the dynamics of real materials including Herbertsmithite.
- Investigate "valley Hall effect" applications in "valleytronics" and tuning these effects with changes to material parameters and applied fields.

High pressures:

- We will continue our work on TMCs looking at TaX_2 and MoX_2 (X = S, Se, and Te) as well as their intercalated complexes.
- We plan to study the effect of pressure on the Cs analogues of the 3D hybrid perovskites, and also plan to investigate the Pb-free double perovskites.
- We will work on the effect of pressure on a series of diamondoids with systematically varying molecular geometries and dimensionalities, ranging from zero-dimensional (0D) adamantane to (3D) pentamantane by combining in situ synchrotron powder x-ray diffraction and Raman spectroscopy.

Structural dynamics:

- Continuation of measurements at UED and LCLS probing dynamics in perovskites. 2D versions of these exhibit broadband emission following photoexcitation and these measurements may enable elucidation of the fundamental mechanisms underlying this opto-electronic functionality.
- Laboratory-scale measurements using THz pulses as an all-optical bias within meta-material-based phase-change materials, studying the processes the enable ultrafast switching of the electronic and structural properties.

2D transition metal dichalchogenides (TMDC):

- We plan to augment our ability to control valley pseudospin by intense optical radiation. So far this capability has been applied only to alter the relative phase between the two valley pseudospin components, but not to alter the relative amplitudes.
- We will also explore to use RIXS for the investigation of the rich physics of transition metal dichalcogenide. To test the feasibility, we have performed a quick testing measurement on the monolayer transition metal diachalcogenide WSe_2 at the APS. At the W L-edge, we observed signatures of orbital excitations, indicating the feasibility of using RIXS to probe the properties of the monolayer WSe_2 film. We have been awarded beamtime at APS to formally investigate the collective excitations in WSe_2 films. The film will be provided by FWP 10027.

Expected Progress in FY2018

- We plan to continue utilizing LCLS to perform advanced x-ray scattering experiments, including time-resolved x-ray diffraction, time-resolved RIXS and inelastic scattering, and pulsed field experiments to address the grand challenge problems of "emergence" in and out of equilibrium.

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

- Our goal is to simultaneously control electron (and valley pseudospin) dynamics and structural dynamics in 2D materials and layers using ultrafast laser excitation. Current efforts have addressed each of these two interrelated facets separately.

- We will continue to study TMCs and their intercalated complexes at high pressure.

- We will continue high pressure studies of 2D- and 3D- hybrid perovskites.

- We will continue to explore carbon-based nanomaterials and whether pressure can induce the addition of foreign dopants into diamondoids and induce emergent properties such as ferroelectricity and superconductivity in these materials.

Collaborations

Bolme, Cindy, LLNL; Brus, Louis, Columbia; Caracas, Razvan, Ecole Normale Superieure de Lyon; Cao, Liyou, North Carolina State; Chen, David Z., Caltech; Chen, Xiaojia, HPSTAR, China; Chow, Paul, CIW; Collins, Gilbert, LLNL; Ding, Yang, APS, ANL; dos Santos, A. ORNL; Eggert, Jon, LLNL; Eng, Peter, APS, ANL; Fratanduono, Dayne, LLNL; Goddard, William A., Caltech; Goncharov, Alexander, CIW; Greer, Julia, Caltech; Greven, Martin, U Minnesota; Haskel, Daniel, APS, ANL; Hawreliak, James, Washington State U; Hemley, Russell, Carnegie Institution of Washington; Kono, Yoshio, CIW; Kraus, Richard, LLNL; Lazicki, Amy, LLNL; Mao, Ho-kwang, CIW; Meng, Yue, CIW; Oganov, Artem, SUNY-Stony Brook; Pascarelli, Sakura, ESRF; Shen, Guoyin, CIW; Shen, Howard, George Mason University; Shahar, Anat, CIW; Shu, Jinfu, CIW; Sinogeikin, Stas, CIW; Struzhkin, Viktor, CIW; Thonhauser, Timo, Wake Forest; Tulk, Chris, ORNL; Yang, Wenge, CIW. Analytis, J G, UC Berkeley; Ando, Yoichi, Osaka University; Banerjee, Tamalika, University of Groningen; Baumberger, Felix, U Geneva; Bluhm, Hendrik, Lawrence Berkeley National Laboratory (LBNL); Chen, Cheng-Chien, Argonne National Laboratory; Chen, Yulin, Oxford University, England; Chuang, Yi-De, LBNL; Delaire, Olivier, Oak Ridge National Laboratory; Fahy, Stephen, University College Cork; Freericks, James K., Georgetown University;.; Fujimori, Atsushi, University of Tokyo, Japan, Greven, Martin, University of Minnesota; He, Rui-Hua, Boston College, Massachusetts; Hemminger,John C., UC Irvine; Hill, John, Brookhaven National Laboratory; Hone, James, Columbia; Hussain, Zahid, LBNL; Johnson, Steven, ETH Zurich; Johnston, Steven, University of Tennessee; Kaindl, Robert A., LBNL; Kampf, Arno P., University of Augsburg; Kemper, Alexander F., LBNL; Krishnamurthy, H. R., Indian Institute of Science, Bangalore, India; Lee, Dung-Hai, UC Berkeley; Lipp, Magnus J.,LLNL; Liu , Amy Y., Georgetown University; Martin, L., UC Berkeley; Mazin, Igor I., Naval Research Laboratory; Meevasana, Worawat, Suranaree University of Technology, Thailand; Merlin, Roberto, U. Michigan; Mishchenko, Andrey S, RIKEN Advanced Science Institute, Japan; Monney, Claude, Fritz-Haber-Institut, Berlin, Germany; Nagaosa, Naoto, University of Tokyo; RIKEN Advanced Science Institute, Japan; Orenstein, Joseph, LBNL; Patthey, Luc, Paul Scherrer Institut, Switzerland; Scalapino, Douglas J., UC Santa Barbara; Scalettar, Richard T., UC Davis; Schmitt, Thorsten, Paul Scherrer Institute, Switzerland; Schoenlein, Robert W., LBNL; Sokolowski-Tinten, Klaus, University of Duisburg-Essen, Germany; Shastry, B. Sriram, UC Santa Cruz; Shen, Kyle M., Cornell University; Singh, Rajiv R. P., UC Davis; Stephenson, G.B., Argonne National Laboratory; Stock, Chris, NIST Center for Neutron Research; Indiana University Cyclotron Facility; Strocov, Vladimir N., Paul Scherrer Institute, Switzerland; Thomale, Ronny, University of Wurzburg, Germany; Tohyama, Takami, Kyoto University; Tongay, Sefaattin, Arizona State; Uchida, Shin-Ichi, University of Tokyo, Japan; van Veenendaal, Michel, Northern Illinois University, Argonne National Laboratory; Vishik, Inna, MIT; Wen, Haidan, ANL; Xu, Xiaodong, Washington; Yang, WanLi, LBNL; Yang, Wenge, CIW; Yabashi, Makina, RIKEN, Japan; Zaanen, Jan, University of Leiden, The Netherlands, Zhu, Diling, SLAC LCLS.

Publications

Peer-Reviewed Journal Articles

1. **Charge Density Wave in $YBa_2Cu_3O_{6.67}$ at High Magnetic Fields,** S. Gerber, H. Jang, H. Nojiri, S. Matsuzawa, Y. Yasumura, D. A. Bonn, R. Liang, H. N. Hardy, Z. Islam, A. Mehta, S. Song, M. Sikorski, D. Stefanescu, Y. Feng, S. A. Kivelson, T. P. Devereaux, Z.-X. Shen, C.-C. Kao, W.-S. Lee, D. Zhu, J.-S. Lee, Science **350**, 949 (2015).

2. **Ultrafast Dynamics of Localized Magnetic Moments in the Unconventional Mott Insulator Sr_2IrO_4,** O. Krupin, G. Dakovski, B. J. Kim, J. W. Kim, J. H. Kim, S. Mishra, Y. D. Chuang, C. Rayan-Serrao, W. S. Lee, W. Schlotter, M. Minitti, D. Zhu, D. Fritz, M. Chollet, R. Ramesh, S. Molodtsov, Turner, Joshua. J. Phys. Cond. Mat., *accepted.*

3. **Raman and fluorescence characteristics of resonant inelastic X-ray scattering from doped superconducting cuprates.** H. Y. Huang, C. J. Jia, Z. Y. Chen, K. Wohlfeld, B. Moritz, T. P. Devereaux, W. B. Wu, J. Okamoto, W. S. Lee, M. Hashimoto, Y. He, Z. X. Shen, Y. Yoshida, H. Eisaki, C. Y. Mou, C. T. Chen, D. J. Huang, Scientific Report **6**, 19657 (2016).

4. **Ultrafast lattice dynamics of the electronically driven, lattice directed charge density wave in $TbTe_3$**. R. G. Moore, W. S. Lee, P. S. Kirchman, Y. D. Chuang, A. F. Kemper, M. Trigo, L. Patthey, D. H. Lu, O. Krupin, M. Yi, D. A. Reis, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, G. Hays, P. Hering, T. Benson, J. -H. Chu, T. P. Devereaux, I. R. Fisher, Z. Hussain, and Z. -X. Shen, Phys. Rev. B **93**, 024304 (2016).

5. **Magnetic order dynamics in optically excited multiferroic $TbMnO_3$.** J. A. Johnson, T. Kubacka, M. C. Hoffmann, C. Vicario, S. de Jong, P. Beaud, S. Grübel, S.-W. Huang, L. Huber, Y. W. Windsor, E. M. Bothschafter, L. Rettig, M. Ramakrishnan, A. Alberca, L. Patthey, Y.-D. Chuang, J. J. Turner, G. L. Dakovski, W.-S. Lee, M. P. Minitti, W. Schlotter, R. G. Moore, C. P. Hauri, S. M. Koohpayeh, V. Scagnoli, G. Ingold, S. L. Johnson, and U. Staub, Phys. Rev. B. **92**, 184429 (2015).

6. **Observation of charge density wave order in 1D mirror twin boundaries of singlelayer $MoSe_2$**, Sara Barja, Sebastian Wickenburg, Zhen-Fei Liu, Yi Zhang, Hyejin Ryu, Miguel M. Ugeda, Zahid Hussain, Z.-X. Shen, Sung-Kwan Mo, Ed Wong, Miquel B. Salmeron, Feng Wang, Michael F Crommie, D. Frank Ogletree, Jeffrey B. Neaton, Alexander Weber-Bargioni; Nature Physics, in press, 2016.

7. **Characterization of collective ground states in single-layer $NbSe_2$**, M.M. Ugeda, A.J. Bradley, Y. Zhang, S. Onishi, Y. Chen, W. Ruan, C. Ojeda-Aristizabal, H. Ryu, M.T. Edmonds, H.Z. Tsai, A. Riss, S.K. Mo, D.H. Lee, A. Zettl, Z. Hussain, Z.X. Shen, M.F. Crommie, Nature Physics, V12, 1 (Jan. 2016)

8. **Dynamic Structural Response and Deformations of Monolayer MoS_2 Visualized by Femtosecond Electron Diffraction**, E. M. Mannebach, R. Li, K-A. Duerloo, C. Nyby, P. Zalden, T. Vecchione, F. Ernst, A. H. Reid, T. Chase, X. Shen, S. Weathersby, C. Hast, R. Hettel, R. Coffee, Nick Hartmann, A. R. Fry, Y. Yu, L. Cao, T. F. Heinz, E. J. Reed, H. A. Dürr, X. Wang, and A. M. Lindenberg, Nano Lett. **15**, 6889-6895 (2015).

9. **Linearly Polarized Excitons in Single- and Few-Layer ReS_2 Crystals**, O. B. Aslan, D. A. Chenet, A. M. van der Zande, J. C. Hone, and T. F. Heinz, ACS Photonics **3**, 96−101 (2016)

10. **Ultrafast Manipulation of Valley Pseudospin**, Z. Ye, D. Sun, and T. F. Heinz, Nature Phys. (under review).

11. **Pressure tuning the lattice and optical response of silver sulfide,** Z. Zhao, H. Wei, and W. L. Mao, Adv. Opt. Mater., submitted.

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

13. **In situ measurements of lithiation-induced stress in silicon nanoparticles using micro-Raman spectroscopy,** Z. Zeng, N. Liu, Q. S. Zeng, S. W. Lee, W. L. Mao, and Y. Cui, Nano Energy **22**, 105-110 (2016).

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

15. **The electronic structure of structurally strained Mn_3O_4 postspinel and the relationship with Mn_3O_4 spinel,** S. Hirai, Y. Goto, Y. Sakai, A. Wakatsuki, Y. Kamihara, and M. Matoba, J Phys. Soc. Japan 84,114602.

16. Shigeto is submitting an erratum which will include SIMES support.

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

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Diamondoid Science and Applications

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Overview

Diamondoids are unique new carbon-based nanomaterials consisting of 1–2 nanometer, fully hydrogen-terminated diamond particles. Unlike their conjugated counterparts, graphene or carbon nanotubes, the carbon atoms in diamondoids are exclusively sp^3-hybridized, leading to unique electronic and mechanical properties. Diamondoids behave much like small molecules, with atomic-level uniformity, flexible chemical functionalization, and systematic series of sizes, shapes and chiralities. At the same time diamondoids offer more mechanical and chemical stability than small molecules, and vastly superior size and shape control compared to inorganic nanoparticles. This family of new carbon nanomaterials is thus an ideal platform for approaching the grand challenges of energy flow at the nanoscale and synthesis of atomically perfect new forms of matter with better precision than any other nanomaterials system.

This program explores and develops diamondoids as a new class of functional nanomaterials based upon their unique electronic, mechanical, and structural properties. This includes all phases of investigation, from diamondoid isolation from petroleum, chemical functionalization, and molecular assembly, as well as electronic, optical and theoretical characterization. We have currently focused on three areas of research: synthesis, electronic properties, and thin film growth. This naturally requires the broad expertise and collaboration between a number of investigators to successfully approach tackle these problems. This approach has yielded fruit, enabling synthesis of a number of new compounds, and exploration of their structural and electronic properties. In particular the ability of these materials to control the flow of electrons and emitted electron energy at the molecular level is an exciting direction for mastering energy flow at the nanoscale. The team meets biweekly to review current progress and initiate new ideas.

Progress in FY2016

As proposed, we prepared completely rigid, nm-sized hydrocarbon structures are accessible through the coupling of diamondoids through their secondary positions. Indeed, nanometer-sized doubly-bonded diamondoid dimers and trimers, which may be viewed as models of diamond with surface sp^2-defects, were prepared from their corresponding ketones *via* a McMurry coupling and were characterized by spectroscopic and crystallographic methods. The neutral hydrocarbons and their radical cations were studied utilizing density functional theory (DFT) and *ab initio* (MP2) methods, which reproduce the experimental geometries and ionization potentials well. The van der Waals complexes of the oligomers with their radical cations that are models for the self-assembly of diamondoids, form highly delocalized and symmetric electron-deficient structures. This implies a rather high degree of □-delocalization within the hydrocarbons not too dissimilar to delocalized π-systems. As a consequence, sp^2-defects are thus also expected to be nonlocal, thereby leading to the observed high surface charge mobilities of diamond-like materials. In order to be able to use the diamondoid oligomers for subsequent surface attachment and modification, their C–H-bond functionalizations were studied and these provided halogen and hydroxy derivatives with conservation of unsaturation. Our studies also help elucidate graphitization and diamond surface defects. As many properties of diamond materials can be traced back to surface impurities, the preparation of such unsaturated larger diamondoid particles with well-defined structures can helps interpret these findings (e.g., EAs, IPs, fluorescence).

One of the most exciting insights from examining self-assembly direct by diamondoids has been realizing under which conditions certain inorganic structures form. Rather than a random relationship between the inorganic/diamondoid species and the resulting architecture, we now believe that the structure arises from the inorganic material's preferred 2D structure (e.g., a triagonal bonding network for CuS), which is then 'wrapped' into lower-dimensional shapes by the steric bulk and intermolecular dispersion attraction of the diamondoids. In Cu-S materials the preferred trigonal bonding network is retained in the diamondoid composite, forming a three triangle nanotube encaged by the adamantane species. Similarly, the 'square-triangle' 2D structure of Ag-S is retained for both adamantane and diamantane directed materials. This is somewhat surprising, as the steric bulk and shape of diamantane is quite different from adamantane. A slight structural shift in the direction the bonding triangles (two in the same direction at once rather than alternating) is observed, yet this change is less dramatic than anticipated. These results seem to indicate that to a large degree the inorganic bonding is determined by the inorganic species, with the geometric 'wrapping' of the structure determined by the organic ligand. This is an important hypothesis for predicting the electronic properties of the new composites, as they could then be viewed as dimensionally restricted subsets of the parent 2D material, rather than an individually unique material where the properties would be different and unpredictable for each structure.

Diamondoids are unique for their true diamond structure that can serve as a homogeneous nucleation site for diamond nucleation and growth. Diamondoid seeding followed by diamond CVD can form high purity,~10 nm nanoparticles or ultra-high seeding density thin films. The small size and high purity makes these ideal candidates for controlling and manipulating optical and quantum coherence through active color centers in diamond. We have exploited the diamondoid's purity and controlled nanoparticle growth to produce the highest-quality optically active diamond nanoparticles and thin films and characterize their performance. Since optical color centers and quantum coherence in nanomaterials is a substantial and expanding discipline, we have collaborated with Prof. Steven Chu and Prof. Jelena Vuckovic to bring their expertise to this project. Together with these groups, we wre able to demonstrate high-quality diamond emitters on both homoepitaxial and heteroepitaxial structures (Nano Lett 2016).

Expected Progress in FY2017

Among developing further methods for the preparation of an even broader variety of functional diamondoid derivatives, we will also plan the preparation of a variety of diamondoid-carbon nanotube (CNTs) adducts and / or hybrids with small graphene models such as pyrene. These adducts will be thoroughly characterized chemically and physically (especially I/V curves via STS) with a keen eye on single-molecule electronics and the dependence on the size, shape, attachment geometry, and functionalization of the diamondoids.

One particular scientifically worthwhile challenge associated with diamondoids is their remarkable ability to stabilize van-der-Waals contact surface through intramolecular dispersion (cf. Schreiner et al. *Nature* **2011**, *477*, 308). This property has not been utilized, for instance in the design of novel materials and catalysts. With regard to materials, we will attempt to prepare the hexaphenylethane (an unknown molecule) analogues with substituents in the *all-meta* positions. The derivative with *all-meta-t*butyl groups indeed is a stable molecule owing to the mutual London dispersion interactions of the *t*butyl groups. Diamondoid groups in the same positions should be even more favorable as the entropic penalty (large for *t*butyl substiuents) is minimized. This approach would give rise to new organic materials that can dissociate at higher temperature, thereby leading to two radicals per molecule and a paramagnetic organic material overall. There are very few examples of such materials that undoubtedly have a large variety of applications, especially in energy science (e.g., conversion of thermal energy into magnetic moment). In the realm of catalysis, we will further develop the use of diamondoids as sterically demanding yet dispersion energy donor binding moieties for ligands (e.g., mixed phospines and others). Finally, we plan on preparing large diamondoid rings connected through saturated and unsaturated moieties for superior adhesion to nonpolar surfaces (utilizing the "Gecko"-effect).

Expected Progress in FY2018

We will further develop and explore the diamondoid nanocrystal growth, synthetic modification of diamondoids, and nano-molecular organization and structure. We will continue to pursue diamond growth using diamondoids as seed particles, and explore which defects can be controllably introduced into different size nanoparticles. We hope to achieve N-V and Si-V centers in sub 5nm diameter diamond particles, which have only been feasible with diamondoid seeding. We will investigate the ultimate stability limit for these defects and measure their environmental stability and emission yield.

Collaborations

Prof. Andrey A. Fokin, Kiev Polytechnic Institute, Ukraine

Prof. Jean-Cyrille Hierso, Université Burgogne, Dijon, France

Prof. Thomas Möller, Techical University of Berlin

Publications

Peer-Reviewed Journal Articles

1. Ultra-low effective work functions from diamondoid modified surfaces. Functionalized Nanodiamonds, part 51. Karthik T. Narasimha, Chenhao Ge, Jason D. Fabbri, William Clay, Boryslav A. Tkachenko, Andrey A. Fokin, Peter R. Schreiner, Jeremy E. Dahl, Robert M. K. Carlson, Z. X. Shen, Nicholas A. Melosh. *Nature Nanotech.* **2016**, *11*, 267–272. DOI: 10.1038/nnano.2015.277

2. Hybrid group IV nanophotonic structures incorporating diamond silicon-vacancy color centers. Functionalized Nanodiamonds, part 52. Jingyuan Linda Zhang, Hitoshi Ishiwata, Thomas M. Babinec, Marina Radulaski, Kai Müller, Konstantinos G. Lagoudakis, Jeremy E. P. Dahl, Robert Edgington, Veronique Souliére, Gabriel Ferro, Andrey A. Fokin, Peter R. Schreiner, Zhi-Xun Shen,* Nick Melosh,* and Jelena Vukovic* *Nano Lett.* **2016**, *15*, 212–217. DOI: 10.1021/acs.nanolett.5b03515

3. Unexpectedly stable primary diamondoid phosphines. Functionalized Nanodiamonds, part 56. Oana Moncea, Maria A. Gunawan, Didier Poinsot, Hélène Cattey, Jonathan Becker, Raisa I. Yurchenko, Ekaterina D. Butova, Heike Hausmann, Marina Šekutor, Andrey A. Fokin,* Jean-Cyrille Hierso,* and Peter R. Schreiner* *J. Org. Chem.* **2016**, *81*, DOI: 10.1021/acs.joc

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7. The Functionalization of Nanodiamonds (*Diamondoids*) as key Parameter of the Easily Controlled Self-Assembly in Micro- and Nanocrystals from the Vapor Phase. Functionalized Nanodiamonds, part 46. Functionalized Nanodiamonds, part 43. Maria A. Gunawan, Didier Poinsot, Bruno Domenichini, Sébastien Chevalier, Céline Dirand, Andrey A. Fokin, Peter R. Schreiner,* and Jean-Cyrille Hierso,* *Nanoscale* **2015**, *8*, 1956–1962. DOI: 10.1039/C4NR04442H. Open Access.

Electronic and Magnetic Structure of Quantum Materials

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Visiting Physicists: Lucio Braicovich, Giacomo Ghiringhelli, Rudolf Hackl, Di-Jinn Huang, Arno Kampf, Xianwen Sun,

Overview

We have made substantial progress on several research fronts to advance our understanding of complex materials through advanced photoelectron spectroscopy techniques coupled with advanced numerical simulations. There are four themes of complementary experimental efforts within this FWP: to study novel superconductors and related materials, to develop in-situ materials synthesis capability, to develop time resolved photoelectron spectroscopy, and to develop spin-resolved photoelectron spectroscopy, and to apply these capabilities to important contemporary material science issues. Through these activities, we also aspire to development scientific coupling with two major scientific user facilities at SLAC- LCLS and SSRL, and to advance complementary tools important to the future of these facilities. These experiments are complemented by closely integrated theoretical simulation and investigations that study model systems with strongly coupled degrees of freedom under equilibrium and non-equilibrium conditions. In the following, we outline our progress through lists of bullets. As this is a brievated version, we will only highlight key results, the full results will be included in the review document.

Progress in FY2016

- ARPES study of the cuprate high-*T*c superconductors
  - Simple BCS-like d-wave superconducting gap has been established in heavily overdoped Bi2212 (p > 0.22), providing simple BCS-like d-wave superconductivity in heavily overdoped Bi2212 (p > 0.22), providing an ideal platform to study the high-Tc superconductivity itself without complex influence of the competing pseudogap.
  - Preliminarily ARPES spectra with improved quality for Tl- and La-based cuprates are obtained at the newly commissioned ARPES endstation at SSRL beamline 5-2.
  - Slightly overdoped Pb-doped Bi2212 has been synthesized by the floating zone method and the gap function has been measured. It showed an anomalous suppression of the gap size around the antinode, which could be explained by the higher harmonics of a d-wave gap or the competition between the pseudogap and superconductivity.
  - Systematic investigation of La2-xSrxCuO4 in the deeply underdoped regime has been performed in order to understand the initial stage of the evolution from a antiferromagnetic Mott insulator to a high temperature superconductor.

- ARPES study of iron-based superconductors
  - Systematic study of the electronic structure in Fe(Te,Se) family reveals incoherent-coherent crossover and orbital dependent band renormaliztion in this model system. The orbital-dependent change in the correlation level agrees with theoretical calculations on the band structure renormalization, and may help to understand the onset of superconductivity in this family (Z. Liu *et al.*, Phys. Rev. B **92**, 235138 (2015)).
  - A case study of $Rb_{0.8}Fe_2(Se_{1-z}S_z)_2$ family compounds (z=0, 0.5, 1) further suggests that instead of the Fermi surface topology, the electronic correlation, as manifested in the quasiparticle bandwidth, is the important tuning parameter for superconductivity, and moderate correlation is essential to achieving high Tc (M. Yi *et al.*, Phys. Rev. Lett. **115**, 256403 (2015)).

- Electronic structure characterization of the topological material $ZrTe_5$
  - Temperature-dependent ARPES reveals Lifshitz transition from electron to hole carriers in bulk, manifest in both the band dispersion and quasiparticle scattering rates
  - High energy- and momentum- resolution laser-based ARPES observes a subtle splitting in the band dispersion, potentially attributable to bulk and surface states. Pending theoretical support, this may represent the first observation by ARPES of the surface state of a weak 3-dimensional topological insulator.

- In-situ ARPES study of MBE grown films
    - Monolayer and multilayer FeSe films on STO have been grown and further characterized in-situ by ARPES
    - High reolution measurements on the monolayer FeSe film reveals a nodeless superconducting gap with moderate anisotropy. The location of the gap maxima cannot be explained by lowest harmonics of sine and cosine function (i.e., or lowest order d-wave, extended s-wave or s± gap function), putting strong constraints on the pairing mechanism of superconductivity. (Y. Zhang *et al.,* arXiv: 1512.06322)
    - The electronic origins of the nematic state in multilayer FeSe films has been studied by both ARPES and STM (Y. Zhang *et al.*, arXiv:1503.01556, W. Li *et al.*, arXiv:1509.01892). The observation of standing wave in STM confirms that the nematicity is driven by electronic rather than lattice degree of freedom. Distinctive momentum dependence of the band reconstruction observed in ARPES suggests that the highly anisotropic nearest-neighbor hopping of dxz and dyz holds the key in understanding the nematicity in iron-based superconductors.
    - Quantum replica bands and Tc enhancement have been observed between the FeSe films on STO(110) and TiO2(100) substrates elucidating the robust nature of the strong, forward focused, electron-phonon coupling.
    - First data has been collected from FeSe films grown and characterized at the new SSRL Beamline 5
    - Oxide films of TiO2 grown on LaAlO3 as well as oxide heterostructures of LaTiO3/SrTiO3 and BaTiO3/SrTiO3 have been developed to control the charge transfer, electron-phonon coupling as well as the O-18 isotope effect between FeSe films and the underlying oxide substrate.
    - Highly uniform ferroelectric films of SrTiO3 have been grown utilizing oxygen-18
    - Recipes of cuprate thin film superconductors are under developement

- Non-equilibrium studies of FeSe films
    - Comparison of time resolved x-ray scattering experiments at LCLS with time resolved ARPES measurements yield a direct measure of the electron-phonon coupling in FeSe films.
    - *Ab initio* calculations of the bandstructure based on photo-modulation of the Se height point to the influence of correlations in tuning the pnictogen and chalcogen height in Fe-based superconductors, as well as a correlation induced, orbitally selective enhancement of electron-phonon coupling in FeSe.

- Time-resolved ARPES studies
    - Investigation of the unoccupied band structure in optimally doped Bi2212 by comparing two-photon photoemission (2PPE) data to cluster perturbation theory (CPT) calculations based on both single- and multi-orbital Hubbard models.
    - Using a 4THz out-of-plane coherent phonon mode in Bi2212 to track the c-axis screening as function of electron momentum, doping and temperature.
    - Near gap excitation of the amplitude mode in the charge density wave system CeTe3 reveals dominant optical transition responsible for collective response.
    - Ultrafast dehybridization between f- and d-states in the heavy-fermion compound YbRh2Si2.
    - Switching into a photo-induced, metastable state in TaS2.

- Spin-dependent optical transitions in the topological insulator Bi_2Se_3
    - Time-resolved ARPES with tunable pump energies in the visible range (2.3 ~ 2.8eV) employed to track optical transitions to and from spin-polarized surface-states in Bi_2Se_3
    - Working to understand how light helicity couples to spin excitations, with ultimate goal of controlled optical spin pumping.

- Spin-texture of unoccupied surface resonances in Bi2Se3
    - In collaboration with A. Lanzara at LBNL, mapped the unoccupied spin-texture of Bi2Se3 using spin- and time-resolved ARPES.
    - Revealed a previously unrecognized surface resonance above the Fermi level, which plays an intimate role in the band-inversion mechanism of topological surface state formation.

- Theory activities:
    - Successfully obtained 10.15M CPU-hours in allocations from the National Energy Research Scientific Computing Center (NERSC) for computational simulations related to x-ray based spectroscopies in correlated materials and non-equilibrium, pump-probe photoemission spectroscopies.

- Using a modified version of our small cluster exact diagonalization (ED) code, we investigated the impact of doping on the observed signatures of electron-phonon coupling in lightly doped $SrTiO_3$ in collaboration with the group of F. Baumberger, Geneva [Z. Wang et al, Nature Materials AOP (2016), doi:10.1038/nmat4623]. With a model of strong forward scattering in the electron-phonon coupling, at very low doping we observe strong phonon shake-off satellites in the single-particle spectra. Keeping the coupling strength fixed and increasing the doping, these satellites naturally decrease in intensity following the trend of experimental observation.
- Using our small cluster exact diagonalization (ED) code and the Krylov-subspace time-evolution method, we have investigated the non-equilibrium dynamics of a photoexcited Mott-Peierls/Hubbard-Holstein system tuned near the cross-over transition [Y. Wang et al., Phys. Rev. Lett. 116, 086401 (2016)]. We observe significant softening of the lattice degrees of freedom approaching the transition from the Peierls side and a momentum dependent softening of the excitations at k_F near the quantum critical cross-over (quantum critical point in the thermodynamic limit), which highlight time-resolved methods with sufficient momentum resolution as ideal tools for characterizing such systems.
- Using a perturbation expansion and Wigner equation-of-motion approach, we have analyzed the response of both s-wave, and now d-wave, superconductors to strong driving fields [A. F. Kemper et al, Phys. Rev. B 92, 224517 (2015)]. We find strong amplitude mode (Higgs) oscillations in both the single-particle spectra, self-energies, and anomalous propagators, which point toward the use of photoemission spectroscopy for observing this phenomena, as already has been done for amplitude mode oscillations in charge density wave materials.
- Studied the doping evolution of spin and charge excitations in the Hubbard model using quantum Monte Carlo (QMC) in comparison to standard random phase approximation (RPA) treatments [Y. F. Kung et al., Phys. Rev. B 92, 195108 (2015)]. We find significant differences between the full QMC results and those from RPA up to substantial doping, well inside the region commonly denoted as Fermi liquid, and only observe good agreement between the full QMC results and the RPA approximation at much higher doping levels. The result constrains conventional RPA treatments for describing multiparticle excitations in the usual doping range of interest for the Hubbard model, as well as any understanding of the influence of these excitations on the complex phase diagram, including superconductivity.
- We have characterized the phase diagram and spectral properties of the multi-orbital Hubbard model, which explicitly incorporates both copper and oxygen degrees of freedom for a more materials oriented treatment of strong correlations [Y. F. Kung et al., Phys. Rev. B 93, 155166 (2016)].
- We have used non-equilibrium dynamical mean-field theory (TD-DMFT) in collaboration with J. K. Freericks, Georgetown, to study the driven charge density wave phase of the Falicov-Kimball model [O. P. Matveev et al., J. Supercond. and Novel Mag. 29, 581-585 (2016); O. P. Matveev et al., Phys. Rev. B 93, 045110 (2016)].
- Using quantum Monte Carlo (QMC) on the multi-orbital Hubbard model, we find evidence for fluctuating spin stripes in the vicinity of 1/8th hole doping with a commensurate ordering wavevector. We further find evidence for softening of the magnetic excitation spectrum in good agreement with the upper branch of the so-called “hourglass” spin dispersion from neutron scattering.
- Collaborating with the group of N. Melosh, SLAC/Stanford/SIMES, we have used density functional theory (DFT) to study both the crystal and electronic structures of self-assembled, quasi-one-dimensional, diamondoid transition-metal chalcogenide nano-wires.
- We have used density functional theory (DFT) to identify the band structure of YSb, which displays extreme magneto-resistance (XMR). The results constrain theories of the XMR mechanism and provide a theoretical analysis to underpin a scenario for XMR based on partial band compensation.
- Using exact diagonalization Krylov-subspace time-evolution, we have investigated the impact of field induced pumping on the multi-particle spectra of the Hubbard model. We find Floquet signatures in the spin and charge response functions and develop a two-particle Floquet description to explain these observations.
- Using cluster perturbation theory, we have investigated the evolution of the single-particle band structure in the Hubbard model as a function of doping, tracking the evolution of distinct spectral features from the Mott insulator to the very weakly interacting metal. These results provide a more complete understanding of the character of the states in the vicinity of the Fermi level and their possible connection to the emergence of the pseudogap and superconductivity with doping.
- We have studied both the geometrical and kinetic driven cross-over between one and two dimensions in the single-band Hubbard model to provide a constraint on spin-charge separation scenarios in the two-dimensional limit.
- We have used quantum Monte Carlo to investigate the phase diagram and spectral properties of the doped Hubbard-Holstein model in collaboration with S. Johnston, Tennessee, and E. A. Nowadnick, Cornell. We find a significant momentum dependence in the self-energy induced by the interplay between the electron-phonon

and electron-electron interactions, as well as strong electron-phonon coupling, albeit in a model with isotropic coupling.
  - Continued development of charge transfer, hybridization, full atomic multiplet code for x-ray spectroscopies in transition metal materials.

- Infrastructure and equipment development
  - First data from the newly commissioned beamline V and related experimental end station – this facility is expected to give five fold increase of the performance, and will substantially extend the photon energy range.
  - Commissioned the chalcogenide MBE system and sample transfer system to couple oxide MBE system, chalcogenide MBE system and PLD system to ARPES endstation at SSRL. First data has been collected for FeSe films grown in situ at the new beamline.
  - Continue design and testing of 4-point probe for in-situ transport measurements of thin films.
  - STM to couple to the MBE/ARPES system at SSRL has been constructed and factory testing complete
  - Completed the development of 11eV picosecond laser, optimized for frequency domain experiments, in collaboration with Lumeras Inc. (Y. He et al., Rev. Sci. Instr. 87, 011301 (2016))
  - Continued development of spin-resolved ARPES system in collaboration with LBNL.
  - 1^{st} steps towards implementing a femtosecond time-resolved 11eV source for trARPES studies with tailored time and energy resolution and unrestricted access to the full Fermi surface of most materials.

Expected Progress in FY2017

- Cuprate phase diagram.
  - Search for the proposed pseudogap reentrant behavior and detailed study of the momentum dependence of the pseudogap-superconductivity competition in Bi2212, especially focusing on the spectral weight.
  - Exploration how the Mott insulator evolves into superconductors, by measuring the electronic structure of La2-xSrxCuO4 using the new ARPES endstation at SSRL beamline 5-2.
  - Single crystal growth of electron-doped cuprates as a collaboration within SIMES (ongoing), aiming for deeper understanding of electron-hole asymmetry in the cuprates using the new ARPES beamline at SSRL.
  - Systematic study of the scattering rate and normal state electronic structure.
- Pairing mechanism in the cuprates
  - Search for the pairing glue, extracting condensation energy and superconducting gap in the pure superconducting phase in the heavily overdoped Bi2212 and Tl2201, by the self-energy analysis and spectral lineshape analysis.
- Competing phase in iron-based superconductors
  - Characterize the underlying electronic structure and its evolution in the C_4 magnetic phase in $Ba_{1-x}Na_xFe_2As_2$ and $Ba_{1-x}K_xFe_2As_2$ system, aiming to understand the nature of complex phase diagram.
  - Systematic study of K-coated multilayer FeSe thin film, in conjunction with data from FeSe single crystals, to elucidate the origin of nematicity and its relationship to superconductivity.
- Role of electron correlations and orbital selectivity to superconductvity
  - Understand the intriguing correlation between Tc and orbital selective band renormalization.
- MBE of oxide films
  - Homoepitaxial STO films grown utilizing O-18 for investigation of isotope effect in monolayer FeSe/STO and investigation of the STO-18 ferroelectric properties
  - TiO2 films will be used for the investigation of the replica bands and O-18 isotope effect in FeSe films.
  - LTO/STO and BTO/STO heterostructures will be used to control the charge transfer and electron-phonon coupling between FeSe and underlying substrate
  - Films of La2CuO4, LSCO and LBCO utilizing ozone assisted MBE will be grown for the exploration of electronic structure evolution with dimension and epitaxial strain via in-situ ARPES and trARPES.
  - Fully commission STM coupled to MBE/ARPES system at SSRL Beamline 5

- Extend time-resolved photoemission studies to systemetaic work on ferro-pnictides
  - Look for signatures of quantum criticality in doping and temperature dependent hot electron lifetimes
  - Investigate electron-phonon coupling strength as function of doping and temperature using out-of-plane A_{1g} and in-plane, 'nematic' E_g modes.
  - Explore how excitation of 'nematic' E_g mode affects band-splitting

- Theory activities:
  - Continued refinement of state-of-the-art quantum Monte Carlo simulations providing for new optical conductivity and Raman response functions in the Hubbard and Hubbard-Holstein models. Extend studies in multi-orbital models for coupling to oxygen B1 bond-buckling and breathing phonon modes identified in experimental studies. Provide insight on the stability of fluctuating stripes in the presence of coupling to lattice degrees of freedom, especially oxygen vibrations.
  - Establish new collaboration with T. Maier, Center for Nanophase Materials Science (CNMS), ORNL. Using the dynamical cluster approximation (DCA++), investigate the single-particle electronic structure and charge and spin structure factors for the single-band Hubbard model as a function of doping. DCA++ provides an embedded cluster, mean-field treatment of the Hubbard model with substantial improvement in the sign-problem allowing for simulations at much lower temperature, while the mean-field embedding ensures all measurements are made in the thermodynamic limit, reducing finite-size effects.
  - Investigate the bi-layer Hubbard model using a non-trivial, sign-problem free implementation of quantum Monte Carlo. Investigate the influence of spin-orbit and strong interlayer couplings on the phase diagram and spectral properties.
  - In collaboration with S. Kivelson and S. Raghu, SLAC/Stanford/SIMES, and D. Scalapino, UCSB, investigate the negative U Hubbard and Holstein models as functions of interaction strength. Specifically, analyze the superconducting transition temperature with increasing interactions to map-out the cross-over to the strong coupling limit and set constraints on the standard Migdal approach.
  - Phenomenological modeling of the photoemission spectrum as a function of momentum in the pseudogap/Fermi arc regime. Study minimal model needed to describe the evolution of peak-dip-hump features, pseudogap, and superconducting signatures in the photoemission response as functions of temperature, momentum, and doping, extending our previous phenomenological treatment restricted to the anti-nodal region [M. Hashimoto et al., Nature Materials 14, 37-42 (2015)].
  - Use the modified Krylov exact diagonalization approach to study time evolution of driven systems, emphasizing the interplay between competing interactions and distinct states of matter. Investigate the possibility of "photoinduced" phase transitions in highly correlated systems, either through applied fields or direct photoexcitation, including the investigation of photoinduced superconductivity by non-trivial means beyond bandwidth control.
  - Continue development of codes for multi-particle response functions appropriate for Keldysh and Krylov subspace methods for systems out of equilibrium such as pump-probe optical conductivity, reflectivity, charge, and spin response functions.
  - Deploy charge-transfer full atomic multiplet code. Improve usability with open-source ab initio back-end support for transition metal oxide, chalcogenide, and pnictide materials. Benchmark the code against existing results in transition metal monoxides and begin tackling signature problems related to catalytic and battery materials. Begin development of an integrated framework to speed production and analysis for different materials.

- Infrastructure and Equipment Development
  - Final commissioning of spin-resolved time-of-flight detector with 11eV laser at SIMES lab
    - First spin-resolved ARPES data on Weyl semimetals and topological materials such as $ZrTe_5$
  - Finish the infrastructure development for new beamline and end station, in-situ sample preparation, time and spin-resolved ARPES, and STM.

Expected Progress in FY2018

- Utilizing the full suite of in situ growth and characterization tools, continue to explore the electronic structure of oxide films and heterostructures as well as oxide/chalcogenide heterostructures
- 1st non-equilibrium trARPES studies using the ultrafast 11eV source: anti-nodal dynamics in cuprates and of superconducting M-pocket in ferro-pnictides, continue to complement ARPES with information about low-energy collective modes and cooperative phenomena of the superconducting phase (Higgs & Leggett modes).
- Start the planning of imaging type and magnetic scattering based spin spectrometer/dector at beamline V.

Collaborations

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Publications

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Correlated Materials – Synthesis and Physical Properties

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Overview

The overarching goal of our research is to understand, and ultimately control, emergent behavior in strongly correlated quantum materials. This broad class of materials holds promise for future applications directly relevant to energy security, affecting technologies from energy distribution, to improved power electronics, to more efficient computing. There are, however, many deep intellectual questions that need to be addressed in order to realize this potential. There are also many opportunities for the development of novel materials with improved properties. The intellectual focus of this FWP sits at the intersection of these challenges and opportunities. Our research combines synthesis, measurement and theory to coherently address questions at the heart of these issues. We use cutting edge, often unique, experimental probes to uncover novel forms of electronic order in a variety of complex materials. Our theoretical work provides a framework to understand the rich variety of possible ordered states, and guides our ongoing measurements and synthesis efforts. Big questions that we collectively address include; what are the rules and organizing principles governing emergent behavior in quantum materials? What is the nature of the coexisting and competing phases in high temperature superconductors, and how do they determine/limit the maximum critical temperatures and fields? And finally, how does quenched disorder affect quantum criticality and inhomogeneous electronic states in strongly correlated materials? Our research addresses these challenging questions in the context of a range of complex quantum materials.

Progress in FY2016

- Ubiquitous signatures of nematic quantum criticality in optimally doped Fe-based superconductors
(Science **352**, 958 (2016))

  A key actor in the conventional theory of superconductivity is the induced interaction between electrons mediated by the exchange of virtual collective fluctuations (originally phonons). Other collective modes that can play the same role, especially spin fluctuations, have been widely discussed in the context of high-temperature and heavy Fermion superconductors. The strength of such collective fluctuations is measured by the associated susceptibility. In this paper, we used differential elastoresistance measurements from five optimally doped iron-based superconductors to show that divergent nematic susceptibility appears to be a generic feature in the optimal doping regime of these materials. This observation motivates consideration of the effects of nematic fluctuations on the superconducting pairing interaction in this family of compounds and possibly beyond.

  One of the particular strengths of our FWP is the intimate connection between theory and experiment. Experiments we perform are motivated by theoretical insights, and results generated from our experiments provoke further development of relevant theories. This paper includes contributions from experiment (IRF) and theory (SAK) in the context of understanding the nematic susceptibility of materials in the presence of disorder in the quantum critical regime.

- Self-Duality and a Hall-insulator phase near the superconductor-insulator transition in InOx
(PNAS 113, 280-285 (2016) and arXiv:1504.08115)

  The magnetic field tuned superconductor-insulator transition (H-SIT) is the paradigmatic quantum phase transition, and along with the quantum-Hall liquid to insulator transition (QHIT), is among the best experimentally studied ones. However, the transition and the ground-state phases proximate it have consistently exhibited features that are seemingly at odds with the generally accepted theoretical "story." In this work we used comprehensive measurements of Hall effect and Magnetoresistance near the H-SIT, allowed us for a first complete characterization of the full resistivity and conductivity tensors in a superconducting thin film in the neighborhood of the (H-SIT). An emergent particle-vortex self-duality at the H-SIT quantum critical point joined by a "Bose insulating" phase above the transition, with a finite Hall resistance, which is fundamentally distinct from a conventional "nderson-insulator," were established for the first time. That these features are analogous to behaviors previously documented near the QHIT supports the existence of the correspondence between the two problems implied by the composite boson theory.

Similar to the previous "bullet", this paper includes contributions from experiment (AK) and theory (SAK). This kind of collaborative approach is an important component of our research.

- Enhanced Superconducting Transition Temperature due to Tetragonal Domains in Two-Dimensionally Doped $SrTiO_3$ and Depth resolved domain mapping in tetragonal $SrTiO_3$ by micro-Laue diffraction

Manuscript in preparation and Applied Physics Letters **108**, 182901 (2016, Editor's Pick).

Strontium titanate is a low-temperature, non-BCS superconductor that superconducts to carrier concentrations lower than in any other system. Neither the mechanism of superconductivity, nor the role of the structure and dielectric properties, are well understood. We studied the effects of twin structure on superconductivity in a 5.5-nm-thick layer of niobium-doped $SrTiO_3$ embedded in undoped $SrTiO_3$. First (manuscript in preparation), we used a scanning superconducting quantum interference device susceptometer to image the local diamagnetic response of the sample as a function of temperature, and observed regions that exhibited a superconducting transition temperature Tc ~ 10% higher than the temperature at which the sample was fully superconducting. The pattern of these regions varied spatially in a manner characteristic of structural twin domains. Second, in collaboiration with HYH from FWP 10069 (Applied Physics Letters **108**, 182901 (2016)), we used depth resolved X-ray micro-Laue diffraction experiments on the low temperature domain structure of $SrTiO_3$. At 80 K, monochromatic X-ray diffraction shows an elongated out-of-plane unit cell axis within a matrix of in-plane oriented tetragonal unit cells. Full deviatoric strain mappings from white beam diffraction show a dominance of two tetragonal domain orientations (x- and z-axes) over a large area of sample surface. This x-ray information sets an upper bound on domain wall widths and offers a method for studying 3D domain structure at low temperatures. The combination of scanning SQUID and X-ray results results emphasize that the anisotropic dielectric properties of $SrTiO_3$ are important for its superconductivity, and need to be considered in any theory of the mechanism of the superconductivity.

Strong collaboration between this FWP and other FWPs in SIMES (in this particular example with FWP 10069) is a characteristic feature of our research.

- Elastoresistance formalism and its use to detect broken symmetries
(Phys. Rev. B **92**, 235147 (2015) and arXiv:1603.03537 (accepted for publication in Reviews of Scientific Instruments))

Resistivity measurements are employed extensively in the field of strongly correlated quantum materials. Since transport properties are determined by the electronic dynamics at the Fermi level, resistivity is often extremely sensitive to Fermi surface changes and electronically-driven phase transitions; however, since resistivity is a second-rank tensor, transport measurements are generically limited in their ability to identify the symmetry properties of the underlying order. In contrast, the elastoresistivity (a fourth-rank tensor defined as the strain derivative of the resistivity) can convey additional information about directional anisotropies and broken point group symmetries which might more subtly manifest in the resistivity itself. Furthermore, since electron-lattice coupling in strongly correlated materials is often large, the order parameter characterizing an electronically-driven phase transition in these materials is often strongly tuned by strain and strongly reflected in transport; the coefficients in the elastoresistivity tensor are then likely to be large, making elastoresistivity very promising from an experimental perspective.

Over the last 2-3 years we have pioneered measurements probing the elastoresistivity of a variety of strongly correlated materials. In these two papers we introduce a general formalism for the elastoresistivity, show how symmetry dictates the form of the elastoresistivity tensor (and hence how elastoresistance measurements can also be used as a probe of broken mirror symmetries) and describe a series of new classes of measurements based on transverse elastoresistance measurements. The latter techniques have a number of specific advantages over earlier manifestations, and are quite broadly applicable. More broadly, this work fits in to our wider investigations of quantum materials in our FWP using strain as a powerful tuning parameter.

- Electronic pair-binding and Hund's rule violations in doped C_{60}
(Phys. Rev. B **93**, 165406 (2016).)

There is strong empirical evidence – especially from experiments on Cs_3C_{60}, that in the Mott insulating phase of doped C_{60} the three electrons form a spin ½ ground-state, rather than the spin 3/2 state that would be expected on the basis of Hund's first rule. The fact that when the electrons are itinerant (for instance, in Cs_3C_{60} under pressure), the electron fluid state that results is superconducting with a relatively high transition temperature suggests that there is an effective attractive interaction between electrons on a C_{60} molecule when the long-range part of the Coulomb energy is collectively screened. What is contravertial is to what extent these behaviors could arise directly from the microscopic repulsive interactions between the electrons, or whether this reflects the physics of the Jahn-Teller coupling of the electrons to an intra-molecular ionic mode. In this paper Kivelson in collaboration with Jiang (an inter-FWP collaboration), successfully carried out a DMRG calculations for various charge states of the t-J model (a strong-coupling limit of the Hubbard model) on the C_{60} lattice. (That convergent results could be obtained for this remarkably large and two dimensional system pushed the limits of what has been achieved with this method.) We have shown that both the Hund's rule violations and the effective attraction between two electrons arise for a broad range of parameters in this model, establishing at least as a point of principle that non-trivial correlation effects may be responsible for the behavior seen in the actual materials.

Expected Progress in FY2017

- Electronic nematicity in Fe based superconductors

Our ongoing experiments (collaboratively combining synthesis, theory and experiment) will target (1) non-linear elastoresistance; (2) use of B_{1g} strain as a transverse field on B_{2g} nematic order; (3) probes of electronic nematicity "beneath" the superconducting dome; and (4) origins and consequences of the re-entrant C_4 phase found for hole-doped systems.

- Elastoresistance measurements of HTSC cuprates

We have begun a series of elastoresistance measurements of single crystal and thin film samples of $La_{2-x}Sr_xCuO_4$ with the aim of investigating the evolution of the nematic susceptibility across the phase diagram in this representative cuprate superconductor. The measurements will potentially address the origin of the HTT to LTO transition and the presence/absence of fluctuating stripe order on the underdoped side of the phase diagram.

- Generalized Superconductor-(metal)-Insulator transitions

To further obtain insight into the H-SIT we propose to use a variety of "knobs" to tune the transition. In particular, to control the disorder, which is a key ingredient for the realization of quantum-H-SIT we plan to control the microstructure of the films by introducing a range of length scales from a microscopic microscopic scale that is realized in amorphous films to intermediate granular (where superconductivity is not supported in the single grain), to large grain islands where superconductivity is supported in the single grain. In addition, the coupling among grains will be modified by either using a back-gate, which modulate the carrier density of an underlying semiconducting layer on which we deposit our films using light when the films are deposited on light-sensitive substrates (e.g. In-doped CdTe). In this collaborative project, magnetotransport measurements will be performed to obtain the full conductivity tensor (AK), and scanning squid magnetometry and susceptometry (KAM) will supplement the transport measurements.

- Photogalvanic effect of topological materials

When light hits an electronic sample momentum is being transferred from the light to the electrons, resulting in measurable current - this is the so-called drag effect. However, electric current can also appear in homogeneous media under uniform illumination due to lack of center of symmetry in the medium. This so-called photogalvanic effect (PGE) was initially detected in complex oxides exhibiting a variety of phenomena associated with the lack of center of symmetry such as magnetoelectric and multiferroic materials. We recently built an apparatus to measure PGE, where we measure the current in different directions of the crystal while controlling the polarization of the uniform illumination (circularly vs. linearly polarized light). We plan to use this apparatus to study topological insulators (e.g.

half-Heuslers) and Weyl semimetals, (e.g. $MoTe_2$) both of which should have pronounced PGE that can shed light on the novel electronic properties of these materials.

- Topology and Superconductivity in epitaxial monolayer metals

Using partial SIMES support we recently completed the construction of a "mini-MBE" system with two effusion sources (K-cells) that is attached to our (also recently constructed) Scanning Tunneling Microscope (STM). The STM system includes a UHV preparation chamber (pressure $<10^{-10}$ torr), and the samples can be prepared (e.g. cleaved) in situ and measured at temperatures below 340 mK, and in the presence of magnetic field up to 12 tesla. For a first experiment we are currently studying single and bi- layers of bismuth epitaxially grown on $NbSe_2$. While the mismatch of the two materials is large, especially in the triangular-lattice direction, a monolayer bismuth does grow epitaxially on $NbSe_2$, exhibiting a variety of charge density wave (CDW) structures that seem to help relieving the large strain in the bismuth layer. We plan to widen our studies to see the effect of strain and CDW on superconductivity which is induced by the substrate, and repeat the study also for Sn.

- Singular signatures of Lifshitz transitions (which change the Fermi surface topology) on the magneto-transport of a Fermi liquid.

In a nematic Fermi liquid, it is possible for a topological transition to occur in which as a function of the magnitude of the nematic order, the Fermi surface passes through a van-Hove point, transitioning from a close to an open Fermi surface. Such a transition can be expected to yield dramatic changes in the magneto-transport. In particular, in the high field limit ($\omega_c\tau >> 1$) for a single- band system with a closed Fermi surface, the sign and magnitude of the Hall number is simply determined by the portion of the Brilluoin zone enclosed by the Fermi surface; however, for an open Fermi surface, or for finite values of , even the Hall number can vary in unexpected ways. In the context of a semiclassical treatment of the transport in a Fermi liquid state, this problem can be solved exactly, and the nature of the critical anomalies apparent in the magneto-transport can be analyzed. The analysis can also be straightforwardly extended to other quantum phase transitions involving changes in Fermi surface topology. The results, therefore, should be useful in designing experimental strategies to explore the nature of putative quantum phase transitions in metals.

- Phenomenological studies of the effect of disorder on the qualitative character of a CDW ground-state.

Incommensurate CDW order is always "fragile" in the sense that even weak quenched randomness destroys the long-range order and, under most circumstances, rounds what would otherwise have been sharply defined CDW phase transitions. Thus, the effect of disorder is of fundamental importance in characterizing such states, and especially the various crossover regimes. In layered systems, for instance, there can be a sharp crossover from a "two-dimensional" regime in which the in-plane correlation length, ξ_{ab}, is large compared to the lattice constant, a, and the interplane correlation length, ξ_c, to an anisotropic "three dimensional" regime, where $\xi_{ab} >> \xi_c >> a$. If unidirectional "stripe" order is favored in the clean limit, then for weak disorder as a function of uniaxial strain, ε, there can be a sharp crossover from a regime where the stripes in different domains are randomly oriented (making the diffraction pattern resemble that expected from bidirectional or ``checkerboard'' order) to a regime in which the unidirectional character of the ideal order is apparent; this occurs at a characteristic value of the strain, ε^*, which is increasingly small the weaker the disorder. There are also interesting differences to be explored between the effects of short-range correlated disorder (such as from random alloying) and long-range correlated disorder (as will arise when the disorders dominantly due to a random distribution of charged impurities). The methods for studying this class of problems using a self-consistent phonon approximation to treat the order parameter fluctuations and the replica trick to handle the disorder averages has been developed, and benchmarked against extensive Monte-Carlo simulations in previous studies. (L. Nie, G. Tarjus, and S. A. Kivelson, "Quenched disorder and vestigial nematicity in the pseudogap regime of the cuprates," Proc. Nat. Acad. of Sci. **111**, 7980-7985 (2014) and L. Nie, L.E. Hayward-Sierens, R. Melko, S. Sachdev, and S. A. Kivelson, "Fluctuating Orders and Quenched Randomness in the Cuprates," Phys. Rev. B **92**, 174505 (2015).) Where appropriate and where possible, we will look for experimental signatures of similar effects in model materials systems, combining theory and experiment.

- Magnetic imaging of strongly correlated materials under strain.

We are investigating the landscapes of magnetism, magnetic susceptibility, and magnetic fluctuations of several families of strongly correlated materials, includes cuprates, pnictides, and Sr_2RuO_4, while applying strain.

- Real-time and -space imaging of spontaneous magnetic fluctuations in spin ices.
  A wide variety of frustrated magnets, both classical and quantum, develop highly degenerate, correlated ground states. We use Superconducting QUantum Interference Device (SQUID) microscopy on classical spin ice and quantum to image the magnetization at the surface, observing and quantifying magnetization landscapes that fluctuate in both time and space and complementing other techniques in studies of emergent phenomena in various classical and quantum magnets by enabling real-space-, -time-, and -energy- resolved detection of spin fluctuations.
- Current-phase relations (CPR) in InAs nanowire Josephson junctions.
  We use scanning superconducting quantum interference device (SQUID) microscopy to directly measure the current-phase relation of InAs nanowire Josephson junctions, demonstrating that the CPR can be tuned by a gate and observing, possibly for the first time, the current-phase relation of a single-mode junction.

Expected Progress in FY2018

- Elastoresistance measurements of strongly correlated materials

We will continue our investigation of the elastoresistance of several families of strongly correlated materials. We will also seek new materials that reveal electronic nematic phases, the study of which might shed light on the significance of nematic fluctuations and nematic quantum criticality in the Fe pnictides and cuprate HTSCs.

- Is an asymptotically approach to a metallic quantum critical point possible?

On a longer time-scale, we will address the issue of whether metallic quantum critical points (MQCP) exist in the true asymptotic sense. In the case in which the system at criticality preserves either time-reversal or inversion symmetry (or both), it is highly probable that the Fermi liquid phases proximate to the MQCP suffer from a Cooper instability, and that the superconducting transition temperature, T_c, does not vanish at the MQCP. In this case, it is not possible to approach asymptotically close to the QCP without a gap developing that changes the character of the critical point. In situations in which time-reversal and inversion symmetry are both broken in the neighborhood of the MQCP, there is generically no Cooper instability; however, the tendency of the quasiparticle effective mass to diverge (at least on certain portions of the Fermi surface) upon approach to a MQCP means that the density of low energy excited states grows correspondingly – this is suggestive that various other sorts of collective organization, resulting in other sorts of broken symmetry phases, may well preempt the putative MQCP even when superconductivity is quenched.

- Investigations of strongly correlated and topological materials

We will continue our investigation of strongly correlated and topological materials using the variety of probes that we developed under this FWP for the past several years. This include STM studies of half-Heusler systems, STM studies of monolayer Bi and Sn and possibly adding In, Photogalvanic effects in Weyl semimetals, and time-reversal symmetry breaking in unconventional superconductrs using the Sagnac effect.

- Magnetic imaging of strongly correlated materials

We will continue to investigate the landscapes of magnetism, magnetic susceptibility, and magnetic fluctuations of several families of strongly correlated materials, includes cuprates, pnictides, and Sr_2RuO_4.

Collaborations

E.D. Bauer (LANL); R.E. Baumbach (NHMFL); E. Berg (Weizmann); N. Breznay (LBNL); Christoph Brüne (Würzburg); Hartmut Buhmann (Würzburg); N. J. Curro (UC Davis); L. DeGiorgi (ETHZ); T. P. Devereaux (Stanford); R. M. Fernandes (UMN); C. Gould (Würzburg);J. J. Hamlin (UF); Ewelina M. Hankiewicz (Würzburg); P. Jarillo-Herrero (MIT); F. Katmis (MIT); H-C. Jiang (Stanford); B. Keimer (Stuttgart); E-A.Kim (Cornell); S. Lederer (MIT); L. Maier (Würzburg); M. B. Maple (UCSD); R. H. McKenzie (Queensland); Laurens W. Molenkamp (Wuerzburg); J.S. Moodera (MIT); M. Norman (ANL); J. Orenstein (UC Berkeley); A. Palevski (TAU); S. Raghu (Stanford);B. Ramshaw (LANL); D. A. Reis (Stanford); F. Ronning (LANL); S. Rosenkranz (ANL); Y. Shattner (Weizmann); Z.-X. Shen (Stanford); B. Spivak (UW); M.A. Steiner (NERL); R. Thomale (Wurzburg); G. Tkachov (Würzburg); S. Uchida (Tokyo); F. Weber (KIT); J. Zaanen (Leiden); D. A. Zocco (KIT)

Publications for FY15 & FY16 (Oct 1st 2014 to date)

Oct 1st 2014 – Dec 31st 2014

1) *Distinguishing bulk and surface electron-phonon coupling in the topological insulator Bi_2Se_3 using time-resolved photoemission spectroscopy*
J. A. Sobota, S.-L. Yang, D. Leuenberger, A. F. Kemper, J. G. Analytis, I. R. Fisher, P. S. Kirchmann, T. P. Devereaux, and Z.-X. Shen
Phys. Rev. Lett. **113**, 157401 (2014) [4 pages] – Published 10 October 2014

2) *Nematic-driven anisotropic electronic properties of underdoped detwinned $Ba(Fe_{1-x}Co_x)_2As_2$ revealed by optical spectroscopy*
C. Mirri, A. Dusza, S. Bastelberger, J.-H. Chu, H.-H. Kuo, I. R. Fisher, and L. Degiorgi
Phys. Rev. B **90**, 155125 (2014) [7 pages] – Published 21 October 2014

3) *Notes on Constraints for the Observation of Polar Kerr Effect in Complex Materials*,
Aharon Kapitulnik,
Physica B **460**, 151-158 (2015). doi:10.1016/j.physb.2014.11.059 – Published online 24 November 2014

4) *Theory of disordered unconventional superconductors*
A. Keles, A. V. Andreev, S. A. Kivelson, and B.Z. Spivak,
JETP **119(**6), 1109 (2015) – Published 1 December 2014

2015

5) *High Temperature Superconductivity in the Cuprates*
B. Keimer, S. A. Kivelson, M. Norman, S. Uchida, and J. Zaanen,
Nature **518**, 179-186 (12 February 2015) doi: 10.1038/nature14165 – Published online 11 February 2015

6) *Erratum: Kerr effect as evidence of gyrotropic order in the cuprates [Phys. Rev. B 87, 115116 (2013)]*
Pavan Hosur, A. Kapitulnik, S. A. Kivelson, J. Orenstein, S. Raghu, W. Cho, and A. Fried
Phys. Rev. B **91**, 039908 – Published 26 January 2015.

7) *Are there quantum oscillations in an incommensurate charge density wave?*
Yi Zhang, Akash V. Maharaj, and Steven A. Kivelson,
Phys. Rev. B **91**, 085105 (2015) – Published 9 February 2015

8) *Nonsinusoidal Current-Phase Relationship in Josephson Junctions from the 3D Topological Insulator HgTe*
Ilya Sochnikov, Luis Maier, Christopher A. Watson, John R. Kirtley, Charles Gould, Grigory Tkachov, Ewelina M. Hankiewicz, Christoph Brüne, Hartmut Buhmann, Laurens W. Molenkamp, and Kathryn A. Moler,
Phys. Rev. Lett. **114**, 066801 – Published 9 February 2015

9) *Evidence for a nematic component to the hidden-order parameter in URu_2Si_2 from differential elastoresistance measurements*
Scott C. Riggs, M.C. Shapiro, Akash V Maharaj, S. Raghu, E.D. Bauer, R.E. Baumbach, P. Giraldo-Gallo, Mark Wartenbe & I.R. Fisher
Nature Communications **6**, 6425 (2015) doi:10.1038/ncomms7425 [6 pages] – Published 06 March 2015

10) *Evidence for broken time-reversal symmetry in the superconducting phase of URu_2Si_2*,
E. R. Schemm, R. E. Baumbach, P. H. Tobash, F. Ronning, E. D. Bauer, A. Kapitulnik,
Phys. Rev. B **91**, 140506(R) – Published 30 April 2015

11) *Pressure dependence of the charge-density-wave and superconducting states in $GdTe_3$, $TbTe_3$, and $DyTe_3$*,
D. A. Zocco, J. J. Hamlin, K. Grube, J.-H. Chu, H.-H. Kuo, I. R. Fisher, and M. B. Maple
Phys. Rev. B **91**, 205114 (2015) [7 pages] – Published 14 May 2015

12) *Classification of Collective Modes in a Charge Density Wave by Momentum-Dependent Modulation of the Electronic Band Structure*,

D. Leuenberger, J. A. Sobota, S.-L. Yang, A. F. Kemper, P. Giraldo-Gallo, R. G. Moore, I. R. Fisher, P. S. Kirchmann, T. P. Devereaux, Z.-X. Shen
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13) *Wave-vector-dependent electron-phonon coupling and the charge-density-wave transition in $TbTe_3$*,
M. Maschek, S. Rosenkranz, R. Heid, A. H. Said, P. Giraldo-Gallo, I.R. Fisher and F. Weber.
Phys. Rev. B **91**, 235146 (2015) – Publised 29 June 2015

14) *Elastoconductivity as a probe of broken mirror symmetries*,
Patrik Hlobil, Akash V. Maharaj, Pavan Hosur, M.C. Shapiro, I.R. Fisher, S. Raghu
Phys. Rev. B **92**, 035148 (2015) - Published 27 July 2015

15) *Observation of universal strong orbital-dependent correlation effects in iron chalcogenides*,
M. Yi, Z. K. Liu, Y. Zhang R. Yu, J. X. Zhu, J. J. Lee, R. G. Moore, F. T. Schmitt, W. Li, S. C. Riggs, J. H. Chu, B. Lv, J. Hu, M. Hashimoto, S. K. Mo, Z. Hussain, Z. Q. Mao, C. W. Chu, I. R. Fisher, Q. Si, Z. X. Shen, D. H. Lu,
Nat. Commun. **6**:7777 doi: 10.1038/ncomms8777 (2015).(published July 23 2015)

16) *Observation of chiral currents at the magnetic domain boundary of a topological insulator*
Y. H. Wang, J. R. Kirtley, F. Katmis, P. Jarillo-Herrero, J. S. Moodera, K. A. Moler
Science (2015), DOI: 10.1126/science.aaa0508 – Published 13 August 2015, Retracted 18 Dec 2015.

17) *Origin of the resistive anisotropy in the electronic nematic phase of $BaFe_2As_2$ revealed by optical spectroscopy*,
C. Mirri, A. Dusza, S. Bastelberger, M. Chinotti, J.-H. Chu, H.-H. Kuo, I.R. Fisher, L. Degiorgi
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18) *Symmetry constraints on the elastoresistivity tensor*,
M. C. Shapiro, Patrik Hlobil, A. T. Hristov, Akash V. Maharaj, and I. R. Fisher,
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2016 (to date)

19) *Self Duality and a possible Hall-insulator phase near the superconductor-to-insulator transition in two-dimensional indium-oxide films*,
Nicholas P. Breznay, Myles A. Steiner, Steven A. Kivelson, Aharon Kapitulnik,
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R.M. Fernandes, S. A. Kivelson, E. Berg,
Phys. Rev. B **93**, 014511 (2016) – Published 19 January 2016

21) *Ultrafast resonant soft x-ray diffraction dynamics of the charge density wave in $TbTe_3$*,
R. G. Moore, W. S. Lee, P. S. Kirchman, Y. D. Chuang, A. F. Kemper, M. Trigo, L. Patthey, D. H. Lu, O. Krupin, M. Yi, D. A. Reis, D. Doering, P. Denes, W. F. Schlotter, J. J. Turner, G. Hays, P. Hering, T. Benson, J.-H. Chu, T. P. Devereaux, I. R. Fisher, Z. Hussain, and Z.-X. Shen,
Phys. Rev. B **93**, 024304 (2016) – Published 25 January 2016

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Phys. Rev. B **93**, 085114 (2016) - Published 5 February 2016

23) *Quantum oscillations in a bilayer with broken mirror symmetry: a minimal model for $YBa_2Cu_3O_{6+\delta}$,*,
A. V. Maharaj, Y. Zhang, B. J. Ramshaw, and S. A. Kivelson
Phys. Rev. B **93**, 094503 (2016) – Published 1 March 2016

24) *NMR Evidence for Inhomogeneous Nematic Fluctuations in $BaFe_2(As_{1-x}P_x)_2$*,

A. P. Dioguardi, T. Kissikov, C. H. Lin, K. R. Shirer, M. M. Lawson, H.-J. Grafe, J.-H. Chu, I. R. Fisher, R. M. Fernandes, and N. J. Curro,
Phys. Rev. Lett. **116**, 107202 (2016) - Published 10 March 2016

25) *Electronic pair-binding and Hund's rule violations in doped* C_{60},
H-C. Jiang and S. A. Kivelson,
Phys. Rev. B **93**, 165406 (2016) – Published 5 April 2016

26) *Depth resolved domain mapping in tetragonal SrTiO3 by micro-Laue diffraction*
Tyler A. Merz, Hilary Noad, R. Xu, H. Inoue, W. Liu, Y. Hikita, A. Vailionis, Kathryn A. Moler and Harold Y. Hwang,
Applied Physics Letters 108 182901 (2016). – Published on 02 May 2016, Editor's Pick.

27) *Ubiquitous signatures of nematic quantum criticality in optimally doped Fe-based superconductors*,
Hsueh-Hui Kuo, Jiun-Haw Chu, Steven A. Kivelson, Ian R. Fisher
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28) *Ising nematic quantum critical point in a metal: a Monte Carlo study*,
Y. Shattner, S. Lederer, S.A. Kivelson, and E. Berg
arXiv:1511.03282

29) *Spin-orbit coupling and odd-parity superconductivity in the quasi-one-dimensional compound,* $Li_{0.9}Mo_6O_{17}$,
C. Platt, W-J. Cho, R.H.McKenzie, R. Thomale, and S. Raghu,
arXiv:1601.04757

30) *Cold-spots and glassy nematicity in underdoped cuprates*,
K. Lee, S.A. Kivelson, and E-H. Kim
arXiv:1603.03104

31) *Measurement of the* B_{1g} *and* B_{2g} *components of the elastoresistivity tensor for tetragonal materials via transverse resistivity configurations*,
M. C. Shapiro, A. T. Hristov, J. C. Palmstrom, Jiun-Haw Chu, and I. R. Fisher
arXiv:1603.03537 (accepted for publication in Reviews of Scientific Instruments)

32) *Electric coupling in scanning SQUID measurements*
Eric M. Spanton, Aaron J. Rosenberg, Yihua H. Wang, John R. Kirtley, Ferhat Katmis, Pablo Jarillo-Herrero, Jagadeesh S. Moodera, Kathryn A. Moler
arXiv: 1512.03373

Spin Physics

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Overview

The Spin Physics program investigates novel phenomena arising from spin interactions and spin-orbit coupling in solids. In conventional semiconductors, spin-orbit coupling gives the possibility of electric manipulation of the spin degrees of freedom, which can be used for data storage and information processing. More recently, it is realized that spin-orbit coupling can lead to a fundamentally new state of matter, the topological insulator. These materials have an energy gap in the bulk, and a conducting topological state on the surface. The spin program develops theoretical concepts and experimental tools to investigate these novel effects.

Progress in FY2016

Zhang's group has theoretically predicted a series of new phenomena on the quantum anomalous Hall (QAH) effect in Cr doped topological insulator (Sb,Bi)2Te3, many of which have been confirmed experimentally. During 2016, his group investigated the possibility of electrically tunable magnetism in magnetic topological insulators. The external controllability of the magnetic properties in topological insulators would be important both for fundamental and practical interests. His group predicts the electric-field control of ferromagnetism in a thin film of insulating magnetic topological insulators. The decrease of band inversion by the application of electric fields results in a reduction of magnetic susceptibility, and hence in the modification of magnetism. Remarkably, the electric field could even induce the magnetic quantum phase transition from ferromagnetism to paramagnetism. His group further proposes a transistor device in which the dissipationless charge transport of chiral edge states is controlled by an electric field. In particular, the field-controlled ferromagnetism in a magnetic topological insulator can be used for voltage based writing of magnetic random access memories in magnetic tunnel junctions. The simultaneous electrical control of magnetic order and chiral edge transport in such devices may lead to electronic and spintronic applications for topological insulators.

Orenstein collaborated with Goldhaber-Gordon on $Cr_2Ge_2Te_6$ substrates. $Cr_2Ge_2Te_6$ is proposed as an insulating ferromagnetic substrate that is ideal for introducing magnetism to 2D metals such as graphene and transition metal dichalcogenides. Orenstein's group is currently investigating the magneto-optical properties of small flakes to assist the Goldhaber-Gordon group in offering feedback to the crystal growers to improve crysal quality, as well as to improve fabrication of devices based on $Cr_2Ge_2Te_6$ substrates: for example, identifying whether $Cr_2Ge_2Te_6$ retains its magnetism after exposure to air for various time periods (difficult to avoid during fabrication). Goldhaber-Gordon has observed indications of magnetic polarization in graphene on $Cr_2Ge_2Te_6$, through Shubnikov-deHaas oscillations enabled by high mobility (routinely 30-40,000 cm2/Vs, much higher than on SiO_2).

Orenstein also worked with Xiang Zhang on transition metal dichalcogenides. They are planning to use the newly acquired magneto-optical cryostat to measure photoluminescence (PL) in transition metal dichalcogenides. The inequivalent valleys of WSe2 in the Brillouin zone can be selectively addressed using circularly polarized light, suggesting the possibility of optical manipulation of the valley pseudo spin degree of freedom. Measurements in applied magnetic fields have shown a small shift of the exciton resonances.

Manoharan, Zhang, and Orenstein continued to work together on the half-metallic surface state of $NaCoO_2$ as a platform for topological superconductivity and Majorana fermions though the mechanism of *s*-wave superconductivity proximity effect. Previous STM measurements of Manoharan on the surface states of $NaCoO_2$ confirmed a bulk bandgap > 1eV, and distinguished the *p*-type doping surface region expected by theory to harbor magnetic surface states. The observed local density of states (LDOS) by STM experiments quantitatively agree with Zhang group's *ab initio* calculations, indicating the single spin-polarized Fermi surface on $NaCoO_2$. The magnetization of the surface states was confirmed by measurements of the magneto-optical Kerr effect by Orenstein group revealing a remnant magnetization of the state with a critical temperature $T \sim 15$ K, in agreement with *T*-dependent scanning tunneling spectroscopy performed by Manoharan group. Now new measurements were obtained by Manoharan on superconductivity induced into the half-metallic surface state by a novel superconducting scanning probe technique. These experiments have revealed superconducting point contact spectra consistent with nodal p-wave superconductivity, the presence of 98% spin polarization in the surface state, and highlighted by the appearance of zero-energy states in concert with p-wave superconductivity; the overall behavior and initial theoretical model indicates a Majorana bound state and topological superconductivity.

Manoharan and Orenstein investigated a new class of 2D materials embedding magnetic dopants into monolayer MoS_2. Manoharan identified single atomic dopants and tunneling spectra consisting with a large spin splitting. Orenstein began Kerr rotation investigations on the same materials to search for dilute magnetism.

In magnetic topological insulators (Cr- and V-doped (Bi,Sb)2Te3, Goldhaber-Gordon has obtained higher activation energies for dissipative transport (~1K vs 200 mK previously) and has made nonlocal measurements which may reveal whether dissipation is associated with edge or bulk states.

Expected Progress in FY2017

Orenstein plans to work on ferroaxial Cu3Nb2O8, which is a ferroaxial magnet, with centrosymmetric triclinic symmetry (space group P1) in the paramagnetic phase. Cu3Nb2O8 orders magnetically at 26 K and develops an electrical polarization of 17μC/m2 below a second magnetic transition at 24 K. In the polar phase below 24 K, a coplanar helicoidal magnetic structure is stabilized with propagation vector km = (0.4876, 0.2813, 0.2029) in the reciprocal space. The electrical polarization in Cu3Nb2O8 is in clear contradiction with the predictions of the cycloidal multiferroics model. Working with Sang-wook Cheong of Rutgers University, he will use our confocal scanning Kerr microscope to help understand the role of domains in determining macroscopic polarization properties.

Orenstein and Zhang plan to investigate the magnetic order in Cr-doped topological insulators, and study the mechanism for ferromagnetism in the insulating regime. Together with Manoharan and Goldhaber-Gordon, Orenstein will perform systematic magneto-optic Kerr measurements on this system. Zhang plans to perform detailed theoretical calculations on the ferromagnetic order and Kerr rotation angle at different chemical potential and compare with the experimental data. Goldhaber-Gordon will manipulate magnetic domain structure using local magnetic fields. Returning to zero ambient magnetic field, this domain structure will be spatially mapped by Orenstein. Domain boundaries are predicted to carry 1D chiral electrical conduction.

Manoharan and Orenstein will investigate highly-doped regions of magnetic monolayer MoS_2 to search for signatures of a dilute magnetic 2D semiconductor. Tunneling measurements by Manoharan will incorporate inelastic tunneling to excite single spin excitations around atomic dopant sites, and Kerr measurements by Orenstein will be coupled with larger domain samples and scanning capabilities.

Manoharan and Zhang will complete the theory of superconducting point contact spectroscopy into a topological superconducting state induced in the half-metallic $NaCoO_2$ surface state. This theory will fit the nodal order parameter and identify other possibilities for zero-energy modes which will then be tested in experiment.

Manoharan will finish investigations of spin splitting observed in a 1D flatband in a linear topological defect assembled into molecular graphene, which also becomes half-metallic at the proper doping, and work with Zhang on a theoretical model based on interactions.

Working with Zhang and motivated by theoretical predictions by Zhang, Goldhaber-Gordon will make superconducting contacts to magnetic topological insulators, and will attempt to measure supercurrent along edges and in bulk in these materials.

Expected Progress in FY2018

Manoharan and Zhang plan to investigate the proximity coupling between superconductors and the quantum anomalous Hall state, and confirm the coupling by measuring the tunneling spectrum. Moreover, Manoharan and Zhang plan to investigate the vortex state of this proximity coupled superconductor, and measure the tunneling spectrum of the core states, to observe possible signatures of the Majorana bound state at zero energy. Goldhaber-Gordon will perform transport measurements on these systems (with nanopatterned electrodes), in order to confirm the chiral topological superconductivity in this system.

Orenstein plans to work on the modes of noncollinear magnets. CrNb3S6, Mn3Sn and Mn3Ge are all examples of noncollinear magnets with interesting properties. CrNb3S6 exhibits a helical phase in zero magnetic field and a soliton lattice in applied field that gives rise to unusual magnetoresistance. Mn3Sn and Mn3Ge are Heusler-based chiral magnets with large anomalous Hall effects owing to Berry curvature. In both samples he will use pump/probe Kerr microscopy to study the magnetic modes of this systems and the relation to transport properties.

Manoharan and Zhang will complete the theory investigation to explain experiment results on spin-polarized topological edge states observed in molecular graphene. This will include a theoretical prediction of the conditions necessary for half-metallicity.

Collaborations

L. Molenkamp (Wuerzburg Germany), K. Wang (UCLA), Q-K Xue (Tsinghua, China), K.He (Tsinghua, China), Yulin Chen (Oxford), Sang-wook Cheong (Rutgers University), David Mandrus, S. Oh (Rutgers University), Xiang Zhang (UC Berkeley/LBNL), Claudia Felser (Max Planck Dresden).

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Atomic Engineering Oxide Heterostructures: Materials by Design

Principal Investigator(s): Harold Y. Hwang (FWP lead), Srinivas Raghu, Yasuyuki Hikita, Jun-Sik Lee

Postdoctoral Scholars and Graduate Students: Xiao Feng, Hisashi Inoue, Tyler Merz, Adrian Swartz, Zhuoyu Chen, Akash Maharaj, Prashant Kumar

Overview

The overarching scientific goals of this FWP are to use techniques we have developed for atomic-scale synthesis of complex oxide heterostructures to address the grand challenges for basic energy sciences. The issues we investigate are central to the challenge of "how do we atomically design and perfect revolutionary new forms of matter with tailored properties", and which are also important to the challenges of controlling processes at the electron level, understanding and creating emergent phenomena, and mastering energy and information on the nanoscale. Keywords for this FWP are *emergence*, *design*, and *engineering*:

- *Emergence* – how can we harness the strongly interacting charge, spin, orbital, and lattice degrees of freedom of transition metal oxides to create new states at their surfaces and interfaces, which exhibit properties beyond their bulk constituents?
- *Design* – how can we use theory to transcend intuition and serendipity, and move towards the rational construction of materials at the atomic scale?
- *Engineering* – how can we use the flexibility and reduced symmetry of oxide interfaces and surfaces to enhance their properties and band lineups for optimal use in energy technologies?

X-ray scattering, spectroscopy, and microscopy are used to examine the surface and interface electronic structure, their nanoscale coupling, and their lateral nanoscale static and dynamic order. Magnetotransport and scanning probes are used to study artificial two-dimensional (2D) superconducting and magnetic oxide heterostructures, towards the development of the mesoscopic physics of *d*-electron systems. Advanced analytical and computational theory techniques are applied to develop a quantitative foundation for analysis and predictive design. In addition to the core mission of DoE BES, these aims are well aligned to the Materials Genome Initiative, and the Mesoscale Materials and Chemistry Initiative currently being developed.

Progress in FY2016

- Carrier density and disorder are two crucial parameters that control the properties of correlated two-dimensional electron (2D) systems. In order to disentangle their individual contributions to quantum phenomena, independent tuning of these two parameters is required. By utilizing a hybrid liquid/solid electric dual-gate geometry acting on the conducting $LaAlO_3/SrTiO_3$ heterointerface, we obtain an additional degree of freedom to strongly modify the electron confinement profile and thus the strength of interfacial scattering, independent from the carrier density. A dual-gate controlled nonlinear Hall effect is a direct manifestation of this profile, which can be quantitatively understood by a Poisson-Schrödinger subband model. In particular, the large nonlinear dielectric response of $SrTiO_3$ enables a very wide range of tunable density and disorder, far beyond that for conventional semiconductors. Our study provides a broad framework for understanding various reported phenomena at the $LaAlO_3/SrTiO_3$ interface, and platform for future work on tuning the superconducting transition.
- We have been theoretically studying the 2D superconductor-insulator quantum phase transition. In recent work, we suggested an explanation for the metallic phase obtained in MoGe and perovskite thin films and heterostructures in

the vicinity of the superconductor-insulator transition. Currently, we are investigating the transition using numerical techniques (DMRG).

- We have completed depth resolved X-ray micro-Laue diffraction experiments on the low temperature domain structure of $SrTiO_3$. At 80 K, monochromatic X-ray diffraction shows an elongated out-of-plane unit cell axis within a matrix of in-plane oriented tetragonal unit cells. Full deviatoric strain mappings from white beam diffraction show a dominance of two tetragonal domain orientations (x- and z-axes) over a large area of sample surface. This information sets an upper bound on domain wall widths and offers a method for studying 3D domain structure at low temperatures.
- We have demonstrated that our novel technique for engineering interface dipole layers can be broadly applied to non-epitaxial interfaces, including non-perovskite systems. This approach has been applied to controlling tunneling barriers for spectroscopy, for manipulating surface photoelectrochemical properties, and artificially tuning band alignments at interfaces.
- Using this dipole tuning approach, we have developed extremely sensitive tunnel junctions which enable us to measure the electron-phonon coupling and superconductivity in doped $SrTiO_3$. Our central finding is that in the normal state, we find large electron-phonon coupling which grows with decreasing carrier density. However, in the superconducting state we measure a gap to T_C ratio consistent with weak coupling superconductivity for all densities. Motivated by these results, we have been theoretically studying strong coupling electron-phonon superconductors using quantum Monte Carlo simulations.
- We are considering scaling theories of electrons in 2D in the presence of both interactions and disorder. We are studying the effect of correlated disorder and Coulomb interactions in a 2DEG and have found new renormalization group fixed point descriptions of electron systems which are metallic, and occur only in the presence of both disorder and Coulomb interactions. We are applying our theory to the phenomenology of the superconductor-insulator transition, as well as the closely related problem of quantum Hall plateau transitions.
- We have demonstrated the selective fabrication of Ruddlesden-Popper (RP) type $SrIrO_3$, $Sr_3Ir_2O_7$, and Sr_2IrO_4 epitaxial thin films from a single $SrIrO_3$ target using pulsed laser deposition (PLD). We identified that the growth conditions stabilizing each phase directly map onto the phase diagram expected from thermodynamic equilibria. This approach allows precise cation stoichiometry control as evidenced by the stabilization of single phase $Sr_3Ir_2O_7$ for the first time, overcoming the close thermodynamic stability between neighboring RP phases. Despite the non-equilibrium nature of PLD, these results highlight the importance of thermodynamic guiding principles to strategically synthesize the targeted phase in complex oxide thin films. These films will be further incorporated in heterostructures to utilize and manipulate the electronic structure arising from strong spin-orbit coupling.

Expected Progress in FY2017

- For the 2D superconductor-insulator quantum phase transition, we will investigate the transition using numerical techniques (DMRG). We are also studying closely related problems of quantum Hall plateau transitions using numerical tools. Experimentally we will used our dual gate device to map out the superconducting phase diagram as a function of density and disorder.
- Using our freestanding thin film growth technique, we will complete our study of the thickness dependent crystalline to amorphous phase transition, and compare with theoretical models of crystalline order in 2D.
- We have been exploring the physics of the half-filled Landau level, focusing on the question of particle-hole symmetry. We will also investigate possible models that display “Hall insulator” behavior. Such an insulating phase may have recently been observed in thin films of indium oxide, and are being explored in other 2D oxide systems.
- We are combining transport with x-ray spectroscopy to examine the evolution of the electronic structure in oxide films gated via solid and ionic-liquid structures.
- We are studying the superconducting properties of quasi-one dimensional systems. We are studying instabilities to triplet superconductivity, as well as the crossover from Luttinger liquid behavior at high temperatures to Fermi liquid behavior at low temperature.

Expected Progress in FY2018

Further theoretical study of strongly enhanced superconducting instabilities near quantum critical points, the goal being to identify limits where higher T_c superconductivity can emerge from a non-Fermi liquid regime, the parametric enhancement of Tc and the effect of quantum critical fluctuations on the superfluid density. Further x-ray probes of magnetic reconstructions in ultrathin magnetic oxide films are planned, first to examine static properties, and eventually dynamical response. Increasing efforts to study magnetotransport in oxides on mesoscopic length scales are planned, as well as the further development and utilization of inelastic tunneling spectroscopy.

Collaborations

T.H. Geballe, S. Kachru, A. Kapitulnik, S. Kivelson, K. A. Moler, Y. Cui, T. P. Devereaux, Z. X. Shen, H. Durr, J. Stohr, J. K. Norskov, A. Nilsson, M. Brongersma, C.-C. Kao, X. Qi (Stanford/SLAC); R. Thomale (ETF Lausanne); H. Akiyama, A. Fujimori, Y. Iwasa, M. Kawasaki, K. Miyano, N. Nagaosa, M. Oshima, S. Shin, H. Takagi, Y. Tokura (Tokyo); T. Kimura, Y. Wakabayashi (Osaka); H. Ohta (Nagoya); T. Egami, H. N. Lee (ORNL); J. Levy (Pittsburgh); Y. Taguchi (RIKEN); D. A. Muller, L. F. Kourkoutis, D. G. Schlom (Cornell); B. G. Kim (Pusan); B. Keimer, J. Mannhart (MPI Stuttgart); T. W. Noh (Seoul); C. Bernard (Fribourg); D. H. A. Blank, G. Rijnders (Twente); R. Ramesh (Berkeley); J. H. Song (Chungnam); A. F. Hebard (Florida); G. A. Sawatzky (UBC); T. Banerjee (Groningen); A. J. Millis (Columbia); F. Baumberger, J. M. Triscone (Geneva); S. J. Allen, D. D. Awschalom, C. Nayak, S. Stemmer, C. Van de Walle (UCSB); S. Rajan (Ohio State); D. Jena (Notre Dame); C. H. Ahn, T. P. Ma (Yale); Y. Dagan (Tel Aviv); J. Aarts, Y. M. Huber (Leiden); C. Attanasio (CNR-INFM); M. G. Blamire (Cambridge); B. Kalisky (Bar-Ilan); H. Kumigashira (KEK, Japan); M. Yu. Kupriyanov (Moscow State); V. N. Kushnir (Belarus State); W. Meevasana (Thailand Center of Excellence in Physics); R. J. Wijngaarden (Vrije).

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Scattering and Spectroscopic Studies of Quantum Materials

Principal Investigator: Professor Young Lee

Collaborators: Hongchen Jiang

Progress in FY2016

Since the start of the FWP, we have made progress on several fronts:

- We have performed inelastic neutron scattering on the quantum spin liquid material herbersmithite in high magnetic fields (strong enough to close the spin gap).
- We have performed density matrix renormalization group (DMRG) calcuations for the structure factor that we can directly compare with the neutron data.
- We have performed and x-ray scattering experiment at the LCLS and observed an enhancement of the charge order in the cuprate $La_{2-x}Cu_xO_4$ in high pulsed magnetic fields up to 30 Tesla.
- Several other scattering experiments are ongoing. Also, numerical calculations are simultaneously being performed to describe the materials we are studying.

Expected Progress in FY2017

We plan to perform further neutron scattering measurements to get a full description of the magnetic excitations in the quantum spin liquid in high magnetic fields. In concert, DMRG calculations will be completed that will predict how the structure factor changes in high fields. We will perform soft x-ray RIXS on the spin liquid to measure the magnetic excitations to high energies. We will synthesize new frustrate magnets and explore their magnetic correlations with novel x-ray techniques (such as using resonant coherent scattering).

Expected Progress in FY2018

We plan to perform further neutron and x-ray scattering measurements on our selected quantum materials (ie, topological magnon insulators, quantum spin liquids, high temperature superconductors). Theoretical tools will be developed to help explore the phase space of new materials to target for synthesis, as well as aid in analysis of the data.

Funding Summary

FY2016

We use our funding to support the core team of research scientists, postdocs and graduate students to perform the research. Also, funds are spent on materials and supplies, as well as traveling to perform the x-ray and neutron scattering research.

FY2017

We plan to fund the core team of research scientists, postdocs and graduate students to perform the research. Also, funds will be spent on materials and supplies, as well as traveling to perform the x-ray and neutron scattering research.

FY2018

We plan to fund the core team of research scientists, postdocs and graduate students to perform the research. Also, funds will be spent on materials and supplies, as well as traveling to perform the x-ray and neutron scattering research.

Collaborations

Takashi Imai (McMaster Univerisity), Michael Norman (Argonne National Lab), Collin Broholm (Johns Hopkins University), Li Lu (University of Michigan), Phuan Ong (Princeton).

Publications

Peer-Reviewed Journal Articles

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Real-time Ptychography of Ion-Insertion Nanomaterials in Liquid

Principal Investigator: William C. Chueh

Progress in FY2016

(A) Development of microfluidic cells for operando X-ray microscopy in liquid environments

We have successfully developed electrochemical liquid X-ray microscopy that probes ion-insertion solids in the soft X-ray regime. The platform combines scanning transmission X-ray microscopy (STXM) with microfluidic liquid cells (Figure 1). The first demonstration was carried out on Li_XFePO_4 microplatelet single crystals, a gold standard material for investigating ion-insertion solids in liquid. The spatio-dynamics of lithium insertion was tracked by monitoring the Fe oxidation state at the nanoscale. By carefully optimizing liquid flow, X-ray dose, and sample preparation, we minimized beam-induced interaction and achieved repeated imaging of the same particle at a spatial resolution of ~ 50 nm (Figure 2). This achievement represents the first successful operando soft X-ray imaging of lithiation/de-lithiation at the sub-particle length scale, and reveals the origin and hysteresis of lithium insertion spatio-dynamics. The result of this work is undergoing final revisions at *Science*.

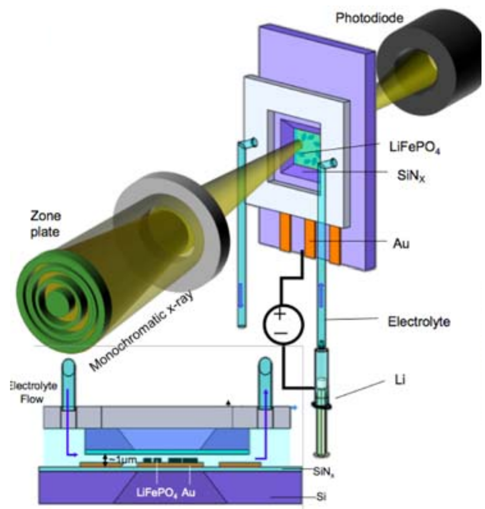

Figure 1: *Schematic of electrochemical liquid transmission X-ray microscopy.*

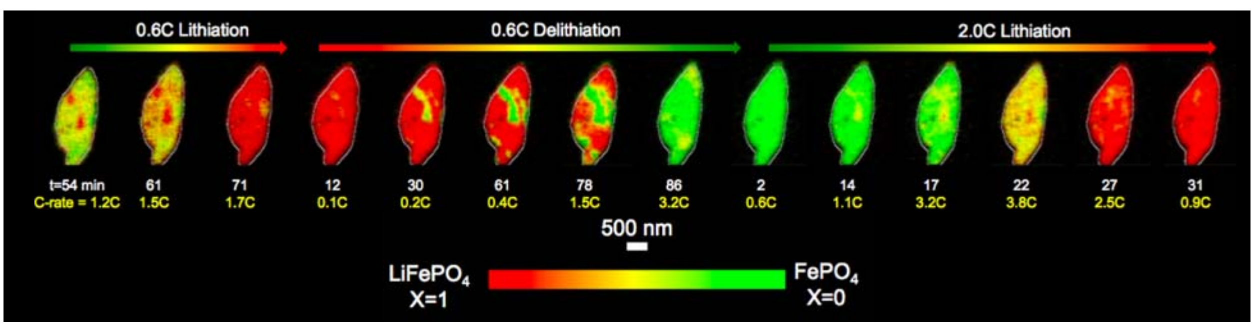

Figure 2: *Spatio-dynamics of lithiation in Li_XFePO_4* measured using electrochemical liquid STXM.

((B) Demonstration of soft-X-ray ptychography in liquid

Having demonstrated electrochemical liquid STXM at 50-nm spatial resolution, we turn toward ptychography using the same microscope and microfluidic cell setup, which promises resolution < 10 nm. Again using Li_XFePO_4 as a model system, we successfully carried out operando liquid ptychography using soft X-rays. In comparison to STXM results, ptychography reconstructions give significant more information. In particular, small microstructural defects not visible in STXM give rise to noticeable contrast, and are providing a rich dataset that correlates nanoscale microstructure defects with redox reactions.

(C) New insights on ion-insertion-induced phase transformation

Simultaneously quantifying nanoscale reaction kinetics and the underlying material composition at the solid-liquid interface is a grand challenge in materials science. By tracking the same particles under multiple lithiation/de-lithiation cycles, we show that nanoscale spatial variations in rate and in composition control the lithiation pathway at the sub-particle length scale, beyond the well-documented phase separation and solid solution pathways at the crystallographic level. Our real-time measurements of the local ion-insertion current density reveal several electrochemical domains within individual primary particles, each of which exhibits a different insertion rate (Figure 2). Upon increased rates of lithiation, we directly observe a transition from compositionally nonuniform domains to a uniform solid solution within these nominally phase-separating particles (Figure 3, top).

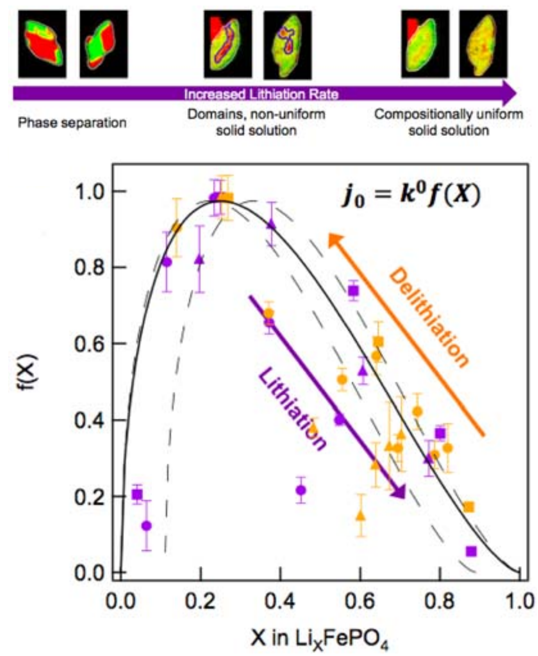

*Figure 3: **(top)** Schematic depicting rate-dependent phase transformation pathway in LiXFePO4. **(bottom)** Composition-dependent exchange current density.*

We further connect the bulk lithiation pathway to the interfacial reaction kinetics by quantifying the spatial and temporal dependence of the interfacial exchange current density (j^0). We demonstrate that spatial variations in j^0 lead to the formation of nonuniform domains, and the composition dependence of j^0 amplifies nonuniformities during de-lithiation but suppresses them during lithiation (Figure 3 ,bottom).

(D) Crucial role of surface diffusion in phase transformation of insertion solids

In nanomaterials, surface transport at the interface of a solid and a fluid becomes more significant in determining the overall transport rate. Despite their crucial important to nanomaterials, the effect of surface transport on solid-state phase transformations pathways is poorly understood, and little is known about how transport rates at surfaces and interfaces ultimately govern phase transformations. We use Li_XFePO_4 as a model system for understanding solid-state phase transformations induced by ion movement. It is well-established both lithium ions and electrons diffuse very quickly in the [010] out-of-plane direction. Diffusion is at least ten orders of magnitude slower in the in-plane directions. We experimentally measure the time required for solid-solution $Li_{0.5}FePO_4$ to separate into Li-rich and Li-poor phases. We observe that moisture and organic solvents increase the rate of surface transport and thus the rate of phase separation by at least two orders of magnitude compared to an inert environment. Our results show that surface diffusion is a necessary prerequisite for phase separation in $LiFePO_4$, and the relative rates of lithium insertion and surface diffusion ultimately determine whether or not a particle phase-separates (Figure 4).

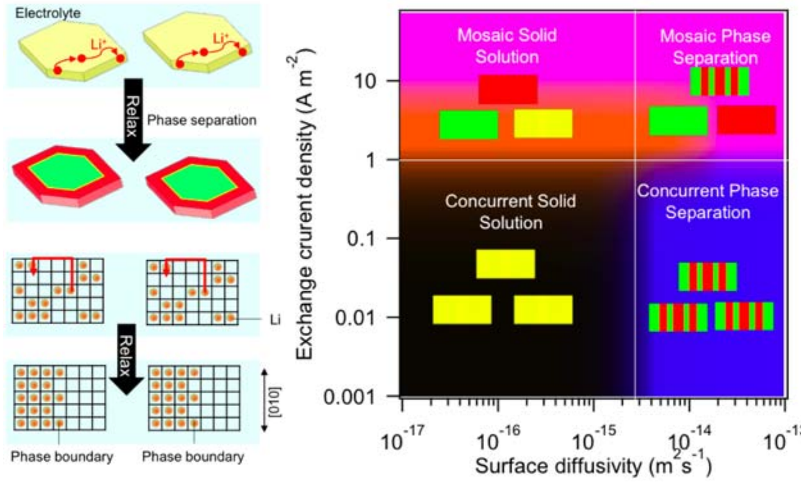

***Figure 4**: (**left**) Schematic showing the role of Li surface diffusion in the phase transformation of metastable solid-solution $Li_{0.5}FePO_4$. (**right**) Calculated phase diagram, validated by experiment, shows that exchange current density and surface diffusivity determines whether or not phase separation takes place.*

(E) Parallel activities using interface-sensitive photoelectron spectroscopy

Whereas STXM and ptychography quantify spatio-dynamics of redox processes, interface-selective spectroscopy such as X-ray photoelectron spectroscopy (XPS) gives the interface chemistry. We have been carrying out ambient pressure XPS to investigate the chemical and electrostatic nature of the gas/solid and liquid/solid interface. Our goal is the combine the interface chemistry with the bulk spatio-dynamics to give a complete picture of ion-insertion reactions. This synergistic effort is supported by a SIMES seed grant.

The result of this has been published in *Advanced Materials*, and an additional manuscript is under consideration at *Nature Materials*.

Expected Progress in FY2017

In the first six months of this seed project, we have made substantial progress in developing X-ray microscopy platform to probe ion-insertion processes in a liquid environment. With the microfluidic-cell-based transmission microscopy platform essentially fully developed, we will focus on the following aspects:

- Exploring oxygen-ion insertion in perovskite oxides in liquid (e.g., $(La,Sr)CoO_{3-x}$)
- Comparing non-equilibrium ion-insertion with equilibrium chemical doping
- Elucidating beam-induced damage mechanisms

Funding Summary

FY2016

Two postdoctoral scholars (2 FTEs) are supported by this $350k seed grant (one started in Oct. 2015, and the other started in Feb. 2016). A custom microfluidic cell for operando X-ray microscopy in liquid has been designed and fabricated, which is supported by this seed grant as well as a $50k seed from SIMES/SLAC. An additional postdoctoral scholar (0.25 FTE) is also being supported by the SIMES seed grant. Our budget is on track for FY16.

Collaborations

D. Shapiro (Advanced Light Source), Johanna Weker Nelson (SSRL), Mike Toney (SSRL), Martin Bazant (MIT), Norman Salmon (Hummingbird), Aleksandra Vojvodic (SLAC), Robert Sinclar (Stanford)

Publications

Peer-Reviewed Journal Articles

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

2. J. Lim, Y. Li, D. H. Alsem, H. So, S. C. Lee, P. Bai, D. A. Cogswell, X. Liu, N. Jin, Y.-S. Yu, N. Salmon, D. Shapiro, M. Z. Bazant, T. Tyliszczak, W. C. Chueh. Nanoscale variation of Li-insertion rate controls compositional spatio-dynamics within battery primary particles. *Science* (2016). *Pending final acceptance*.

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