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Final Technical Report

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

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Topic Area:	X-ray Scattering
Topic Area Program Manager:	Lane Wilson

FINAL TECHNICAL REPORT

1. Major Goal of the Project

This research program aimed to address the scientific questions related to the emergence and control of non-equilibrium electronic phases of matter in strongly-correlated Mott oxides and their interfaces. We were focusing specifically on exploiting the interfaces in heterostructures and superlattices, containing Mott oxides $CaMnO_3$ and $LaNiO_3$ because in such systems, precise control of electronic and magnetic structure in the ground state can be achieved through dimensionality, heterostructuring, interface termination, and lattice strain. We utilized advanced x-ray spectroscopic and scattering techniques, to investigate these phenomena. Additionally, we used intense THz electric-field pulses generated by a femtosecond laser to directly modify the electronic structure and magnetic states of the ultrathin $LaNiO_3$ and $CaMnO_3$ layers in such heterostructures, with the objectives of disentangling, understanding, and harnessing control over the intricate competing interactions responsible for two-dimensional magnetism and metal-insulator transition at the interfaces.

2. What was accomplished under these goals?

During the performance period of this project, we achieved several significant accomplishments directly aligned with the major goals of investigating strongly-correlated materials and two-dimensional electronic systems. Our efforts included the investigation and synthesis of several Mott oxide superlattice systems, combining these materials into heterostructures with atomically precise quasi-2D interfaces. These interfaces exhibit emergent electronic, magnetic, and structural phenomena essential for understanding phase transitions and their potential applications in logic and memory device science.

We focused our studies on probing the electronic structure and magnetic states of these materials, demonstrating new capabilities using soft x-rays and standing-wave excitation. Specifically, we achieved momentum-resolved analysis of quasi-2D oxide layers and accomplished single-unit-cell resolution in depth-dependent probing of electronic structures in oxide superlattices. These advancements are crucial for our ongoing research, particularly for studying buried interfaces with free-electron lasers (FELs).

Further enhancing our research capabilities, we expanded our ultrafast THz activities, conducting extensive measurements using ultrafast THz-pump optical-probe techniques on $CaMnO_3$ and $LaNiO_3$-containing superlattices. We combined various ultrafast detection methods, such as reflection- and transmission-based time-resolved magneto-optical Kerr effect (tr-MOKE) and balanced-diode detection for reflectivity and transmission measurements. These methods enable simultaneous probing of spin dynamics and field-induced insulator-metal transitions at cryogenic temperatures and in applied magnetic fields, offering insights into ferromagnetism control via insulator-metal transitions.

Our investigations also extended to comprehensive thickness, temperature-, and fluence-dependent measurements to separate the electronic and magnetic components of the ultrafast responses. These were coupled with polarization-dependent soft x-ray resonant magnetic scattering measurements, elucidating the interfacial origin of magnetism in these materials.

We continued our static synchrotron-based characterization and optimized the in-situ pulsed laser deposition (PLD) synthesis of ultrathin $CaMnO_3/LaNiO_3$ superlattices for surface-sensitive angle-resolved photoemission spectroscopy measurements. Additionally, we developed a novel soft x-ray standing-wave photoemission technique using second-order Bragg reflection to enhance depth resolution, enabling focused probing into narrower regions of the sample, approximately one unit cell in depth. This innovative technique allowed us to discover charge reconstruction at the interfaces of $CaMnO_3$/$LaNiO_3$ superlattices, critical for the emergent ferromagnetism observed only in superlattices with metallic $LaNiO_3$ layers thicker than four unit cells.

These comprehensive investigations not only advanced our understanding of strongly-correlated systems and two-dimensional electronic structures but also significantly contributed to the development of techniques crucial for exploring new material systems and their interfaces.

In total, the scientific output of this project includes:

9 peer-reviewed articles

2 peer-reviewed *review* articles

1 peer-reviewed article currently under review

2 Ph.D. theses

14 invited talks at various national and international conferences

6 contributed talks at various national and international conferences

4 awards

Below, we present brief summaries of the main accomplishments, including relevant background information and select results.

1. Direct experimental evidence of tunable charge transfer at the $LaNiO_3$/$CaMnO_3$ ferromagnetic interface

J. R. Paudel *et al.*, ***Phys. Rev. B*** **108**, 054441 (2023). ***Alexander Gray - lead PI***

Interfacial charge transfer in oxide heterostructures gives rise to a rich variety of electronic and magnetic phenomena. Designing heterostructures where one of the thin-film components exhibits a metal-insulator transition opens a promising avenue for controlling such phenomena both statically and dynamically. In this study, we utilized a combination of depth-resolved soft x-ray standing-wave and hard x-ray photoelectron spectroscopies in conjunction with polarization-dependent x-ray absorption spectroscopy to investigate the effects of the metal-insulator transition in $LaNiO_3$ on the electronic and magnetic states at the $LaNiO_3$/$CaMnO_3$ interface. We reported a direct observation of the reduced effective valence state of the interfacial Mn cations in the metallic superlattice with an above-critical $LaNiO_3$ thickness (6 unit cells, u.c.) facilitated by the charge transfer of itinerant Ni 3d e_g electrons into the interfacial $CaMnO_3$ layer. Conversely, in an insulating superlattice with a below-critical $LaNiO_3$ thickness of 2 u.c., a homogeneous effective valence state of Mn is observed throughout the $CaMnO_3$ layers due to the blockage of charge transfer across the interface. The ability to switch and tune interfacial charge transfer enables precise control of the emergent ferromagnetic state at the $LaNiO_3$/$CaMnO_3$ interface and, thus, has far-reaching consequences on the future strategies for the design of next-generation spintronic devices.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Jak Chakhalian (Rutgers University), ***Experiments performed at:*** **Advanced Light Source (LBNL, DOE Lab)**, Swiss Light Source (Paul Scherrer Institute)

DOI: 10.1103/PhysRevB.108.054441

2. Modulation-doping a correlated electron insulator

D. Mondal *et al.*, ***Nature Comm.*** **14**, 6210 (2023). ***Alexander Gray - lead co-PI***

Correlated electron materials (CEM) host a rich variety of condensed matter phases. Vanadium dioxide (VO_2) is a prototypical CEM with a temperature dependent metal-to-insulator (MIT) transition with a concomitant crystal symmetry change. External control of MIT in VO_2 - especially without inducing structural changes - has been a long-standing challenge. In this work, we designed and synthesized modulation-doped VO_2-based thin film heterostructures that closely emulate a textbook example of filling control in a correlated electron insulator. Using a combination of hard X-ray photoelectron spectroscopy, charge transport, and structural characterization, we showed that the insulating state can be doped to achieve carrier densities greater than 5×10^{21} cm^{-3} without inducing any measurable structural changes. We found that the MIT temperature continuously decreases with increasing carrier concentration. Remarkably, the insulating state is robust even at doping concentrations as high as ~0.2 e−/vanadium. Finally, our work revealed modulation-doping as a viable method for electronic control of phase transitions in correlated electron oxides with the potential for use in future devices based on electric-field controlled phase transitions.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Naga Phani Aetukuri (Indian Institute of Science), ***Theory:*** Frank M. F. DeGroot (Utrecht University), ***Experiments performed at:*** Temple University (HAXPES Lab) and DESY (PETRA III)

DOI: 10.1038/s41467-023-41816-3

3. Electronic Structure of a Graphene-like Artificial Crystal of $NdNiO_3$

A. Arab *et al.*, ***Nano Lett.*** **19**, 8311 (2019). ***Alexander Gray - lead PI***

Artificial complex-oxide heterostructures containing ultrathin buried layers grown along the pseudocubic [111] direction have been predicted to host a plethora of exotic quantum states arising from the graphene-like lattice geometry and the interplay between strong electronic correlations and band topology. To date, however, electronic-structural investigations of such atomic layers remain an immense challenge due to the shortcomings of conventional surface-sensitive probes with typical information depths of a few angstroms. In this study, we used a combination of bulk-sensitive soft X-ray angle-resolved photoelectron spectroscopy (SX-ARPES), hard X-ray photoelectron spectroscopy (HAXPES), and state-of-the-art first-principles calculations to demonstrate a direct and robust method for extracting momentum-resolved and angle-integrated valence-band electronic structure of an ultrathin buckled graphene-like layer of $NdNiO_3$ confined between two 4-unit cell-thick layers of insulating $LaAlO_3$. The momentum-resolved dispersion of the buried Ni *d* states near the Fermi level obtained via SXARPES is in excellent agreement with the first-principles calculations and establishes the realization of an antiferro-orbital order in this artificial lattice. The HAXPES measurements reveal the presence of a valence-band bandgap of 265 meV. Our findings opened a promising avenue for designing and investigating quantum states of matter with exotic order and topology in a few buried layers.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Jak Chakhalian (Rutgers University), ***Theory:*** Rossitza Pentcheva (University of Duisburg-Essen), ***Experiments performed at:*** Diamond Light Source (UK), Swiss Light Source (Paul Scherrer Institute)

DOI: 10.1021/acs.nanolett.9b03962

4. Probing single unit-cell resolved electronic structure modulations in oxide superlattices with standing-wave photoemission

W. Yang *et al.*, ***Phys. Rev. B*** **100**, 125119 (2019). ***Alexander Gray - lead PI***

Control of structural coupling at complex-oxide interfaces is a powerful platform for creating ultrathin layers with electronic and magnetic properties unattainable in the bulk. However, with the capability to design and control the electronic structure of such buried layers and interfaces at a unit-cell level, a new challenge emerges to be able to probe these engineered emergent phenomena with depth-dependent atomic resolution as well as element- and orbital selectivity. In this study, we utilized a combination of core-level and valence-band soft x-ray standing-wave photoemission spectroscopy, in conjunction with scanning transmission electron microscopy, to probe the depth-dependent and single-unit-cell resolved electronic structure of an isovalent manganite superlattice $[Eu_{0.7}Sr_{0.3}MnO_3/La_{0.7}Sr_{0.3}MnO_3]\times15$ wherein the electronic-structural properties were intentionally modulated with depth via engineered oxygen octahedra rotations/tilts and A-site displacements. Our unit-cell resolved measurements revealed significant transformations in the local chemical and electronic valence-band states, which were consistent with the layer-resolved first-principles theoretical calculations, thus opening the door for future depth-resolved studies of a wide variety of heteroengineered material systems.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Steven May (Drexel University), ***Theory:*** James Rondinelli (Northwestern University), ***Experiments performed at:*** ***Advanced Light Source (LBNL, DOE Lab)***, ***Molecular Foundry (LBNL, DOE Lab)***, Temple University (HAXPES Lab), Swiss Light Source (Paul Scherrer Institute)

DOI: 10.1103/PhysRevB.100.125119

5. Ultrafast terahertz field control of the emergent magnetic and electronic interactions at oxide interfaces

A. M. Derrico *et al.*, ***submitted*** (2024) **arXiv:2402.04302**. ***Alexander Gray - lead PI***

Ultrafast electric-field control of emergent electronic and magnetic states at oxide interfaces offers exciting prospects for the development of new generations of energy-efficient devices. In this study, we demonstrated that the electronic structure and emergent ferromagnetic interfacial state in epitaxial $LaNiO_3/CaMnO_3$ superlattices can be effectively controlled using intense, single-cycle THz electric-field pulses. We employed a suite of advanced X-ray spectroscopic techniques to measure a detailed magneto-optical profile and the thickness of the ferromagnetic interfacial layer. Then, we used a combination of time-resolved and temperature-dependent optical measurements to disentangle multiple correlated electronic and magnetic processes driven by ultrafast, high-field THz pulses. We observe sub-picosecond non-equilibrium Joule heating of the electronic system, ultrafast demagnetization of the ferromagnetic interfacial layer, and slower dynamics indicative of a change in the magnetic state of the superlattice due to the transfer of spin-angular momentum to the lattice. Our findings suggest a promising avenue for the efficient control of two-dimensional ferromagnetic states at oxide interfaces using ultrafast electric-field pulses

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Jak Chakhalian (Rutgers University), ***Experiments performed at:*** ***Advanced Light Source (LBNL, DOE Lab)***

COLLABORATIVE PROJECTS:

During the period of performance of the grant we have also actively participated in five collaborative projects that were directly relevant to the key goals of this program.

6. Strain-induced anion ordering in perovskite oxyfluoride films

J. Wang *et al.*, ***Chem. Mater.*** **33**, 1811 (2021). ***Alexander Gray - lead co-PI***

Anion ordering is a promising route to engineer physical properties in functional heteroanionic materials. A central challenge in the study of anion-ordered compounds lies in developing robust synthetic strategies to control anion occupation and in understanding the resultant implications for electronic structure. In this study, we showed that epitaxial strain induces preferential occupation of F and O on the anion-sites in perovskite oxyfluoride $SrMnO2_{.5-\delta}F_{\gamma}$ films grown on different substrates. Under compressive strain, F tends to occupy the apical-like sites, which was revealed by F and O *K*-edge linearly polarized X-ray absorption spectroscopy and density functional theory calculations, resulting in an enhanced c-axis expansion. Under tensile strain, F tends to occupy the equatorial-like sites, enabling the longer Mn-F bonds to lie within the plane. The oxyfluoride films exhibit a significant orbital polarization of the 3d electrons, distinct F-site dependence to their valence band density of states, and an enhanced resistivity when F occupies the apical-like anion-site compared to the equatorial-like site. By demonstrating a general strategy for inducing preferential anion-site occupancy in oxyfluoride perovskites, this work lays the foundation for future materials design and synthesis efforts that leverage this greater degree of atomic control to realize new polar or quasi-two-dimensional materials.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Steven May (Drexel University), ***Theory:*** James Rondinelli (Northwestern University), ***Experiments performed at:*** ***Advanced Light Source (LBNL, DOE Lab)***, Temple University (HAXPES Lab), Swiss Light Source (Paul Scherrer Institute)

DOI: 10.1021/acs.chemmater.0c04793

7. Correlating electronic properties with M-site composition in solid solution $Ti_yNb_{2-y}CT_x$ MXenes

Y. Yang *et al.*, ***2D Materials*** **10**, 014011 (2023). ***Alexander Gray - lead co-PI***

High electrical conductivity is desired in MXene films for applications such as electromagnetic interference shielding, antennas, and electrodes for electrochemical energy storage and conversion applications. Due to the acid etching-based synthesis method, it is challenging to deconvolute the relative importance that factors such as chemical composition and flake size contribute to resistivity. To understand the intrinsic and extrinsic contributions to the macroscopic electronic transport properties, a systematic study controlling compositional and structural parameters was conducted with eight solid solutions in the TiyNb2−yCTx system. In particular, we investigated the different roles played by metal (M)-site composition, flake size, and d-spacing on macroscopic transport. Hard x-ray photoemission spectroscopy and spectroscopic ellipsometry revealed changes to electronic structure induced by the M-site alloying. Consistent with the spectroscopic results, the low- and room-temperature conductivities and effective carrier mobility are correlated with the Ti content, while the impact of flake size and d-spacing is most prominent in low-temperature transport. The results provide guidance for designing and engineering MXenes with a wide range of conductivities.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Steven May, Yuri Gogotsi (Drexel University), ***Experiments performed at:*** Temple University (HAXPES Lab)

DOI: 10.1088/2053-1583/ac9e68

8. Ultra-thin Epitaxial MgB_2 on SiC: Substrate Surface Polarity Dependent Properties

W. Yang *et al.*, ***Phys. Rev. Mater.*** **7**, 014803 (2023). ***Alexander Gray – collaborator (experiment)***

High-quality, ultrathin superconducting films are required for advanced devices such as hot-electron bolometers, superconducting nanowire single-photon detectors, and quantum applications. Using hybrid physical-chemical vapor deposition, we showed that MgB_2 films as thin as 4 nm can be fabricated on the carbon-terminated 6H-SiC (0001) surface with a superconducting transition temperature above 33 K and a rms roughness of 0.7 nm. Remarkably, the film quality is a function of the SiC surface termination, with the C-terminated surface preferred to the Si-terminated surface. To understand the MgB_2 thin film/SiC substrate interactions giving rise to this difference, we characterized the interfacial structures using Rutherford backscattering spectroscopy/channeling, electron-energy-loss spectroscopy, and x-ray photoemission spectroscopy. The MgB_2/SiC interface structure is complex and different for the two terminations. Both terminations incorporate substantial unintentional oxide layers influencing MgB_2 growth and morphology, but with a different extent, intermixing, and interface chemistry. In this study, we reported measurements of electronic structure, transport, resistivity, and the critical superconducting temperature of MgB_2/SiC that are different for the two terminations, and they linked interfacial structure variations to observed differences. The result showed that the C face of SiC is a preferred substrate for the deposition of ultrathin superconducting MgB_2 films.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Xiaoxing Xi (Temple University), ***Experiments performed at:*** Temple University (HAXPES Lab), Rutgers University

DOI: 10.1103/PhysRevMaterials.7.014803

9. Bulk Electronic Structure of Lanthanum Hexaboride (LaB_6) by Hard X-ray Angle-Resolved Photoelectron Spectroscopy

A. Rattanachata *et al.*, ***Phys. Rev. Mater.*** **5**, 055002 (2021). ***Alexander Gray – collaborator (experiment)***

In the last decade rare-earth hexaborides have been investigated for their fundamental importance in condensed matter, and for their applications in advanced technological fields. Among these compounds, LaB_6 has a special place, being a traditional *d*-band metal without additional *f* bands. In order to understand the bulk electronic structure of the more complex rare-earth hexaborides, in this study we investigated the bulk electronic structure of LaB_6 using tender/hard x-ray photoemission spectroscopy, measuring both core-level and angle-resolved valence-band spectra. Furthermore, we compared the La 3*d* core level spectrum to cluster model calculations in order to understand the bulk-like core-hole screening effects. The results showed that the La 3*d* well-screened peak is at a lower binding energy compared to the main poorly screened peak; the relative intensity between these peaks depends on how strong the hybridization is between La and B atoms. We showed that the recoil effect, negligible in the soft x-ray regime, becomes prominent at higher kinetic energies for lighter elements, such as boron, but is still negligible for heavy elements, such as lanthanum. In addition, we reported the bulk-like band structure of LaB_6 determined by tender/hard x-ray angle-resolved photoemission spectroscopy (HARPES). We compared HARPES experimental results to the free-electron final-state calculations and to the more precise one-step photoemission theory including matrix element and phonon excitation effects. The agreement between the features present in the experimental ARPES data and the theoretical calculations is very good. In addition, we consider the nature and the magnitude of phonon excitations in order to interpret HARPES experimental data measured at different temperatures and excitation energies. We demonstrated that the one-step theory of photoemission and HARPES experiments provides, at present, the only approach capable of probing, both experimentally and theoretically, true "bulk-like" electronic band structure of rare-earth hexaborides and strongly correlated materials.

Experiment: Alexander Gray (Temple University), **Theory:** Jan Minar (University of West Bohemia), **Experiments performed at:** SPring-8 (Japan), ***Advanced Light Source (LBNL, DOE Lab)***

DOI: 10.1103/PhysRevMaterials.5.055002

10. Tuning band alignment at a semiconductor-crystalline oxide heterojunction via electrostatic modulation of the interfacial dipole

M. Chrysler *et al.*, ***Phys. Rev. Mater.*** **5**, 104603 (2021). ***Alexander Gray – collaborator (experiment)***

In this study, we demonstrated that the interfacial dipole associated with bonding across the $SrTiO_3$/Si heterojunction can be tuned through space charge, thereby enabling the band alignment to be altered via doping. Oxygen impurities in Si act as donors that create space charge by transferring electrons across the interface into $SrTiO_3$. The space charge induces an electric field that modifies the interfacial dipole, thereby tuning the band alignment from type II to III. The transferred charge, accompanying built-in electric fields, and change in band alignment are manifested in electrical transport and hard x-ray photoelectron spectroscopy measurements. Ab initio models revealed the interplay between polarization and band offsets. We found that band offsets can be tuned by modulating the density of space charge across the interface. Modulating the interface dipole to enable electrostatic altering of band alignment opens additional pathways to realize functional behavior in semiconducting hybrid heterojunctions.

Experiment: Alexander Gray (Temple University), ***Sample Synthesis:*** Scott Chambers (PNNL, DOE Lab), ***Experiments performed at:*** Temple University (HAXPES Lab), Diamond Light Source (UK)

DOI: 10.1103/PhysRevMaterials.5.104603

INVITED REVIEW ARTICLES:

Our body of work on the oxide materials as well as in the development of x-ray photoemission and scattering techniques has been summarized in two invited review articles.

11. Emergent phenomena at oxide interfaces studied with standing-wave photoelectron spectroscopy

C.-T. Kuo *et al.*, ***J. Vac. Sci. Technol. A*** **40**, 020801 (2022). ***Alexander Gray - lead author***

Emergent phenomena at complex-oxide interfaces have become a vibrant field of study in the past two decades due to the rich physics and a wide range of possibilities for creating new states of matter and novel functionalities for potential devices. The electronic-structural characterization of such phenomena presents a unique challenge due to the lack of direct yet nondestructive techniques for probing buried layers and interfaces with the required Ångstrom-level resolution, as well as element and orbital specificity. In this Review, we surveyed several recent studies wherein soft x-ray standing-wave photoelectron spectroscopy - a relatively newly developed technique — is used to investigate buried oxide interfaces exhibiting emergent phenomena such as metal-insulator transition, interfacial ferromagnetism, and two-dimensional electron gas. The advantages, challenges, and future applications of this methodology were also discussed.

DOI: 10.1116/6.0001584

12. Hard x-ray photoelectron spectroscopy: a snapshot of the state-of-the-art in 2020

C. Kalhaz *et al.*, ***J. Phys.: Condens. Matter*** **33**, 233001 (2021). ***Alexander Gray - contributing author***

Hard x-ray photoelectron spectroscopy (HAXPES) is establishing itself as an essential technique for the characterization of materials. The number of specialized photoelectron spectroscopy techniques making use of hard x-rays is steadily increasing and ever more complex experimental designs enable truly transformative insights into the chemical, electronic, magnetic, and structural nature of materials. This review begins with a short historic perspective of HAXPES and spans from developments in the early days of photoelectron spectroscopy to provide an understanding of the origin and initial development of the technique to state-of-the-art instrumentation and experimental capabilities. The main motivation for and focus of this paper is to provide a picture of the technique in 2020, including a detailed overview of available experimental systems worldwide and insights into a range of specific measurement modi and approaches. We also aim to provide a glimpse into the future of the technique including possible developments and opportunities.

DOI: 10.1088/1361-648X/abeacd

DOCTORAL THESES:

Two graduate students supported (fully or partially) by this program have successfully completed their doctoral degrees in Physics, and are currently continuing to pursue careers in STEM:

13. Investigating Interfacial Ferromagnetism in Oxide Heterostructures Using Advanced X-Ray Spectroscopic and Scattering Techniques

Jay R. Paudel, Temple University, ProQuest Dissertations Publishing, 2024.

Next Position: Postdoc, Lawrence Berkeley National Laboratory, Advanced Light Source, Berkeley, USA

14. Probing the Surface- and Interface-Sensitive Momentum-Resolved Electronic Structure of Advanced Quantum Materials and Interfaces

Arian Arab, Temple University, ProQuest Dissertations Publishing, 2019.

Next Position: Postdoc, Paul Scherrer Institute, Swiss Light Source, Villigen, Switzerland. **Current Position:** Staff Scientist, Federal Food and Drug Administration

3. What opportunities for training and professional development has the project provided?

During the period of performance, the grant supported three graduate students: Jay Paudel (full-time), Arian Arab (part-time), and Alexander Courchene-Trackman (part-time). These students participated in multiple experiments, meetings with collaborators, and in-house lab work.

In addition to the graduate student training and development, the project has also provided research experience for three undergraduate Physics students: Abigail Derrico (now at UC Berkeley), Kethmi Samarasinghe (now at the University of Pennsylvania), and Joseph Grassi (now at Cornell University).

During the period of performance, the students that were supported by this project participated in multiple synchrotron experiments at the following facilities:

1. Advanced Light Source (LBNL, USA) 6 experiments
2. Elettra Synchrotron (Italy) 3 experiments
3. BESSY II (HZB, Germany) 3 experiments
4. Swiss Light Source (PSI, Switzerland) 2 experiments
5. PETRA III (DESY, Germany) 1 experiment

The students learned to operate all a wide variety of x-ray scattering and spectroscopy instruments, as well as to analyze and interpret the data.

Awards: During the period of performance of the grant, the PI and the students that were supported (fully or partially) by this project received the following awards:

1. PI: Alexander Gray – Humboldt Research Fellowship for Experienced Researchers, Alexander von Humboldt foundation, 2022-2024.
2. Jay Paudel - Peter Havas Humanitarian Scholarship for Outstanding Physics Graduate Students, Temple University, 2022. *[for research on interfacial ferromagnetism]*
3. Abigail Derrico – Diamond Research Scholar Fellowship for Undergraduate Students, Temple University, 2022. *[for research on ultrafast control of magnetism in oxide interfaces]*
4. Kethmi Samarasinghe – Frances A. Velay Research Fellowship for Undergraduate Students, Temple University. *[for research on the development of the SW-PEEM technique]*

4. How have the results been disseminated to communities of interest?

During the period of performance of the grant, we have published 11 peer-reviewed articles:

1. **Probing single unit-cell resolved electronic structure modulations in oxide superlattices with standing-wave photoemission,** W. Yang, R. U. Chandrasena, M. Gu, R. M. S. dos Reis, E. J. Moon, Arian Arab, M.-A. Husanu, J. Ciston, V. N. Strocov, J. M. Rondinelli, S. J. May, and A. X. Gray, ***Phys. Rev. B*** **100**, 125119 (2019).
2. **Electronic structure of a graphene-like artificial crystal of $NdNiO_3$,** A. Arab, X. Liu, O. Köksal, W. Yang, R. U. Chandrasena, S. Middey, M. Kareev, S. Kumar, M.-A. Husanu, Z. Yang, L. Gu, V. N. Strocov, T.-L. Lee, J. Minár, R. Pentcheva, J. Chakhalian, and A. X. Gray, ***Nano Lett.*** **19**, 8311 (2019).
3. **Strain-induced anion ordering in perovskite oxyfluoride films**, J. Wang, Y. Shin, J. R. Paudel, J. D. Grassi, R. K. Sah, W. Yang, E. Karapetrova, A. Zaidan, V. N. Strocov, C. Klewe, P. Shafer, A. X. Gray, J. M. Rondinelli, and S. J. May, ***Chem. Mater.*** **33,** 1811 (2021).
4. **Hard X-ray Photoelectron Spectroscopy: A Snapshot of the State-of-the-Art in 2020,** C. Kalhaz, N. K. Fernandoz, P. Bhatt, S. Siol, L. P.H. Jeurgens, C. Cancellieri, K. Rossnagel, K. Medjanik, G. Schönhense, M. Simon, A. X. Gray, S. Nemšák, C. Schlueter, and A. Regoutz, ***J. Phys.: Condens. Matter*** **33**, 233001 (2021).
5. **Bulk Electronic Structure of Lanthanum Hexaboride (LaB_6) by Hard X-ray Angle-Resolved Photoelectron Spectroscopy,** A. Rattanachata, L. Nicolaï, H. P. Martins, G. Conti, M. J. Verstraete, M. Gehlmann, S. Ueda, K. Kobayashi, I. Vishik, C. M. Schneider, C. S. Fadley, A. X. Gray, J. Minár, and S. Nemšák, ***Phys. Rev. Mater.*** **5**, 055002 (2021).
6. **Tuning Band-Alignment at a Semiconductor-Crystalline Oxide Heterojunction via Electrostatic Modulation of the Interfacial Dipole,** M. Chrysler, J. Gabel, T.-L. Lee, A. N. Penn, B. E. Matthews, D. M. Kepaptsoglou, Q. M. Ramasse, J. R. Paudel, R. K. Sah, J. D. Grassi, Z. Zhu, A. X. Gray, J. M. LeBeau, S. R. Spurgeon, S. A. Chambers, P. V. Sushko, and J. H. Ngai, ***Phys. Rev. Mater.*** **5**, 104603 (2021).
7. **Emergent phenomena at oxide interfaces studied with standing-wave photoelectron spectroscopy**, C.-T. Kuo, G. Conti, J. E. Rault, C. M. Schneider, S. Nemšák, and A. X. Gray, ***J. Vac. Sci. Technol. A*** **40**, 020801 (2022).
8. **Correlating electronic properties with M-site composition in solid solution $Ti_yNb_{2-y}CT_x$ MXenes**, Y. Yang, M. Han, C. E. Shuck, R. K. Sah, J. R. Paudel, A. X. Gray, Y. Gogotsi, and S. J. May, ***2D Materials*** **10**, 014011 (2023).
9. **Ultra-thin Epitaxial MgB_2 on SiC: Substrate Surface Polarity Dependent Properties**, W. Yang, L. Kasaei, H. Hijazi, S. Rangan, Y.-W. Yeh, R. K. Sah, J. R. Paudel, K. Chen, A. X. Gray, P. Batson, L. C. Feldman, and X. X. Xi, ***Phys. Rev. Mater.*** **7**, 014803 (2023).
10. **Direct experimental evidence of tunable charge transfer at the $LaNiO_3/CaMnO_3$ ferromagnetic interface**, J. R. Paudel, M. Terilli, T.-C. Wu, J. D. Grassi, A. M. Derrico, R. K. Sah, M. Kareev, F. Wen, C. Klewe, P. Shafer, A. Gloskovskii, C. Schlueter, V. N. Strocov, J. Chakhalian, and A. X. Gray, ***Phys. Rev. B*** **108**, 054441 (2023).

11. **Modulation-Doping a Correlated Electron Insulator**, D. Mondal, S. Mahapatra, A. M. Derrico, R. Rai, J. R. Paudel, C. Schlueter, A. Gloskovskii, R. Banerjee, A. Hariki, F. M. F. DeGroot, D. D. Sarma, A. Narayan, P. Nukala, A. X. Gray, and N. P. B. Aetukuri, ***Nature Comm.*** **14**, 6210 (2023).

Additionally, one research article is currently under review by the journal ***Science Advances***, and the preprint is posted on arXiv:

12. **Ultrafast terahertz field control of the emergent magnetic and electronic interactions at oxide interfaces,** A. M. Derrico, M. Basini, V. Unikandanunni, J. R. Paudel, M. Kareev, M. Terilli, T.-C. Wu, A. Alostaz, C. Klewe, P. Shafer, A. Gloskovskii, C. Schlueter, C. M. Schneider, J. Chakhalian, S. Bonetti, and A. X. Gray, submitted (2024). arXiv:2402.04302

Furthermore, the PI and the students presented the latest results in **20 invited and contributed talks** at the following international conferences:

Invited talks at International Conferences (presented by the PI):

1. **Atomic-level design and ultrafast THz E-field control of the emergent ferromagnetism at oxide interfaces**, Invited talk presented at the 10th International Symposium on Ultrafast Dynamics and Ultrafast Bandgap Photonics, June 4-10, 2023, Hersonissos, Greece.

2. **Synergies Between Synchrotron and Lab-based X-ray Techniques for the Studies of Complex Materials and Interfaces**, Invited talk presented at the AVS Pacific Rim Symposium on Surfaces, Coatings and Interfaces (PacSurf 2022), December 11-15, 2022, Hawaii.

3. **Ultrafast THz E-field control of the emergent electronic and magnetic interactions at the $CaMnO_3/LaNiO_3$ ferromagnetic interface**, Invited talk presented at the Ultrafast Dynamics and Metastability Conference, Georgetown University, November 14-17, 2022, Washington, DC.

4. **Origins of the emergent phenomena at oxide interfaces studied with complementary x-ray spectroscopic and scattering techniques**, Invited talk presented at the 68th Annual AVS International Symposium and Exhibition (AVS 2022), November 6-11, 2022, Pittsburg, Pennsylvania.

5. **Future opportunities for the momentum microscopy studies of novel materials and interfaces - depth, spin, and time resolution**, Invited talk presented at the SSRL/LCLS Users Meeting, September 26-30, 2022, SLAC National Accelerator Laboratory, Menlo Park, California.

6. **Atomic-level design and ultrafast terahertz electric-field control of emergent electronic and magnetic phenomena at oxide interfaces**, Invited talk presented at the International Conference on Quantum in Complex Matter: Superconductivity, Magnetism and Ferroelectricity (Superstripes 2022), June 20-24, 2022, Rome, Italy.

7. **Combining Multiple X-Ray Spectroscopic and Scattering Techniques to Probe Emergent Electronic Phenomena at Oxide Interfaces**, Invited talk presented at the 67th Annual AVS International Symposium and Exhibition (AVS 2021), October 24-29, 2021, Charlotte, North Carolina.

8. **Synergies between Synchrotron and Lab-Based X-Ray Techniques for the Studies of Complex Materials and Interfaces**, Invited talk presented at the 67th Annual AVS International Symposium and Exhibition (AVS 2021), October 24-29, 2021, Charlotte, North Carolina

9. **Enabling Depth and Time Resolution for X-ray Spectroscopic and Scattering Techniques**, Invited tutorial presented at the Dual Nature of f-Electrons Meeting, June 21-24, 2021, Dresden, Germany.

10. **New Frontiers in Electron Spectroscopies: Novel Techniques, Time Resolution and Extreme Conditions**, Invited lecture presented at the School on "Fermi surface and novel phases in strongly correlated electron systems" at the École de Physique des Houches, October 13-19, 2019, Les Houches, France.

11. **Rational Design of Low-Dimensional Electronic Phenomena at Mott Interfaces**, Invited talk presented at the International Conference on Quantum in Complex Matter: Superconductivity, Magnetism and Ferroelectricity (Superstripes 2019), June 23-29, 2019, Ischia, Italy.

12. **Future Directions in X-ray Photoelectron Spectroscopy: Standing-Waves**, Bulk Sensitivity and Time Resolution, Invited talk presented at the Ultrafast Dynamics and Metastability Conference, Georgetown University, April 15-17, 2019, Washington, DC.

13. **Probing Ultrathin Functional Layers and Buried Interfaces with Advanced X-ray Spectroscopic Techniques**, Invited talk presented at the APS March Meeting, March 4-8, 2019, Boston, Massachusetts.

14. **Combining Hard and Soft X-ray Angle-resolved Photoemission to Probe the Bulk Electronic Structure of Engineered Quantum Solids**, Invited talk presented at the 65th Annual AVS International Symposium and Exhibition (AVS 2018), October 21-26, 2018, Long Beach, California.

<u>Contributed Talks at International Conferences (presented by the sponsored students):</u>

15. **Probing depth-resolved electronic structure of two-dimensional layered materials and their heterostructures using standing-wave photoemission microscopy**, presented by Jay Paudel at the APS March Meeting 2023, Las Vegas, Nevada.

16. **Combining ultrafast optical and x-ray spectroscopies for the study of emergent ferromagnetism at the $LaNiO_3/CaMnO_3$ interface**, presented by Abigail Derrico at the APS March Meeting 2023, Las Vegas, Nevada.

17. **Combining depth-sensitive X-ray spectroscopic and scattering techniques to probe interfacial magnetic phenomena in oxide superlattices**, presented by Jay Paudel at the 9th International Conference on Hard X-ray Photoelectron Spectroscopy (HAXPES 2022), Himeji, Japan.

18. **Depth-resolved X-ray characterization of interfacial ferromagnetism in oxide superlattices**, presented by Jay Paudel at the APS March Meeting 2022, Chicago, Illinois.

19. **Ultrafast terahertz field control of the emergent electronic and magnetic interactions at the $CaMnO_3/LaNiO_3$ ferromagnetic interface**, presented by Abigail Derrico at the APS March Meeting 2022, Chicago, Illinois.

20. **Probing interfacial ferromagnetism in oxide superlattices using depth-resolved X-ray spectroscopic and scattering techniques**, presented by Jay Paudel at the 67th Annual AVS International Symposium and Exhibition (AVS 2021), Charlotte, North Carolina.

5. Instrumentation Development

On the instrumentation development side of the project, we have completed construction of the lab-based 5.4 keV HAXPES spectrometer designed specifically for the depth- and momentum-resolved studies of buried layers and interfaces (see Fig. 1 below). The instrument, currently unique in the U.S., is equipped with a 6-axis cryogenic goniometer as well as a wide-acceptance-angle electron analyzer with a 2D photoelectron detector (Scienta EW4000).

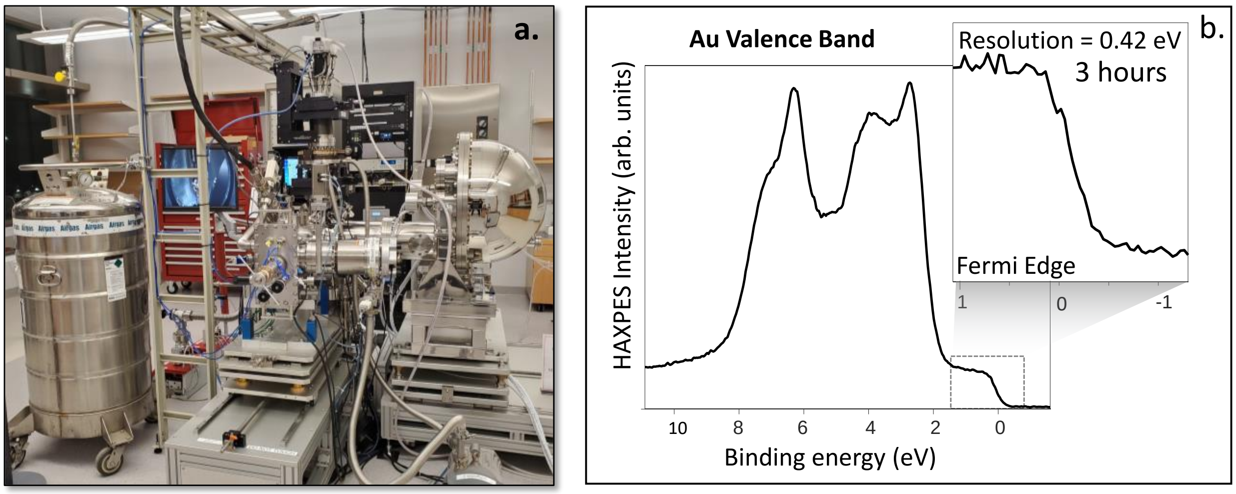

Figure 1. a. Photo of the completed and commissioned tender x-ray HAXPES instrument in the PI's lab at Temple University. **b.** Valence-band spectrum of gold measured with typical settings, providing total experimental energy resolution of 0.42 eV.