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Inversion symmetry breaking cobaltates and vanadates for orbital FETs

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14. ABSTRACT
The project aims to develop new materials with new and enhanced functionalities, enabling new platforms, such as the development of a conducting channel of a logic switch that relies on orbital polarization. The approach we propose takes advantage of the unique properties of complex oxides, which exhibit a wide range of electronic and magnetic phenomena, including magnetism, metal-insulator transitions and ferroelectricity. A key challenge for this project is to understand the orbital and electronic states of transition metal oxides and how their performance can be enhanced using dimensional confinement and interfacial coupling. The approach of the project is to devise new materials implementing oxide heterostructures that exhibit enhanced magnetic and conductive properties. We use a combination of experimental techniques and theoretical analyses to show how charge and spin order parameters are coupled and how to unglue and modify them by the two distinct effects of heterostructuring, namely dimensional confinement and interfacial reconstructions. The reduced dimensionality of transition metal oxides results in novel properties, which are not found in bulk.

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Accomplishments

Research Objectives

The project aims to develop new materials with new and enhanced functionalities, enabling new platforms, such as the development of a conducting channel of a logic switch that relies on orbital polarization. The approach we propose takes advantage of the unique properties of complex oxides, which exhibit a wide range of electronic and magnetic phenomena, including magnetism, metal-insulator transitions and ferroelectricity. A key challenge for this project is to understand the orbital and electronic states of transition metal oxides and how their performance can be enhanced using dimensional confinement and interfacial coupling. The approach of the project is to devise new materials implementing oxide heterostructures that exhibit enhanced magnetic and conductive properties. We use a combination of experimental techniques and theoretical analyses to show how charge and spin order parameters are coupled and how to unglue and modify them by the two distinct effects of heterostructuring, namely dimensional confinement and interfacial reconstructions. The reduced dimensionality of transition metal oxides results in novel properties, which are not found in bulk. The electronic reconstructions imposed by the interface, on the other hand, lead to new properties and phases. This unique phase control can be generally applied to develop otherwise hidden electronic and magnetic behavior in a wide range of materials, such as the superconductor FeSe, topological insulators, nickelates, and cobaltates. This project also provides a rich research environment for students by providing opportunities for international collaborations to perform and propose experiments at international synchrotron facilities.

Correlated oxides are well-known for the existence of intertwined phases of long-range order. One of the objectives in this project is to create a new methodology to control the expression of phase behavior in such systems, the effectiveness of which we demonstrate by unveiling previously unobserved phase behavior. In the first example, we use an approach that breaks inversion symmetry by incorporating the transition metal oxide under study, $LaCoO_3$, into superlattice form with the correlated insulator $LaTiO_3$. This layering breaks inversion symmetry locally and leads to strong orbital polarization. Second, we focus on $NdNiO_3$ thin films and $(NdNiO_3)_m/(NdAlO_3)_4$ superlattices (periodic heterostructure with m-uc $NdNiO_3$ and 4-uc $NdAlO_3$) and study the effect of dimensional confinement and interfacial reconstructions. In the third and fourth examples, we use heterostructures to control the properties of chalcogenide materials. We also report on breakthroughs that use similar principles when applied to complex oxide-chalcogenide interfaces, where the topology of the electronic structure can be controlled by breaking mirror symmetry in the topological crystalline insulator. A key requirement for the advances we report here is the synthesis and microscopic characterization of atomically abrupt heterointerfaces.

Significant results:

Cobaltate-titanate superlattices, Ref. 1.

Achieving an LTO/LCO superlattice structure with well-defined, atomically abrupt layers is a key requirement to engineering and understanding the microscopic origin of orbital polarization. To examine our superlattices, we have used a combination of scanning transmission electron microscopy (STEM) and x-ray diffraction measurements to demonstrate that we have synthesized abrupt, alternating layers of $LaCoO_3$ and $LaTiO_3$ in superlattice form. This is particularly important to show for cobaltate-titanate superlattices because an intermixed double-perovskite compound, La_2CoTiO_6 is the ground state for the superlattice structure. As shown below, we avoid intermixing and fabricate the layered structure using MBE.

First, we present STEM measurements of a $[(LTO)_2/(LCO)_2]\times10$ superlattice[1]. The high-angle annular dark field (HAADF) STEM image in Fig. 1(a) shows that the crystalline structure is maintained throughout the entire film, without any visible defects. In order to image the chemical composition of the superlattice, our collaborators at Brookhaven National Laboratory have measured the electron energy loss spectroscopy (EELS) spectrum of this system (yellow dotted overlay in Fig. 1(a)). Fig. 1(b) shows element-specific maps of La, Ti, Co, and Ti+Co, respectively, and one can see clearly an atomically sharp interface between the cobaltate and titanate layers. One can further analyze the data by plotting the intensity of the Ti and Co EELS peaks as a function of distance along the growth direction [Fig. 1(c)]. These EELS maps demonstrate atomically abrupt interfaces. Furthermore, the La EELS map in Fig. 1(b) shows a uniform electron density distribution of La throughout the region. If there were modulation of the

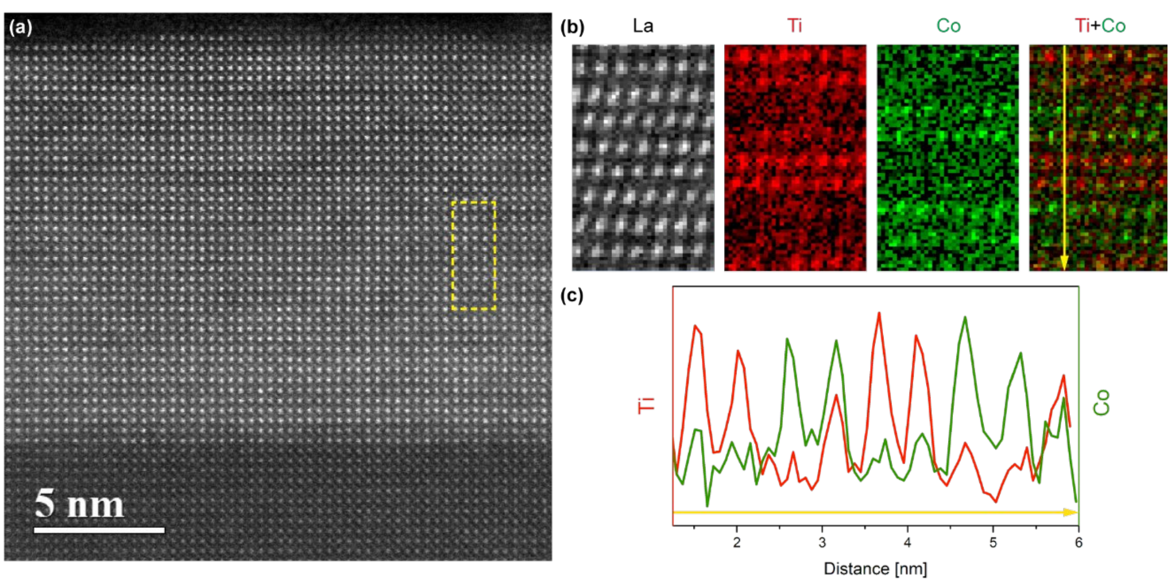

Figure 1. *Structural characterization of cobaltate-titanate superlattices*. (a) HAADF STEM image of an $[(LTO)_2/(LCO)_2]\times10$ superlattice. (b) Element-specific EELS map of the region specified by the yellow box in (a). (c) Intensity of the Ti and Co signal derived from the EELS map as a function of distance along the yellow allow (z-direction) drawn in (b). Figure adapted from Lee et al, Phys. Rev. Lett. **123**, 117201 (2019) [1].

La valence state in the titanate and cobaltate layers or if there were La vacancies, they would be visible in the La EELS map or HAADF STEM image, which is not observed.

To verify the expected periodicity throughout the film, we have performed x-ray diffraction (XRD) and x-ray reflectivity (XRR) along the (00L) direction, which show sharp superlattice peaks around (0 0 3/4) and (0 0 5/4), indicating that the repeating unit consists of four atomic layers. The intensity of these superlattice peaks is sensitive to the quality of the interface and would disappear in the case of an intermixed Co-Ti interface. The superlattice peak is also clearly visible in the XRR as a peak at a two-theta value near 5.2 degrees, which is the expected position for our superlattice structure. These measurements, in combination with STEM-EELS observations, demonstrate the existence of sharp interfaces throughout the entire film.

Nickelate superlattices, Ref. 2.

$NdNiO_3$ exhibits a metal-insulator transition, as shown in in Fig. 2[2], where a sharp increase in resistivity is observed at the MI transition temperature, T_{MI}, for a 50 uc-thick film (similar to the bulk). This MI transition in $NdNiO_3$ is accompanied by a charge order and anti-ferromagnetic phase transition, where all three phase transitions are inextricably linked. This work shows how the phase transitions can be separated by incorporating the $NdNiO_3$ into a superlattice with a band insulator, $NdAlO_3$. Using x-ray absorption spectroscopy (XAS), resonant soft x-ray scattering, and electrical transport, the transition temperature for each phase can be determined, as shown in Fig. 3.

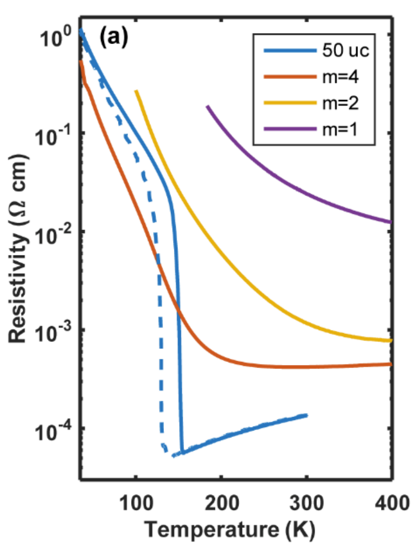

Figure 2. Resistivity vs. temperature for $NdNiO_3$ film and superlattices (solid and dashed line for 50 uc film shows resistance measured during heating and cooling, respectively) Adapted from Ref. 2.

The $NdNiO_3$ superlattices show an increase in the MI transition temperature with dimensional confinement, as the number of $NdNiO_3$ layers, *m*, is decreased, as shown in Fig. 2. However, the confinement in $NdNiO_3$ leads to a separation of the charge and spin ordering transition from the onset of the insulating state (*m*=4 and 2) and an eventual collapse of the charge/spin ordered state altogether for the single $NdNiO_3$ layer superalttice (*m*=1).

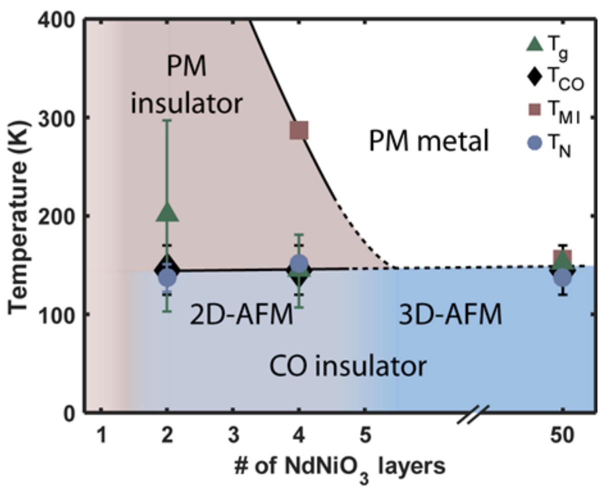

Figure 3. Phase diagram of $NdNiO_3$ superlattices as a function of the number of confined $NdNiO_3$ layers, m, along with data from a 50 uc thick $NdNiO_3$ film (PM = paramagnetic, AFM = antiferromagnetic, CO = charge ordered). T_{MI} (red squares) and T_g (green triangles) are determined from transport, T_{CO} is determined from XAS, and T_N (blue circles) is determined from RSXS. Error bars denote uncertainty in fits to experimental data. Solid and dashed lines are guides to the eye. Adapted from Ref. 2.

T_{CO} is determined by characterizing changes in spectral features from synchrotron XAS measurements at the Ni L_3 edge. T_N indicates the onset temperature for antiferromagnetic order and was determined from synchrotron-based resonant soft x-ray scattering measurements (RSXS) at the Ni L edge. For the 50uc film, the metal-insulator transition, charge order transition and magnetic transition are all intertwined, occurring at the same temperature. As the number of confined $NdNiO_3$ layers, m, decreases, the metal-insulator transition becomes isolated from the charge order and AFM transitions.

The reason for the suppression of the phase transitions for the *m*=1 superlattice can be determined by probing the orbital symmetry using x-ray linear dichroism (XLD). For the *m*=1 $NdNiO_3$ layer superlattice, the $3d(3z^2\text{-}r^2)$ energy level is lowered relative to $3d(x^2\text{-}y^2)$, resulting in significant orbital polarization. The e_g orbital splitting can be related to increased positive ionic charge of the Al cation relative to Ni, resulting from more ionic Al-O bonds compared to Ni-O bonds.

In bulk $NdNiO_3$, orbital degeneracy is preserved upon entering into the ordered phase. If the e_g orbital energy splitting is significantly larger compared to the Hund's coupling energy, J, charge ordering and the accompanying antiferromagnetic alignment are suppressed. This case occurs in the m=1 superlattice, and the development of a conventional charge-transfer or Mott insulating state is observed. Unlike the m=1 superlattice, m=4 and 2 superlattices lack orbital polarization, despite containing confined quasi-2D $NdNiO_3$ layers. Bulk-like order dominates at low temperatures, but large charge and spin fluctuations due to the reduced dimensionality can have the effect of broadening the metal-insulator transition. This 2D fluctuation scenario is also supported by the observation of a non-saturating magnetic scattering moment for the superlattices in RSXS measurements.

Topological SnTe, a prototype chalcogenide Ref. 3.

Topological insulators offer several promising properties for novel electronic devices, including dissipation-free transport and magnetic field control of transport. Topological crystalline insulators (TCIs), such as SnTe, display spin-momentum locking due to their crystalline structure; the transport is also controllable with an electric field when integrated with conventional oxide field effect devices. Here, we report on ultrathin films of SnTe-based topological devices grown on single crystal $SrTiO_3$ substrates[3]; the ultrathin nature is critical to avoid bulk conduction in the SnTe interior. X-ray diffraction and atomic force microscopy confirm that by using a modified molecular beam epitaxy process that takes advantage of net film sublimation during deposition, we can synthesize single-domain, continuous SnTe films. The hole carrier density over a range of film thicknesses, extracted from Hall measurements, reveals two-dimensional carriers confined to the SnTe/STO interface. This film-substrate interface is protected from the ambient environment, a key advantage for making practical devices. Magnetoconductance measurements reveal weak antilocalization behavior, pointing to two-dimensional conduction consistent with topological states. This work provides a new method for integrating topological crystalline insulators with complex oxide materials, making possible new electric field-controlled TCI devices.

We start by growing SnTe films using a conventional MBE approach via thermal evaporation of SnTe source material onto atomically flat single-crystal (001) $SrTiO_3$ (STO). For films that are 30 unit cells (uc)-thick, reflection high-energy electron diffraction (RHEED) images [Fig. 4(a)] show two sets of streaks, marked by triangles and arrows, suggesting multiple domains. The formation of multiple domains is also observed using x-ray diffraction. The XRD patterns show two orientations of the films, as seen by the appearance of (222) and (004) SnTe reflections [not shown]. Diffraction features in RHEED [Fig. 4(b)] and XRD characteristic of a [111] oriented film disappear as the film becomes thicker. The picture that emerges from this data is that SnTe nucleates at the STO surface with two out-of-plane orientations with a single (001) orientation dominating as the films become thicker.

This observation of the relative stability of the two orientations serves as the basis for modifying the conventional MBE process to achieve single-orientation, ultrathin, and continuous SnTe films for transport measurements and device applications. We adapt a deposition method that controls the growth rate by balancing sublimation from the growing film at elevated substrate temperatures with deposition from the SnTe source, which allows us to thin down SnTe films to a few atomic layers in thickness to achieve single-oriented (001) SnTe films. At elevated substrate temperatures, while maintaining a constant SnTe flux, a net sublimation of SnTe from the film takes place, resulting in a negative growth rate that gradually reduces the film thickness. This process is optimized to achieve continuous SnTe films with thicknesses ranging from 10–40 uc-thick. Atomically flat crystal terraces are observed on the surface of the films, as seen by AFM and SEM [Figs. 4(f) and (i)], with pinholes making up < 5 % of the area. RHEED [Fig. 4 (c)] and XRD measurements [not shown] confirm that the SnTe films grown by this method possess only (001) SnTe grains. This "gentle polishing" minimizes the bulk volume relative to surface area while maintaining the continuity of the SnTe films, leading to a substantial relative suppression of conduction in the trivial bulk states, a critical step towards the fabrication of devices with electrical transport dominated by topological states.

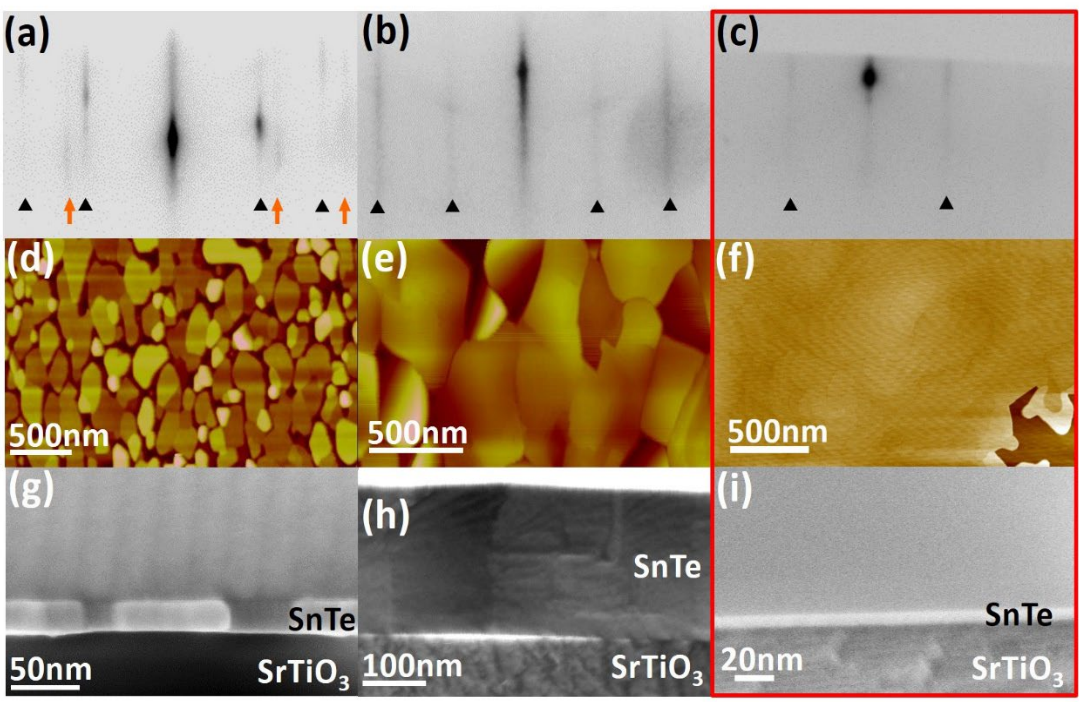

Figure 4. *SnTe film structure.* Reflection high-energy electron diffraction images of (**a**) 30 uc and (**b**) 400 uc SnTe films grown by conventional MBE and (**c**) a 10 uc SnTe film achieved by co-sublimation-deposition on STO looking down the [110] STO axis. Black triangles and orange arrows highlight diffraction from the two epitaxial orientations. Atomic force microscopy images of (**d**) 30 uc, (**e**) 400 uc, and (**f**) 10 uc SnTe films with a vertical scale of 20 nm. Scanning electron microscopy images of (**g**) 30 uc, (**h**) 400 uc, and (**i**) 10 uc SnTe films. Figure taken from Zou et al, APL Materials **7**, 051106 (2019).

Superconducting FeSe-SrTiO3 picoscale characterization, Refs. 4 and 5.

The discovery of a high superconducting transition temperature (T_c) in the FeSe-$SrTiO_3$ interfacial system has led to intense research in the superconductivity community. This material is a prototypical interfacial superconductor, with the mechanism behind the Tc enhancement being highly debated. An understanding of the mechanism will substantially aid the search for new interfacial superconductors, pushing the frontiers of superconductivity research. To date, the FeSe-$SrTiO_3$ interface has proven to be a singular example of a system with greatly enhanced T_c among interfacial superconductors. In addition, it has been found that the superconducting T_c of the FeSe-$SrTiO_3$ interface varies with surface capping and with slight variations in processing conditions. These findings highlight the importance of understanding the microscopic physical origin of superconductivity enhancement at an interface. To address this challenge, which will enable further developments of interfacial superconductors, it is crucial to determine the picoscale atomic structure of the superconducting FeSe-$SrTiO_3$ interface using *in situ* x-ray diffraction and show how it relates to superconductivity[4,5].

Through a complementary analysis of scanning transmission electron microscopy and *in situ* surface x-ray diffraction approaching picometer resolution, we resolve the registry and buckling of atoms at the interface of the FeSe-$SrTiO_3$ system (see Fig. 5). The atomic-scale structure of the FeSe-$SrTiO_3$ interface is an important determinant of the magnetic and interfacial electron-phonon interactions and is thus a key ingredient to understanding high T_c superconductivity in this system. We find that the interface is more strongly bonded for a particular registry and facilitates electron transfer and electron-phonon interactions. Other structural configurations reduce the bonding

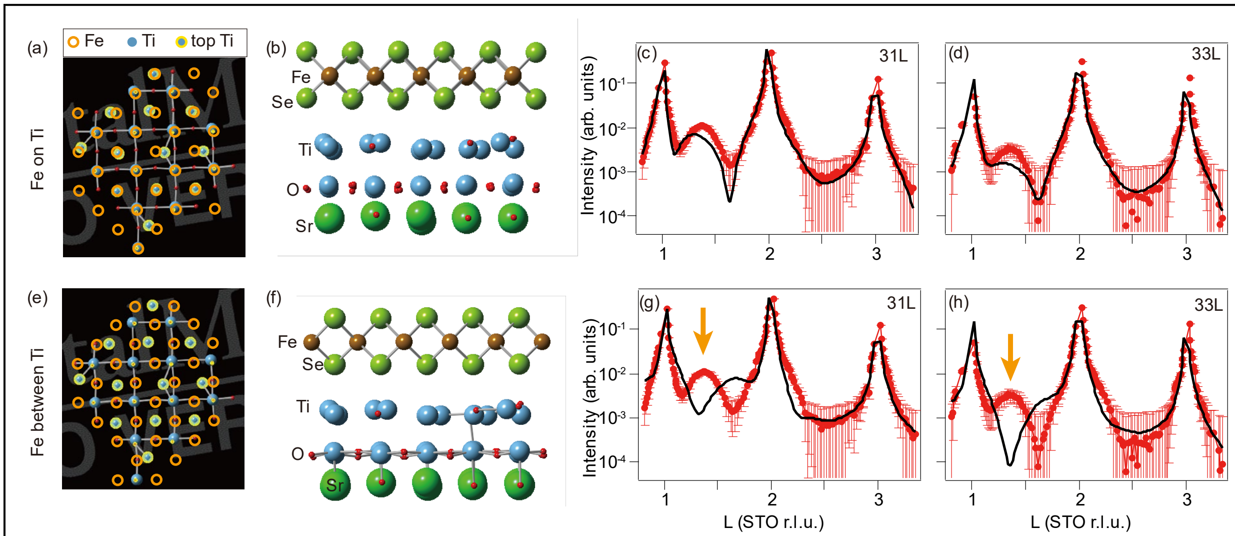

Figure 5. *In situ* x-ray diffraction from a STO-ML FeSe-vacuum heterostructure. Panels a),b) e) and f) show conceptual atomic structures with distinct ways of fitting FeSe to the SrTiO3 surface. Measurements of synchrotron x-ray diffraction (red points in panels c), d), g), and h)) from a film grown in specially designed MBE chamber, allow us to determine the interface structure. Simulations of diffraction from the two different ways of fitting FeSe to SrTiO3 are shown by the black solid lines. A better fit of the structure shown in panels a) and b) demonstrates that this is the structure of the interface. Adapted from Ref. 4.

strength, which explains the extreme sensitivity of superconductivity to capping layers and annealing. Furthermore, the strong bonding for this particular registry acts to strain the monolayer FeSe to an optimal bond angle that may further enhance T_c.

Our results pin down the structural origin of the high-T_c mechanism of $FeSe/SrTiO_3$ and have strong implications on strategies for seeking new higher-T_c materials based on the interfacial structural framework established here.

Impacts

A unique convergence: Many materials derive unique properties from picometer scale distortions of the bonds connecting atoms in the material. These structural modifications affect the electronic states and properties. As part of this project, we have further developed PECAN (Picoscale Engineering of Complex Advanced Nanomaterials) as an approach to manipulating the physical and electronic structure at the picoscale using a multidisciplinary collaboration between theory and experiment aimed at understanding changes of key electronic properties. This approach has been used in the projects described in this report. The interdisciplinary PECAN approach is itself cutting-edge and uses advanced synthesis and characterization tools for realizing targeted materials properties that address grand challenges in basic science and technology. This approach is currently being applied by us[6-8] and other researchers to (a) create novel magnetic, superconducting, or conductive oxide systems that are based on creating orbital configurations of electrons unachievable by bulk synthesis or strain engineering, (b) create new catalysts for challenging chemical reactions, (c) create efficient catalysts for difficult chemical reactions and (d) create materials structures that result in desired quantum electronic phases in layered chalcogenides. These aspects are reviewed and described in S. Ismail-Beigi, F. J. Walker, A. S. Disa, K. M. Rabe, and C. H. Ahn, “Picoscale materials engineering. Nature Reviews Materials” Nature Review Materials (2017)[9]. This published review was supported in part by this program and highlights the impact of the AFOSR funded research described in this final report.

Senior research scientist Fred Walker, supported in part by this project, has also made an impact on the development of beamlines at the National Synchrotron Light Source II, Brookhaven National Laboratory, by participating with the scientific advisory council in reviewing their soft coherent x-ray scattering beamline.

Publications related to AFOSR award:

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