Research Areas

- Electrochemical Materials & Devices
- Electronic, Magnetic & Photonic Materials
- Energy
- Materials Processing
- Nanomaterials & Nanotechnology

Research Interests

Electronic and magnetic materials are the central focus of our group’s research. We study a wide variety of types of materials such as nanostructures, thin films, multilayered heterostructures, and bulk polycrystals and single crystals. We have interests in several areas including the interplay between electronic transport and magnetism in novel materials, and the study of interfaces between dissimilar materials, particularly metals, oxides, and sulfides. The intention is to focus on topics that are attractive from the viewpoint of fundamental science but lie in close proximity to important technological applications such as information storage and microelectronics. Each of the projects requires fabrication of magnetic/electronic materials and/or structures, detailed atomic level characterization, and in-depth measurement by numerous techniques, particularly electronic transport, magnetometry, and neutron scattering. The work often requires that collaborations be forged, both within the University of Minnesota and with external investigators.

The bulk of our current research can be divided into seven primary categories:

(i) magnetism in perovskite oxides,
(ii) perovskite oxide heterostructures,
(iii) spin transport in metals,
(iv) sulfide-based photovoltaics,

(v) novel magnetic alloys,

(vi) magnetic nanostructures, and

(vii) transport in conductive polymers and small molecule systems.

(i) Magnetism in the perovskite oxides: Our work on bulk perovskite cobaltites mostly involves the study of a fascinating phenomenon known as magneto-electronic phase separation, where chemically homogeneous materials are found to exhibit intrinsic inhomogeneities in electronic and magnetic properties. These inhomogeneities correlate with some of the most important properties of complex oxides such as high temperature superconductivity and colossal magnetoresistance. In our work on cobaltites we are examining the phenomenology, consequences, and origins of the formation of inhomogeneous magnetic states by combining a wide array of bulk property measurements (e.g. magnetometry, transport, heat capacity, etc.) with powerful local probes such as NMR and small-angle neutron scattering. The ultimate goal is a fundamental understanding of the origin of the phase separation effects in these model systems. We have focused on the important effects of local doping fluctuations at the nanoscale, which can explain many of the observed features of the electronic inhomogeneity in these systems. We have also recently expanded the work to include narrow bandwidth systems such as (Pr,Ca)CoO3, (Pr,Y)CaCoO3, and (Nd,Ca)CoO3, as well as lightly hole-doped LaCoO3. In the latter we are studying the crossover from polaronic to clustered states, while in Pr-containing systems we are focusing on the remarkable Pr-valence transition.

(ii) Perovskite oxide heterostructures: We are also exploring the area of perovskite oxide heterostructures. Perovskites offer unique opportunities for heterostructure fabrication as they enable the assembly of chemically compatible lattice-matched interfaces between materials with widely varied electronic and magnetic properties. We are pursuing various concepts in this general area, using high pressure reactive magnetron sputtering for deposition of epitaxial thin films. Examples include the use of heterostructures containing doped cobaltite components for studies of dead layer effects, interfacial magnetic phase separation and oxygen vacancy ordering, the investigation of the transport properties of semiconducting SrTiO3 and BaSnO3, and spin injection into complex oxide metals and semiconductors. The major part of our recent work has focused on dead layer effects at cobaltite/titanate interfaces, which is closely related to the strain-induced O vacancy ordering in these materials. In collaborative work with Prof. Bharat Jalan (CEMS, UMN) we are also working on stannate films, with an emphasis on doping and electronic transport. Optical spin injection is being studied in collaboration with Scott Crooker of Los Alamos.

(iii) Spin transport in metals: In a collaborative project with Prof. Paul Crowell's group (Physics, UMN) we are studying spin transport in conventional metallic systems. We are fabricating nanoscopic lateral non-local spin valves to probe spin injection, spin diffusion, and spin relaxation in non-magnetic metals. The ultimate goal of the work is to systematically unravel the factors that limit spin diffusion lengths in metals, considering magnetic and spin-orbit point defects, grain boundaries, surfaces, interfaces, etc. In addition to being of high fundamental interest, such work is important for the development of low resistance-area product all-metal field sensors for next generation hard disk drive technology. Our initial work has highlighted the importance of even ppm-level magnetic impurities, demonstrating that the puzzling non-monotonicity of the spin accumulation signal in such structures is due to a novel manifestation of the Kondo effect. Further quantification is underway via systematic annealing experiments, along with studies of ferromagnetic contact induced relaxation effects, as well as channel thickness effects.

(iv) Sulfide-based photovoltaics: Due to their outstanding potential as next generation solar absorber materials, we are also working on sulfides for photovoltaics. In collaborative work with Prof. Eray Aydil (CEMS, UMN) we are working on Cu2ZnSnS4, an excellent candidate for a low cost solar absorber based on low toxicity high abundance elements. We are depositing thin films via ex situ sulfidation and reactive sputtering and attempting to understand and control doping and electronic properties, eventually for inclusion in solar cells. Highlights from our recent work include studies of the thermodynamics of CZTS formation, the key role of Group I impurities, and the fundamentals of electronic conduction in CZTS. We are also studying FeS2 in this regard, a semiconductor that is well known to have outstanding (unfulfilled) potential as a solar absorber. In our first work on this material we have examined in detail the mechanisms of electronic transport in ex situ sulfidized thin film samples. The data reveal an unexpected crossover from nanoscopic intergranular hopping to conventional charge transport, a result with important
consequences in terms of previous conclusions regarding the doping type and conduction mechanism. Our most recent work is studying the contentious issue of phase stability/purity, again with implications for electronic transport.

(v) Novel magnetic alloys: In collaboration with Prof. R. James (UMN Aerospace Engineering and Mechanics) we are working to understand the magnetic properties of a set of off-stoichiometric Heusler alloys of the form Ni$_{50-x}$Co$_4$Mn$_{25+y}$Sn$_{25-y}$. These fascinating and highly functional alloys result from a program of alloy development guided by a theory of James et al predicting unusually low thermal hysteresis across the martensitic phase transformation under certain conditions. The materials have rich magnetic properties around certain critical compositions, which are challenging to understand. In particular we are trying to make progress with the striking inhomogeneity in their magnetic properties, which bears strong resemblance to some of the phenomena discussed in (i) above.

(vi) Magnetic nanostructures: In a project with Prof. Marc Hillmyer (UMN Chemistry) aimed at developing methods for facile synthesis of extremely high density magnetic features we are using block copolymer thin films as templates for fabrication of large area arrays of magnetic nanostructures. Our prior work focused on the important issue of characterizing and understanding the pattern transfer with these block copolymer lithography techniques, demonstrating 35 nm dot arrays by "lift-off" techniques, 25 nm diameter antidot arrays using pattern transfer methods, and a method for achieving spontaneous perpendicular alignment of minority phase cylinders. In more recent work we have developed a method to fabricate 25 nm diameter magnetic nanodots with exceptional long-range order, monodispersity, and magnetization retention, at the same time avoiding lift-off and etch damage. This "damascene-type" process, which employs solvent annealing, is now being used in studies of single crystal magnetic dot arrays, as well as investigations of complex oxide antidot networks to study electronic phase separation. Very recent developments include contributions to the understanding of the process of solvent vapor annealing, and the use of sacrificial low temperature conformal ALD layers (with Prof. Wayne Gladfelter, UMN Chemistry) to achieve size control and high temperature processing compatibility.

(vii) Transport in conductive polymers and small molecule systems: In a collaboration with Prof. Dan Frisbie (CEMS, UMN) we are studying the details of the electronic transport mechanisms in polymeric and small molecule semiconductors. We use the recently developed ion-gel based electrostatic and electrochemical gating techniques to achieve very high charge densities in thin film transistors of these materials for low temperature and high magnetic field experiments. Our recent work on P3HT has elucidated the hopping conduction in these systems, in addition to the unique features of the approach to the insulator-metal transition in these highly-disordered conductors. We find that the onset of metallic conductivity is suppressed due to doping-induced localization at extreme electrochemically-induced charge densities, a result with important consequences for polymer semiconductor thin film transistors. Nevertheless, at the highest charge densities and mobilities attainable in our experiments we have observed the Hall effect for the first time in a polymer semiconductor transistor. Remarkably, the data are suggestive of a crossover to a regime of diffusive, “band-like”, transport in these highly disordered solution processed polymer semiconductors. More recently, similar methods have been applied to rubrene, generating very high charge densities and mobilities that, at the highest charge densities and mobilities attainable in our experiments, we have observed the Hall effect for the first time in a polymer semiconductor transistor. Remarkably, the data are suggestive of a crossover to a regime of diffusive, “band-like”, transport in these highly disordered solution processed polymer semiconductors. More recently, similar methods have been applied to rubrene, generating very high charge densities and mobilities. The primary interest here is that, in comparison to vacuum-gap devices, we can generate three orders of magnitude higher hole densities, but with only a factor of 3-5 reduction in mobility. The massive increase in conductance leaves us remarkably close to a 2D metallic state on the surface of rubrene.

In terms of experimental techniques our work involves bulk fabrication methods such as solid-state reaction and chemical vapor transport single crystal growth, in addition to thin film growth by sputtering and UHV molecular beam epitaxy. Structural characterization methods such as high-resolution x-ray diffraction and reflectivity, scanning probe microscopy, and various forms of spectroscopy and electron microscopy are of vital importance. The measurement techniques we employ include magnetometry, magnetotransport, and, importantly, various forms of neutron scattering and reflectivity.

Awards

Cozzarelli Prize (with F. Bates and S. Lee), Proceedings of the National Academy of Sciences, 2015
Tate Award for Excellence in Undergraduate Advising, UMN, 2015
Selected Publications
From 2017 and 2016:


“Electrostatic vs. electrochemical doping and control of ferromagnetism in ion-gel-gated ultrathin La0.5Sr0.5CoO3-d”, J. Walter, H. Wang, C.D. Frisbie and C. Leighton, ACS Nano 10, 7799 (2016).


“Simultaneous first-order valence and oxygen vacancy order/disorder transitions in (Pr0.85Y0.15)0.7Ca0.3CoO3-d via analytical transmission electron microscopy”, A. Gulec, D.P. Phelan, C. Leighton and R.F. Klie, ACS Nano 10, 938 (2016).