Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoM

Spectroscopy, Microscopy and Dichroism of Actinides and Rare Earths
Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:20am **AC+AS+MI+SA+SS-MoM1 Novel Synthetic and Spectroscopic Techniques in Actinide Materials Chemistry**, ***Stefan Minasian***, Lawrence Berkeley National Laboratory, *E. Batista,* Los Alamos National Laboratory, *C.H. Booth,* Lawrence Berkeley National Laboratory, *D. Clark,* Los Alamos National Laboratory, *J. Keith,* Colgate University, *W. Lukens,* Lawrence Berkeley National Laboratory, *S. Kozimor, R.L. Martin,* Los Alamos National Laboratory, *D. Nordlund,* SLAC National Accelerator Laboratory, *D. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory, *D. Sokaras,* SLAC National Accelerator Laboratory, *X.-D. Weng,* Los Alamos National Laboratory, *T.-C. Weng*, SLAC National Accelerator Laboratory **INVITED**

The development of a detailed, quantitative understanding of electronic structure and bonding for a broad range actinide materials remains a significant scientific challenge. Recent advances have shown that the 1s to np transition intensities measured by Cl and S K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing in M–Cl and M–S bonds. The scientific progress associated with these Cl and S XAS studies suggests that using synchrotron-generated radiation to quantify covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in two well defined series of f-element materials. The actinide sandwich complexes, “actinocenes,” $(C_8H_8)_2An$ (An = Th, Pa, U, Np, Pu) have played a central role in the development of organoactinide chemistry. Results showed two contrasting trends in actinide–carbon orbital mixing, and evidence that covalency does not increase uniformly as the actinide series is traversed. Additionally, the C K-edge XAS spectrum of thorocene represents the first experimental evidence of a ϕ-type orbital interaction. Oxygen K-edge XAS measurements and DFT studies began the lanthanide dioxides LnO_2 (Ln = Ce, Pr, Tb), because their electronic structures are well-established from hard X-ray spectroscopies. Preliminary efforts to use lanthanide oxides and lanthanide organometallics as experimental benchmarks for quantitative determinations of covalency in d-block and f-block materials will also be discussed.

9:00am **AC+AS+MI+SA+SS-MoM3 X-ray Magnetic Circular Dichroism of Actinides**, ***Andrei Rogalev***, *F. Wilhelm*, European Synchrotron Radiation Facility (ESRF), France **INVITED**

Actinides compounds, which are straddling the magnetic properties of rare-earths and transition metals, have been the subject of increasing interest due to their very different properties, such as Pauli paramagnets, localized and itinerant ferromagnets, and heavy fermion superconductors. The key parameter responsible for the large variety of magnetic properties is obviously degree of localization of the 5f states which are indeed involved in both the chemical bonding and the magnetism. To unravel the details of the electronic structure and magnetic properties of these 5f states, polarization dependent X-ray spectroscopy at the $M_{4,5}$ edges appears as the most suitable experimental tools. At the third generation synchrotron radiation facilities, small x-ray beam with flexible polarization sized down to few microns can be routinely achieved. This technique is thus perfectly suited for studying minute samples (a few micrograms) of transuranium materials. This talk reviews recent advances in use of polarized x-rays to study local magnetic properties and electronic structure of actinides compounds.

The magnetic properties are mostly studied with X-ray Magnetic Circular Dichroism (XMCD). The great advantage of this technique is its capability to probe the orbital and spin magnetization of 5f states separately. XMCD experiments have been reported for a great number of uranium compounds and have permitted to understand, at least qualitatively, which is the ground state despite the difficulty over assigning a valency. It has also revealed differences between localized and itinerant systems that are not yet fully understood. To our knowledge there are very few reports on XMCD measurements on other trans-uranium materials. This is unfortunate, as the questions of localization of 5*f* states become more interesting as the 5*f* count increases. In order to improve our understanding of the magnetism of actinides, which is based up to now solely on uranium compounds, and thus better to describe the differences between localized and itinerant 5*f* systems, we report a thorough XMCD study of a series of ferromagnetic $AnFe_2$ Laves-phase compounds. Moreover, we show that additional information regarding exchange interaction between neighboring actinides atoms can be extracted from the XMCD measurements performed at absorption edges of other "nonmagnetic" atoms in the compounds.

Finally, we demonstrate that the study of the branching ratio in $M_{4,5}$ absorption spectra can bring valuable information regarding the coupling scheme, within which to discuss the electronic and magnetic properties of actinides atoms.

9:40am **AC+AS+MI+SA+SS-MoM5 Magnetic Circular Dichroism Measured with Transmission Electron Microscope**, ***Jan Rusz***, Uppsala University, Sweden **INVITED**

X-ray magnetic circular dichroism (XMCD; [1]) is an established experimental probe of atom-specific magnetic properties of lanthanides and actinides. In XMCD, a photon of well-defined energy and polarization is absorbed by an atom in the sample with a probability that is proportional to the number available unoccupied states with an energy that allows fulfilling the energy conservation and selection rules. An essential element of XMCD are so called sum rules [2,3], which relate the XMCD spectra to the spin and orbital angular momenta, respectively.

Recently, a new experimental method has been developed that is closely related to XMCD. It was named electron magnetic circular (or chiral) dichroism (EMCD) and it is measured with a transmission electron microscope (TEM) instead of a synchrotron beam-line. We will review the short history of this method starting from its proposal in 2003 [4], first experimental proof-of-the-concept in 2006 [5], formulation of the theory [6] and sum rules [7,8] in 2007 to the present state-of-the-art and early applications, for example [9-12]. Yet, despite intense efforts, EMCD is still in its development phase, particularly from the point of view of quantitative studies. On the other hand, qualitative EMCD experiments have reached resolutions below 2nm [13].

The primary advantages of the EMCD, when compared to XMCD, are costs, availability and lateral resolution. Even a state-of-the-art TEM is a device considerably cheaper than a synchrotron beam-line and as such it can be available locally to a research group. TEM is also a very versatile instrument that combines diffraction experiments, elemental analysis, local electronic structure studies via electron energy loss spectroscopy [14] and now also magnetism via EMCD.

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10:40am **AC+AS+MI+SA+SS-MoM8 The Microstructure of Plutonium Hydride Growth Sites**, ***Martin Brierley***, *J.P. Knowles,* AWE, UK, *M. Preuss, A.H. Sherry*, University of Manchester, UK

Under certain conditions plutonium is able to form plutonium hydride during long term storage [1]. Plutonium is radioactive, decaying via release of an alpha particle. Alpha particles are particularly damaging within the body and every attempt should be made to limit the distribution of loose material. Plutonium hydrides have been shown to be pyrophoric when exposed to oxygen; a reaction that could potentially liberate loose particulate outside of suitable containment.

Previous work into the hydriding rate of plutonium has investigated the reaction rate of various hydrides on the surface of these materials; specifically the nucleation rate, the lateral growth rate and the specific hydriding rate [2, 3]. Plutonium is a reactive metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed at discrete sites on the surface, which then grow radially across the surface [1]. Recent work has suggested a grain boundary enhanced growth rate [4].

In the present study, the microstructure associated with selected plutonium hydride growth sites was studied to provide information regarding the nucleation and growth mechanisms that govern the formation of plutonium-hydride. The samples were ground to 600 grit and evacuated before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 1000 mbar for sufficient time to have nucleated a number of hydride sites.

Post-test analysis was performed using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth sites. The morphology of individual hydride growth sites indicates that the hydride-metal interface has a highly discontinuous boundary, resulting from enhanced grain boundary diffusion and spears of transformed material; the microstructure within the plutonium hydride growth sites indicates that a preferred growth habit was adopted by the hydride product.

References

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11:00am **AC+AS+MI+SA+SS-MoM9 Hydrides of U-Mo and U-Zr Alloys: Structure and Electronic Properties**, ***Ladislav Havela***, *M. Paukov, I. Tkach, D. Drozdenko, M. Cieslar, Z. Matej*, Charles University, Czech Republic

When U metal (α-U) is exposed to H gas, it forms a stable hydride β-UH_3. The lattice expansion stabilizes the ferromagnetic order with the Curie temperature around 170 K. The metastable form, α-UH_3, could not be synthesized as a pure phase, and the admixture of β-UH_3 did not allow to determine reliably its intrinsic magnetic properties. We have been testing the reaction to H exposure of γ-U (bcc), which was synthesized as a single phase by combination of Mo or Zr doping into U and ultrafast cooling. We found that such alloys need high H_2 pressure and long exposure to absorb hydrogen. The products can be characterized by the formula $UH_3Mo(Zr)_x$. The hydrides with Mo have a structure corresponding to β-UH_3 with grain size around 1 nm, i.e. almost amorphous. Its ordering temperatures increase to 200 K for $UH_3Mo_{0.18}$ and then decrease for higher Mo concentrations. The hydrides UH_3Zr_x exhibit the UH_3 structure (bcc U lattice filled with H atoms). Their Curie temperature weakly decreases with increasing Zr concentration and the extrapolation to Zr-free state indicates T_C = 170 K, i.e. identical to β-UH_3. The results can be compared with numerous hydrides obtained by hydrogenation of U_6X compounds (X = Mn, Fe, Co, Ni), all probably having similar magnetic properties. We present a detailed study of magnetic properties, electrical resistivity and specific heat. The structure characterization of initial alloys and the hydrides has been done by means of XRD, SEM with EBSD and TEM. The hydrides represent and new class of U materials, which exhibit, irrespective of details of composition or crystal structure, strong ferromagnetism with relatively very high ordering temperatures, quite surprising at materials at which the inter-U spacing does not exceed appreciably the Hill limit 340-360 pm. At last, the variations using double doping (both Mo and Zr) will be presented.

11:20am **AC+AS+MI+SA+SS-MoM10 Unraveling the Mystery of Reactively-Sputtered UO(4+x)**, ***David Allred***, *R.S. Turley, B.S. McKeon, A. Diwan, E.A. Scott, R.R. Vanfleet*, Brigham Young University

We recently found EDX and XPS evidence in reactive sputtered uranium oxide thin films of higher oxygen-to-uranium ratios than the 3-to-1 allowed by stoichiometry. We used reactive, DC-magnetron sputtering in 100% oxygen to prepare uranium-oxide thin films on silicon wafer with the highest possible oxygen content to investigate this. Both EDX & XPS showed that the ratio of oxygen-to-uranium in freshly samples was at least 4-to-1, with compositions approached 5 to 1. The potential explanations are uranates or peroxides. Detecting hydrogen- and an element difficult to detect in thin films-is crucial in understanding what is happening chemically. Uranates require cations. The only one possible in our films would be hydrogen. Similarly, bulk uranium peroxides without water/ hydrogen peroxide of hydration are not known. (We have found evidence of uranium trioxide being weekly hygroscopic and stored samples in a dry environment, nonetheless these samples show high oxygen contents as prepared.) We report our chemistry and structural (TEM and XRD) attempts to solve this mystery. We also report are measurement of extreme ultraviolet reflectance of this material. (ALS-beamline 6.3.2)

11:40am **AC+AS+MI+SA+SS-MoM11 Cathodoluminescence and Band Gap Studies of Single Crystal $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22)**, ***David Turner***, Oak Ridge Institute for Science and Education, *J. Reding, R. Hengehold, T. Kelly,* Air Force Institute of Technology, *J.M. Mann,* Air Force Research Laboratory, *J. Kolis,* Clemson University, *J. Petrosky*, Air Force Institute of Technology

Analyses of depth- and temperature-resolved cathodoluminescence experimental techniques have identified many previously unobserved spectral characteristics in $U_xTh_{1-x}O_2$ compounds grown using a slow growth hydrothermal method. Three $U_xTh_{1-x}O_2$ (x = 0.00, 0.01, 0.22) hydrothermally grown, single crystals were examined using cathodoluminescence. Unique luminescence features were identified as a function of uranium concentration. In the undoped and x = 0.01 $U_xTh_{1-x}O_2$, an electronic phase transition is observed as a 20 nm (0.21 eV) red-shift in the wavelength of maximum emission. This red-shift appears when the crystals are heated during both 5 and 10 keV electron beam irradiation. Conversely, a similar phase transition is not observed in the $U_xTh_{1-x}O_2$ alloy (x = 0.22). Instead, the wavelength of maximum emission remains constant at 305 nm (4.07 eV). Ultimately, the addition of uranium to the ThO_2 lattice increases the band gap of the material which is identified as a 10 nm (0.13 eV) blue shift if the luminescence. Finally, a quadrupole transition is observed in the uranium-containing crystals (O 2p to U 5f) at approximately 600 nm (2.07 eV).

Electronic Materials and Processing
Room: 314 - Session EM+MI+NS-MoM

Complex Oxides and Their Interfaces

Moderator: Jessica Hilton, Mantis Deposition, Lisa M. Porter, Carnegie Mellon University

8:20am **EM+MI+NS-MoM1 Emergent Phenomena at Complex Oxide Interfaces**, ***Susanne Stemmer***, University of California at Santa Barbara **INVITED**

Two-dimensional electron gases (2DEGs) at interfaces between two insulating oxides have attracted significant attention because they can exhibit unique properties, such as strong electron correlations, superconductivity, and magnetism. In this presentation, we will discuss properties arising from strong electron correlations in narrow quantum wells of the band insulator $SrTiO_3$, sandwiched between Mott insulating rare earth titanates, $SmTiO_3$ and $GdTiO_3$, respectively. These quantum wells exhibit very high sheet electron high-densities, of approximately 1 electron per planar unit cell of the quantum well. We demonstrate electron correlation effects due to short-range Coulomb interactions, including mass enhancement, interface-induced magnetism in the electron gas, and a transition to a correlated insulator at the lowest thickness in quantum wells bound by ferrimagnetic $GdTiO_3$. We show that the metal-insulator transition is coupled with the sudden onset of structural distortions in the quantum well. In contrast, quantum wells bound by antiferromagnetic $SmTiO_3$ exhibit almost no structural distortions, incipient antiferromagnetism, no metal-insulator transition, and non-Fermi liquid behavior. We will discuss the implications of the results in the context of two-dimensional electron correlation physics.

This work was performed in collaboration with Clayton Jackson, Pouya Moetakef, Jack Zhang, Jinwoo Hwang, Leon Balents, and Jim Allen.

9:00am **EM+MI+NS-MoM3 Atomic and Electronic Structure of the Ferroelectric $BaTiO_3$-Ge (001) Interface**, ***Kurt Fredrickson***, The University of Texas at Austin, *P. Ponath, A.B. Posadas,* University of Texas at Austin, *M.R. McCartney, T. Aoki, D.J. Smith,* Arizona State University, *A.A. Demkov*, University of Texas at Austin

In this study, we demonstrate the epitaxial growth of $BaTiO_3$ on Ge(001) by molecular beam epitaxy using a thin Zintl template buffer layer. A combination of density functional theory, atomic-resolution electron microscopy and *in situ* photoemission spectroscopy is used to investigate the electronic properties and atomic structure of the $BaTiO_3$/Ge interface. Aberration-corrected scanning transmission electron micrographs reveal that the Ge(001) 2x1 surface reconstruction remains intact during the subsequent $BaTiO_3$ growth, thereby enabling a choice to be made between several theoretically predicted interface structures. The measured valence band offset of 2.7 eV matches well with the theoretical value of 2.5 eV based on the model structure for an in-plane-polarized interface. The agreement between the calculated and measured band offsets, which is highly sensitive to the detailed atomic arrangement, indicates that the most likely $BaTiO_3$/Ge(001) interface structure has been identified.

9:20am **EM+MI+NS-MoM4 Strain-Controlled Stochiometry Variations in $CaMnO_3$ Epitaxial Thin Films**, ***Rajeswari Kolagani***, *G. Yong, Z. Warecki, C. Stumpf, D. Schaefer, P. Sharma, C. Hart, A. Burger*, Towson University

$CaMnO_3$ is a material of interest for application in novel energy technologies such as thermoelectric power generation, and as a photo catalyst for hydrogen energy storage. We are currently investigating the properties of epitaxial thin films of $CaMnO_3$ (CMO) and its electron doped derivatives towards tuning material properties that enable these applications. Oxygen stoichiometry and its effect on structural and electronic properties are key variables in optimizing thin films of these materials. We will present our studies of CMO thin films grown epitaxially by Pulsed Laser Deposition on several compatible oxide substrates with varying degrees of tensile and compressive lattice mismatch. Lattice mismatch results in the distortion of the unit cell symmetry from cubic to tetragonal. In hole-doped rare earth manganites such as La $_{0.7}CaMnO_3$, tensile as well as compressive lattice mismatch strain is known to cause a suppression of the insulator-metal transition, leading to an increase in electrical resistivity. In contrast, our studies of the structural and electrical properties of CMO thin films indicate that tensile strain causes a pronounced decrease in the electrical resistivity. The strained films have an expanded out of plane lattice parameter which is consistent with reduced oxygen stoichiometry. These results indicate that the tensile strain causes CMO thin films to be more susceptible to the formation of oxygen vacancies, thus reducing electrical resistivity. This is in agreement with recent theoretical predictions correlating strain and oxygen vacancies, where tensile strain induced in-plane expansion of the unit cell is shown to favor oxygen deficiency. The potential for employing lattice mismatch strain for tuning film composition has important implications for technological applications. We will present our detailed investigations of the correlation of strain and oxygen stoichiometry in $CaMnO_{3-d}$ andrelated manganite compositions, employing high resolution X-ray diffraction, temperature dependent resistivity measurements, and characterization of the film surface morphology using atomic force microscopy.

9:40am **EM+MI+NS-MoM5 Controlling Complex Oxide Chemistry to Enable Advanced Dielectric, Ferroelectric, and Electronic Applications**, ***Lane Martin***, University of California, Berkeley **INVITED**

Current and next-generation advanced functional materials are testing our ability to produce high-quality, complex materials with ever increasing precision. Particular interest has been given to candidate complex oxide materials which present a diverse range of material properties and functionality not easily produced in other classes of materials. The ultimate integration and utilization of these materials, however, will require that we can carefully and deterministically balance the intrinsic phenomena of interest in these materials with a knowledge of the potential extrinsic effects that can arise form defects which result from our inability to produce these complex materials with the precision we desire. This is made more challenging by the fact that these complex oxide systems are prone to and can accommodate large densities of point defects through a range of internal compensation mechanisms. In this presentation, we will explore the interrelationship between the complex oxide growth process, the chemical nature of these complex materials, the resulting structure and strain evolution, and the ultimate effect on properties in a range of prototypical complex oxide materials. We will explore these interrelationships in model systems including the classic dielectric materials $SrTiO_3$ and $LaAlO_3$, highly-controlled heterointerfaces that exhibit exotic physics including the $LaAlO_3/SrTiO_3$ system, and ferroic systems such as $BaTiO_3$ and others. In this context, we will demonstrate routes by which we can deterministically utilize the tendency for these materials to form point defects to enhance epitaxial thin film strain, developing new modalities of strain control of thin-film materials that go beyond traditional lattice mismatch effects, and how the combination of epitaxial strain and defects in materials can be used to enhance performance, independently tune susceptibilities, and provide new insights into the nature of these complex materials. For instance, in $BaTiO_3$ we will illustrate how one can couple epitaxial strain to defect structures to provide an additional out-of-plane strain component that can dramatically enhance ordering temperatures and will explore the use of compositionally-graded heterostructures to further extend what can be done with epitaxial strain to manipulate dielectric, ferroelectric, and electronic properties of materials.

10:40am **EM+MI+NS-MoM8 Monolithic Integration of Epitaxial $BaTiO_3$ on Si and SiGe for Ferroelectric Devices**, *L. Mazet, R. Bachelet, G. Saint-Girons,* Institut des Nanotechnologies de Lyon (INL) - CNRS - ECL, France, *D. Albertini, B. Gautier,* Institut des Nanotechnologies de Lyon (INL) - CNRS - INSA de Lyon, France, *M.M. Frank, J. Jordan-Sweet, I. Lauer, V. Narayanan,* IBM T.J. Watson Research Center, *M. Hytch, S. Schamm-Chardon,* CEMES - CNRS - Université de Toulouse, France, ***Catherine Dubourdieu***, Institut des Nanotechnologies de Lyon (INL) - CNRS - ECL, France **INVITED**

Ferroelectric oxides integrated on a semiconductor substrate are of particular interest for various applications such as memory or logic devices, electro-optic devices or as piezoelectric materials for sensors and actuators. Among the ferroelectric compounds, $BaTiO_3$ is an attractive candidate for large-scale applications compared to Pb- or Bi-based oxides. It is a well-known perovskite largely studied for its dielectric, piezoelectric and ferroelectric properties.

In this talk, I will briefly review the challenges associated with the monolithic integration of crystalline complex oxides on a semiconductor and more particularly with the integration of ferroelectrics. Molecular Beam Epitaxy (MBE) provides unique advantages to precisely construct, almost atom by atom, the oxide/semiconductor interface.

I will then present an experimental work on the epitaxy of $BaTiO_3$ thin films (1.2 - 20 nm) on silicon and $Si_{1-x}Ge_x$ substrates. Films are grown by MBE, in the thickness range of 1.2-20 nm. Different growth conditions such as temperature and oxygen pressure are explored to optimize the $BaTiO_3$ film quality and to minimize the SiO_2 interfacial layer regrowth between Si and the $SrTiO_3$ buffer layer. The surface quality is monitored *in-situ* by reflection high-energy electron diffraction (RHEED) and *ex-situ* by X-ray reflectometry (XRR) and atomic force microscopy (AFM). The crystalline structure is studied by conventional and synchrotron X-ray diffraction. It is also investigated at the nanoscale using advanced transmission electron microscopy techniques. Strain maps determined with high precision (0.05%), 5 nm spatial resolution and with a large field of view (1 µm) using dark field electron holography will be discussed for selected samples. The crystalline domain orientations (*c*- versus *a*-domains) will be discussed with respect to the growth conditions and thickness. The ferroelectric properties are investigated by piezoresponse force microscopy (PFM). Ferroelectric films are obtained in optimized conditions that will be discussed. Ultrathin films of few monolayers are investigated to determine the onset of ferroelectricity.

I will conclude with ongoing perspectives on the integration of such heterostructures in new field-effect devices for low power logic applications.

11:20am **EM+MI+NS-MoM10 The Surface Study of Hexagonal $LuFeO_3$ Multiferroic Thin Films**, ***Shi Cao***, *X.S. Xu, T. Paudel, E.Y. Tsymbal, P.A. Dowben*, University of Nebraska-Lincoln

The surface properties of hexagonal $LuFeO_3$ thin film have been studied by ultra-high vacuum based characterization technologies such as X-ray/ultra-violet photoemission spectroscopy (XPS/UPS), inverse photoemission spectroscopy (IPES) and XMCD-PEEM. Hexagonal $LuFeO_3$ is a stable multiferroic at room temperature with potential magneto-electric properties. The application of this material in voltage controlled magnetic devices depends very significantly on the interface composition and interface magnetism. The angle resolved XPS shows the possible iron-rich termination and the oxygen deficiency due to the sensitivity of the surface to the of sample preparation methods. The combined UPS and IPES allow us to infer that this multiferroic oxide, $LuFeO_3$, has a band gap about 2.35eV. All these characterizations are consistent with the density function theory calculations of the surface and bulk band structure.

11:40am **EM+MI+NS-MoM11 Integration of Ferroelectric Perovskites on Ge(001) by ALD: A Case Study of $BaTiO_3$**, ***Thong Ngo***, *M.D. McDaniel, S.N. Chopra, J.G. Ekerdt, A.B. Posadas, A.A. Demkov*, The University of Texas at Austin

Gemanium, which exhibits higher hole and electron mobilities than silicon, might become a candidate to replace silicon as a channel material in a field effect transistor (FET) beyond the 3D FET generation. Unlike Si, when the high-κ dielectrics are integrated on Ge, the chemical instability of GeO_2 is an advantage. Moreover, the instability of GeO_2 also enables epitaxial functional oxides on Ge. Crystalline perovskites can be high-κ insulating, with many also being ferromagnetic, ferroelectric, multiferroic, or superconducting. This wide range of properties, combined with possibilities for lattice match to Ge(001), allows for multi-functional oxides to be engineered on Ge(001).

Epitaxial integration of ferroelectric barium titanate, $BaTiO_3$ (BTO), on Ge has attracted much attention due to the low lattice mismatch between Ge(001) and BTO (0.25% above Curie temperature, T_c = 120 °C). The efforts to epitaxially integrate ferroelectric BTO on Ge(001) have been demonstrated using molecular beam epitaxy (MBE) by several groups. However, for device manufacturing applications, atomic layer deposition (ALD) has advantages over MBE due to its high step coverage, significantly low thermal budget, scalability, and low cost.

We demonstrate an all-chemical route to epitaxially integrate BTO directly on Ge(001). Amorphous BTO films were grown on the 2×1 reconstructed, clean Ge(001) surface at 225 °C using ALD. Barium bis(triisopropylcyclopentadienyl), titanium tetraisopropoxide, and water were employed as co-reactants. The films become highly crystalline after a vacuum anneal at 600–700 °C. In-situ x-ray photoelectron spectroscopy confirms the stoichiometry of the BTO films with no detectable GeOx formation or carbon incorporation. In-situ reflection high energy electron diffraction (RHEED) shows high order of BTO film crystallinity after vacuum annealing. X-ray diffraction (XRD) is used to determine the crystallinity and the orientation of BTO films. Electrical characterization, including capacitance-voltage, leakage current, interface trap density, and piezoresponse force microscopy measurements will also be performed to explore the high-κ insulating and ferroelectric properties of BTO films on Ge(001). The integration of BTO films on Ge(001) by ALD is a promising method for fabricating a ferroelectric FET at production scale.

Magnetic Interfaces and Nanostructures
Room: 311 - Session MI+EM-MoM

Interfacial Effects in Oxide Heterostructures
Moderator: Greg Szulczewski, The University of Alabama

8:40am **MI+EM-MoM2 Linear Dichroism of $La_{0.7}Sr_{0.3}MnO_3$ Magnetic Dead Layers**, ***Robbyn Trappen***, *M.B. Holcomb, J. Zhou, C.-Y. Huang,* West Virginia University, *Y.-H. Chu, V. Tra*, National Chiao Tung University, Taiwan, Republic of China

Magnetic dead layers are a phenomenon in which a normally ferromagnetic material loses its magnetization below a critical thickness, which poses a problem for thin film applications. Density functional calculations predict the behavior of the dead layer in complex oxide films to be antiferromagnetic, which is attributed to interdiffusion of the magnetic film into the neighboring layers. Here, we investigate the transition from ferromagnetic to antiferromagnetic behavior in the complex oxide $La_{0.7}Sr_{0.3}MnO_3$ using x ray magnetic linear and circular dichroism on the Mn L-edge (2p to 3d transition). These measurements were taken at the Advanced Light Source at Lawrence Berkeley National Labs. If the mechanism of the formation of the dead layers is understood, it can potentially be reversed and the same physics may be able to even enhance the magnetization beyond its bulk parameter.

9:00am **MI+EM-MoM3 Magnetotransport at the Superconducting $LaAlO_3/SrTiO_3$ Interface**, ***Stefano Gariglio***, *D. Li, A. Fête, W. Liu, J.-M. Triscone*, University of Geneva, Switzerland **INVITED**

The conducting interface between the two band insulators $LaAlO_3$ and $SrTiO_3$ has drawn a large share of attention, as it presents a variety of exciting electronic properties that are tunable by an electric field [1].

At low temperatures, magnetotransport analysis has revealed a strong Rashba spin-orbit interaction originating from the breaking of inversion symmetry [2] and, in field effect devices, the ground state has been tuned from an insulating to a superconducting state. I will discuss these results in light of recent magnetotransport experiments in field-effect devices to probe the evolution across the phase diagram of the weak localization /weak anti-localization transport regime, its relation to the strength and anisotropy of the superconducting state.

Moreover, this interface naturally provides a versatile system to artificially build stacks of multiple 2D superconductors that would allow coupled 2D superconducting layers to be studied. I will show that we can prepare metallic and superconducting interfaces with $LaAlO_3$ layers grown on an artificial $SrTiO_3$ film [3].

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9:40am **MI+EM-MoM5 Symmetry Breaking in Strained Vanadium Dioxide Films**, ***Mengkun Liu***, UC San Diego **INVITED**

We report on nanoscopic aspects of the insulator-to-metal transition (IMT) in a canonical correlated electron material, vanadium dioxide (VO2). Using scattering-type scanning near-field optical microscopy (s-SNOM) and spectroscopy (nano-FTIR), we revealed unique phase separation in strained VO2 films at sub-micrometer scale over a wide temperature range (320K-380K). Investigating the three dimensional formation of this microscopic stripe state, we resolved the enigma of the macroscopic electronic anisotropy and disentangled distinct stages of the VO2 phase transition with spontaneous symmetry breaking [Phys. Rev. Lett. 111 (9), 096602 (2013), Appl. Phys. Lett. 104 (12), 121905 (2014) and follow-up studies]. With these results we demonstrated that the novel spectroscopic techniques of near-field optics provide powerful and universal methodologies for studying mesoscopic and interfacial physics for many classes of transition metal oxides and phase transition materials.

10:40am **MI+EM-MoM8 Interface Assisted Molecular Spintronics**, ***Karthik Raman***, Indian Institute of Science, India **INVITED**

The adsorption of molecules on magnetic surfaces offers a new directionality to the study of molecular spintronics. The creation of new interface states formed by the hybridization of molecular orbitals with the spin-polarized bands of the surface leads to the development of a unique electronic and magnetic character. Such a richness of the interface spin-chemistry allows developing new handles to functionalize the properties of the adsorbed molecules, opening up a molecular-genome initiative to develop spin-functional tailor-made devices. Along with the exploration of single molecular magnets, the use of carbon based aromatic molecules, both non-magnetic and open shell magnetic systems, have presented many interesting interface phenomena. In addition to the experimental demonstrations, these studies share a strong theoretical support from computational *ab initio* interface modeling. The mechanism of inducing molecular magnetism with stability up to room temperature, inducing interface magnetic exchange coupling with strengthens of the order of thermal energy at and above room temperature, enhancement in the magnetic anisotropy of the surface and the spin-filtering property demonstrating interfacial magnetoresistance opens up a new channel to develop molecular designs for applications in sensor, memory and computing applications. This talk shall drive interest in the emergent subfield of interface assisted molecular spintronics, by presenting a strong foundation of the interface spin-physics and spin-chemistry and propose novel schemes promoting the use of advanced spectroscopy tools for the investigation of molecular spin responses. Efforts to template molecules on surfaces offer a way forward towards molecular scaling-up, providing a future outlook to the field.

References:

1. N. Atodiresei & K. V. Raman, “Interface assisted spintronics: tailoring at the molecular scale”, MRS Bulletin (**July** 2014).

2. K. V. Raman, ‘Focusing on the molecular scale’, Nature Nanotechnology ***8***, 886 (2013).

3. K. V. Raman *et. al.*, ‘Interface engineered templates for molecular spin memory devices’, Nature ***493***, 509 (2013).

4. K. V. Raman, J. Chang, J. S. Moodera, ‘New method of spin injection into organic semiconductors using spin filtering tunnel barriers’, *Org. Electronics***12**, 1275 (2011).

5. K. V. Raman, S. M. Watson, J. H. Shim, J. A. Borchers, J. Chang, J. S. Moodera , "Effect of molecular ordering on spin and charge injection in rubrene", *Phy. Rev. B***80**, 195212 (2009).

11:20am **MI+EM-MoM10 Coverage-Dependent Surface Magnetism of Iron Phthalocyanine on an O-Fe(110) Surface**, ***Jack Rowe****, D.B. Dougherty,* North Carolina State University*, E. Vescovo*, National Synchrotron Light Source

Iron phthalocyanine adsorbed on an oxygen covered Fe(110) surface shows a complex coverage-dependent spin polarization during growth of the first molecular monolayer. Spin polarization is modified at low submonolayer coverages, absent at intermediate submonolayer coverages, and re-appears in modified form for a complete monolayer. This is attributed to coverage-dependent adsorption configurations from a random adsorption system to a packed monolayer with a well-defined interfacial spin polarization. In addition, we report on the observation of a rotation of the spin direction of photoelectrons in the presence of molecules, which is attributed to molecular modifications of surface magnetic anisotropy.

11:40am **MI+EM-MoM11 Time Resolved Imaging At 10Ghz And Beyond Using The Ssrl Scanning Transmission X-Ray Microscope**, ***Hendrik Ohldag***, SLAC National Accelerator Laboratory, *S. Bonetti, R. Kukreja,* Stanford University, *J. Frisch, H. Duerr, J. Stoehr*, SLAC National Accelerator Laboratory

Understanding magnetic properties at ultrafast timescales is crucial for the development of new generations of magnetic devices. Such devices will employ the spin torque or spin Hall effect, whose manifestation at the nanoscale is not yet sufficiently understood, which is why studies addressing these effects are of great fundamental significance as well. The samples of interest are often thin film magnetic multilayers with thicknesses in the range of a atomic layers. This fact alone presents a sensitivity challenge in STXM microscopy, which is more suited toward studying thicker samples. In addition the relevant time scale is of the order of 10 ps, which is well below the typical x-ray pulse length of 50 – 100 ps. Altogether this means that pushing the time resolution of a synchrotron x-ray microscopy experiment is synonymous with improving the signal to noise ratio on the detector and providing stable, low jitter excitation to not further dilute the already small magnetic signals.

The SSRL STXM is equipped with a single photon counting electronics that effectively allows us to use a double lock-in detection at 476MHz (the x-ray pulse frequency) and 1.28MHz (the synchrotron revelation frequency). The pulsed or continuous sample excitation source is synchronized with the synchrotron source with a few picosecond drift over 24 hours. This setup currently allows us to achieve a signal to noise ratio of better than 10000, enabling us to detect miniscule variations of the x-ray absorption cross section.

In this talk I will describe the time resolved STXM setup developed at SSRL and present firsts results that have been obtained using the instrument in collaboration with an outstanding group of external users. The instrument operates in ultra high vacuum (~10^{-8}torr) and allows us to apply electrical pulses to our samples that can be placed in out of plane magnetic fields up to 0.8 Tesla or in plane magnetic fields up to 0.3 Tesla. We have used the instrument to successfully image spin waves excited in spin-torque and spin Hall oscillators with nano contacts of the size of ~100nm. We also succeeded in imaging different excitation modes of magnetic samples in ferromagnetic resonance at 9.6GHz excitation frequency, where the opening angle of the precession cone is of the order of 10mrad.

The facility that is dedicated to ultrafast studies of materials under electric and magnetic fields is open to general users who are interested in this field.

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-MoA

Theoretical Modeling of f Electron Systems
Moderator: Ladislav Havela, Charles University, Czech Republic

2:00pm **AC+AS+MI+SA+SS-MoA1 Nonmagnetic Ground State of PuO_2**, ***Jindrich Kolorenc***, Academy of Sciences of the Czech Republic **INVITED**

The correlated band theory implemented as a combination of the local density approximation with the dynamical mean-field theory is applied to PuO_2. We obtain an insulating electronic structure consistent with the experimental photoemission spectra, and a nonmagnetic ground state that is characterized by a noninteger filling of the plutonium f shell ($n_f \approx 4.4$). Due to a sizable hybridization of the f shell with the p states of oxygen, the ground state is more complex than the four-electron Russell–Saunders $^5I_4$ manifold split by the crystal field. The dynamical mean-field theory, which in the present case can be schematically viewed as an extension of the crystal-field model with hybridization terms, improves the agreement between the theory and experiment for the magnetic susceptibility [1]. Encouraged by the good accuracy achieved for PuO_2 , we apply the theory to several other tetravalent actinide oxides.

[1] A. B. Shick, J. Kolorenč, L. Havela, T. Gouder, and R. Caciuffo, Phys. Rev. B **89**, 041109 (2014).

2:40pm **AC+AS+MI+SA+SS-MoA3 DMFT Modeling of Electronic Spectral Properties in Pu-based Actinides**, ***Jian-Xin Zhu***, Los Alamos National Laboratory **INVITED**

Plutonium-based materials have been studied for many years due to their importance in nuclear energy applications. Scientifically, these materials exhibit highly complex properties. Pu metal shows a significant volume expansion and anomalous magnetic properties; while Pu-115 (like $PuCoGa_5$) are found to be superconductors. These intriguing phenomena originate from the special location of Pu in the Periodic Table, which is at the boundary between the light actinides that have itinerant 5f electrons and the heavy actinides with localized 5f electrons. They call out the notion of strong correlation of 5f electrons. In this talk, I will present a study of the electronic structure of Pu metals and its 115 compounds in the framework of the combination of local density functional approximation and dynamical mean-field theory. In particular, the results on momentum-resolved spectral functions will be presented and be compared with those based on the LDA only. In addition, the effect of Pu 5f electron occupancy on the electronic structure of these systems will also be discussed. The test of these results by future angle-resolved photoemission spectroscopy measurements will give a stringent constraint on the theoretical approach.

3:40pm **AC+AS+MI+SA+SS-MoA6 The Evolution in Pu Nanocluster Electronic Structure: From Atomicity to Three-Dimensionality**, ***James Tobin***, *S.W. Yu, B.W. Chung,* Lawrence Livermore National Laboratory, *M.V. Ryzhkov,* Russian Academy of Science-Urals, *A. Mirmelstein*, Russian Federation Nuclear Lab (VNIITF)

The development of electronic structure in solid systems as a function of size has long been a subject of great interest and extensive scientific investigation. Experimentally, the transition, from nanoscale or mesoscopic to bulk behavior in metal clusters, was reported in 1981 by Mason and co-workers. Similarly, the evolution from two-dimensional to three-dimensional band structure in metal overlayers and the manifestation of nanoscale effects in compound semiconductor have also observed. In the area of actinide materials, the progress has been slowed by the limitations imposed by the highly radioactive, chemically toxic and pyrolytic nature of these materials. Havela and Gouder and colleagues performed investigations upon Plutonium (Pu) ultra-thin films, deposited in situ by means of a discharge-plasma, and Trelenberg and co-workers developed an approach using laser ablation of Uranium (U). Gas phase studies of actinides have also been pursued including atoms, molecules and reactions. Recent theoretical studies include UO_2 molecules, solid actinide oxides, and actinide carbide clusters. A new approach to cluster calculations has been taken in this study. Past cluster calculations were arranged in such a way that the central atom would exist in a bulk like environment. In calculations herein, it is expected that the central atom will be in the most bulk-like environment as well. However, just as in any finite size object, there will be variation of potential at the positions of symmetry non-equivalent atoms within the simulated cluster. Hence, averaging over all of the atoms in the cluster will give a measure of the effect of size. We will use this aspect of cluster calculations to investigate size related effects. Here, we report the result of the calculation of the electronic structure of clusters of Pu and their comparison to bulk spectroscopic results. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract No. DE-AC52- 07NA27344. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported

by the DOE Office of Science, Office of Basic Energy Science. For more detail see:M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin, “Probing Actinide Electronic Structure through Pu Cluster Calculations,” Intl. J. Quantum Chem. **113**, 1957 (2013); COVER ARTICLE .

4:00pm **AC+AS+MI+SA+SS-MoA7 First-Principles Density Functional Theory Simulation on Rare-Earth-Based Oxides as Fast Oxygen Ion Conductors**, ***Mamoru Sakaue***, *M. Alaydrus, H. Kasai,* Osaka University, Japan, *T. Ishihara*, Kyushu University, Japan

Development of novel fast ion conductors is a crucial issue for realizing solid oxide fuel cells (SOFCs) which can operate in low temperatures. While yttria-stabilized zirconia (YSZ) had been well-studied both by experiments and theories, exploration of other types of materials retaining high ionic conductivities in lower temperatures is still desired. Experimental studies in the recent twenty years have found some rare-earth-based oxides having higher ionic conductivities to be promising for operation below 600°C, and first-principles simulation studies on the materials have begun.

We studied atomic and electronic properties on oxygen-ionic conduction of $LaGaO_3$-, La_2GeO_5-, Pr_2NiO_4- and CeO_2-based materials by first-principles calculations based on density functional theory (DFT). We analyzed stable structures, electronic densities of states, oxygen migration paths and activation energies in the paths of pure and doped materials in order to evaluate their capabilities in application to electrolytes or electrodes. The obtained results of the activation energies showed good agreements with experiments in several aspects. However, for Pr_2NiO_4- and CeO_2-based materials that contain lanthanoid elements, there remains an open question about theoretical treatment of 4*f* electron states. The strong localization was found to affect oxygen ion motions fundamentally as well as electronic/magnetic properties. Then the strong electron-electron correlation modifies simple trends in activation energies found for the lanthanoid series within an approximation in which the correlation effects were neglected [1].

While fundamental reproduction of the strong electron-electron correlation in localized states by DFT is extremely difficult, empirical corrections by Hubbard *U* terms enable a practical solution to this problem. Here, the *U* value can be determined only by comparison with experiments in most cases because the value is affected by environment of the lanthanoid atoms. However, a theoretical study based on an empirical model demonstrated that the environment effects on 4*f* orbitals can be small if its strong localization is maintained [2]. In the presentation, we confirm this rule based on the results by the DFT first-principles calculations with Hubbard *U* corrections and discuss possibilities of computational materials design of lanthanoid-doped ceria ($Ce_{1-x}Ln_xO_{2-x/2}$) as electrolyte materials.

[1] M. Alaydrus, M. Sakaue, S. M. Aspera, T. D. K. Wungu, T. P. T. Linh, H. Kasai, T. Ishihara and T. Mohri, J. Phys. Condens. Matter **25**, 225401 (2013).

[2] E. Rogers, P. Dorenbos and E. van der Kolk, New J. Phys. **13**, 093038 (2011).

4:20pm **AC+AS+MI+SA+SS-MoA8 Electronic Structure, Magnetic Properties, and Magneto-Structural Transformations of Rare Earth Magneto-Caloric Materials**, ***Durga Paudyal***, Ames Laboratory, *V.K. Pecharsky, K.A. Gschneidner, Jr.*, Ames Laboratory and Iowa State University **INVITED**

We present first principles modeling of structural and magnetic properties of Gd_5Ge_4 based magneto-caloric materials. The total energy as a function of the shear displacement of slabs confirms stability of experimentally observed crystal and magnetic structures. Small substitutions of the Gd by Y and Lu lead to a catastrophic loss of ferromagnetism, but the substitutions by La have no effect on the magnetism. Furthermore, substitutions of the Ge by Si exert chemical pressure and transform the antiferromagnetic O(II) to the ferromagnetic O(I) ground state. In addition, we present a pathway for estimating the magnetic entropy change in the room temperature giant magnetocaloric compounds, i.e. $Gd_5Si_2Ge_2$, by coupling first principles outputs with the established magneto-thermodynamic models. The theoretical values of the magnetic entropy change compare well with experimental results.

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.

Magnetic Interfaces and Nanostructures
Room: 311 - Session MI-MoA

Topological Insulators/Rashba Effect
Moderator: Rosa Alejandra Lukaszew, The College of William and Mary

2:00pm **MI-MoA1 Spin-Polarized Electronic Structure at Strongly Spin-Orbit Coupled Surface**, ***Koji Miyamoto***, Hiroshima Synchrotron Radiation Center, Japan **INVITED**

Topological insulators and Rashba systems possess peculiar spin dependent electronic structure arising from a combination between a broken space inversion symmetry and strong spin-orbit interaction and are expected as key materials to revolutionize spin current devices without external magnetic field. However, the spin-orbit interaction cause the spin diffuse scattering and spin relaxation time shortens. For promoting practical use, it is necessary to enhance the short spin relaxation time. Topological insulators and Rashba systems possess peculiar spin dependent electronic structure arising from a combination between a broken space inversion symmetry and strong spin-orbit interaction and are expected as key materials to revolutionize spin current devices without external magnetic field. However, the spin-orbit interaction cause the spin diffuse scattering and spin relaxation time shortens.

For promoting practical use, it is necessary to enhance the short spin relaxation time. The spin relaxation time is also dependent on the spin texture caused by spin-orbit interaction, therefore, it enhance demand to directly observe the spin dependent electronic structure. The spin- and angle-resolved photoemission spectroscopy (spin-ARPES) is a most powerful tool to do it. However, it is not enough energy- and angle-resolution ($\Delta E \sim 100$ meV, $\Delta\theta \sim 2°$) of common spin-ARPES systems to clarify the detail spin texture due to the low efficiency ($\varepsilon \sim 10^{-4}$) of the conventional Mott-type spin detector. Recently, our group have developed novel high-efficient spin-ARPES system[1]. The system consists of a highe performance hemispherical analyzer (VG-Scienta R-4000) and high efficient spin detector based on very low energy electron diffraction of Fe(001)p(1x1)-O, which has 100 times higher efficiency. Finally, the highest ΔE and $\Delta\theta$ have been improved to 8meV and 0.37°.

In this symposium, I present the researches on spin texture for several strongly spin-orbit coupled system such as Rashba systems [2] and topological insulators [3] studied by our developed high efficient spin-ARPES system.

Reference

[1] T. Okuda, K. Miyamoto et al., Rev. Sci. Instrum. **82**, 103302 (2011).

[2] K. Miyamoto et al., New. J. Phys. accepted.

[3] K. Miyamoto et al., Phys. Rev. Lett. **109**, 166802(2012).

2:40pm **MI-MoA3 Spin Chirality in Momentum Space for Surface States on Tl/Si(111) and Tl/Ge(111)**, ***Markus Donath***, *S.D. Stolwijk, P. Eickholt, A.B. Schmidt,* Muenster University, Germany, *K. Sakamoto,* Chiba University, Japan, *P. Krueger*, Muenster University, Germany

The Tl/Si(111)-(1x1) surface is known for its outstanding properties due to spin-orbit interaction: a rotating spin pattern in momentum space and an unoccupied surface state with giant spin splitting at the K point [1,2]. In this contribution, we focus on the unoccupied surface electronic structure along the ΓM and MK high-symmetry directions. Spin- and angle-resolved inverse-photoemission experiments with sensitivity to the in-plane and the out-of-plane components of the spin-polarization vector were performed with our recently developed rotatable spin-polarized electron source [3]. Along both high-symmetry directions, our experiments reveal a surface-derived state with giant spin-orbit-induced splitting, in agreement with our theoretical findings. The state is purely in-plane polarized along ΓM, whereas the out-of-plane component is dominant along KM. As a consequence, spin chirality is found in momentum space around the M point.

We will compare our results for Tl/Si(111) with data for the isoelectronic Tl/Ge(111) surface. Differences in the surface electronic structure between the two surfaces appear along ΓM, where the Rashba-type spin-split surface state on Tl/Ge(111) lies within a band gap, while it is degenerate with bulk bands on the Si substrate. Consequences for the spin texture will be discussed.

[1] K. Sakamoto *et al*., Nature Commun. **4**, 2073 (2013).

[2] S.D. Stolwijk *et al*., Phys. Rev. Lett. **111**, 176402 (2013).

[3] S.D. Stolwijk *et al*., Rev. Sci. Instrum. **85**, 013306 (2014).

3:00pm **MI-MoA4 Spin-Orbit-Induced Spin Polarization in the Unoccupied Electronic Structure of W(110)**, ***Henry Wortelen****, Westfälische Wilhelms-Universität Münster, Germany, *H. Mirhosseini,* Johannes Gutenberg-Universität, Germany, *J. Henk,* Martin-Luther-Universität Halle-Wittenberg, Germany, *A.B. Schmidt, M. Donath*, Westfälische Wilhelms-Universität Münster, Germany

The spin texture in the electronic structure of heavy elements and topological insulators, which is caused by spin-orbit interaction, is a hot topic of today´s research in condensed matter physics. On W(110), a spin-polarized Dirac-cone-like surface state has been found recently, which is reminiscent of topological surface states [1, 2]. While the occupied bands including this surface state are well investigated by spin- and angle-resolved photoemission, there is basically a blank area on the $E(k_{\|})$-map above the Fermi level.

We present a combined experimental and theoretical study on the unoccupied electronic structure of W(110). We interpret our spin- and angle-resolved inverse photoemission experiments on the basis of band structure and one-step-model calculations. We compare results for Γ-N and Γ-H, which are nonequivalent due to the two-fold symmetry of the W(110) surface.

A complex spin structure is observed for the surface-state emissions, in which the symmetry of the respective states plays a crucial role. Using several photon detectors and therefore being sensitive to different photon takeoff angles result in different spin-polarization signals of the same electronic state even for normal electron incidence. This shows that the measured spin polarization is highly dependent on the geometry of the experimental setup and does not necessarily resemble the spin structure of the state under investigation. To derive the spin texture of the electronic states experimentally, the photon-emission process has to be taken into account. In this context, we will address how the symmetry of the states influences the observed spin polarization.

[1] K. Miyamoto *et al.*, Phys. Rev. Lett. **108**, 066808 (2012)

[2] H. Mirhosseini *et al*., New J. Phys. **15**, 033019 (2013)

3:40pm **MI-MoA6 Reorganization and Annihilation of Topologically Nontrivial Surface and Interface States**, ***Jürgen Henk***, Martin Luther University Halle-Wittenberg, Germany **INVITED**

Topological insulators are characterized by an insulating bulk and topologically protected surface states. The latter bridge the fundamental band gap und often show linear dispersion, i.e., a Dirac cone. In this presentation, I am going to answer two questions: how is the Dirac surface state of Bi_2Te_3 modified upon deposition of noble metal atoms? And second, is it possible to confine nontrivial interface states between two topological insulators? The findings have impact for spin-dependent transport.

The electronic structure of Au-covered Bi_2Te_3 is investigated by first-principles calculations [1]. The Dirac surface state of Bi_2Te_3 hybridizes with the Au sp states, which gives rise to strong reorganization of the surface electronic structure. Striking features of the modified Dirac surface state are (i) the introduction of new Dirac points within the fundamental band gap of Bi_2Te_3, (ii) an extremely weak dispersion, and (iii) an anisotropic number of conducting channels in the fundamental band gap of Bi_2Te_3 which leads to a complicated Fermi surface.

I shall also show that nontrivial electronic states exist at an interface of a Z_2 topological insulator and a topological crystalline insulator [2]. At the exemplary (111) interface between Bi_2Te_3 and SnTe, the two Dirac surface states at the Brillouin zone center annihilate upon approaching the semi-infinite subsystems but one topologically protected Dirac surface state remains at each time-reversal invariant momentum M. This leads to a highly conducting spin-momentum-locked channel at the interface but insulating bulk regions. For the Sb_2Te_3/Bi_2Te_3 interface, there is complete annihilation of Dirac states because both subsystems belong to the same topology class.

This work is supported by the Priority Program 1666 of DFG.

[1] Francisco Muñoz, Jürgen Henk, and Ingrid Mertig, submitted (2014).

*** Falicov Student Award Finalist**

[2] Tomáš Rauch, Markus Flieger, Jürgen Henk, and Ingrid Mertig, Phys. Rev. B **88** (2013) 245120.

4:20pm **MI-MoA8 Unconventional Relativistic Electron Structure on Polar Bi Chalcogenide Sufaces**, ***Andrew Weber****, University of Missouri-Kansas City, *I. Pletikosic, Q.D. Gibson, H. Ji,* Princeton University, *T. Yilmaz,* University of Connecticut, *J.T. Sadowski, E. Vescovo,* Brookhaven National Laboratory, *A.V. Fedorov,* Lawrence Berkeley National Laboratory, *A.N. Caruso,* University of Missouri-Kansas City, *G. Gu,* Brookhaven National Laboratory, *B. Sinkovic,* University of Connecticut, *R.J. Cava,* Princeton University, *T. Valla*, Brookhaven National Laboratory

Spin-polarized surface electronic structures arising from broken inversion symmetry and a topologically non-trivial excitation gap in the underlying bulk show promise as platforms for realizing of exotic quantum phases (e.g. Majorana fermion modes) and spin-filter transport applications, however, the opportunities presented by these systems for exploring fundamental aspects of the spin-orbit interaction (SOI) in 2D have been underemphasized. The effect of SOI in solids can deviate from conventional models because it is sensitive to the full quantum description of the system, including atomic quantum numbers, the effective electric field, and spatial orbital and crystal symmetries. Together, these conditions shape the band structure and spin- and orbital-texture, and dictate the strength and anisotropy of interband hybridizations. Through spin- and angle-resolved photoemission spectroscopy of semi-ionic topological $(Bi_2)_m(Bi_2X_3)_n$ (X= Se, Te) superlattice materials, we have identified a variety of unconventional SOI effects acting on topological surface states. We will discuss how tuning the surface charge dipole and termination chemistry controls: (1) the electron band dispersion, (2) interband hybridizations, (3) the size, shape, and spin-topology of the Fermi surface and (4) the sign and magnitude of the Fermi velocity.

4:40pm **MI-MoA9 Identifying the Intrinsic Atomic Defects in Bi_2Se_3 with Scanning Tunneling Microscopy**, ***Jixia Dai***, Rutgers University, *D. West,* Rensselaer Polytechnic Institute, *X.-Y. Wang, Y.-Z. Wang, D. Kwok,* Rutgers University, *S.B. Zhang,* Rensselaer Polytechnic Institute, *S.-W. Cheong, W. Wu*, Rutgers University

In topological insulators the helical Dirac fermions are immune to backscattering as long as the time reversal symmetry is preserved. However, the existence of intrinsic atomic defects in materials such as Bi_2Se_3 and Bi_2Te_3 still represents one of the major issues for applications. Intrinsic atomic defects such as vacancies or antisites not only could dope charges, make the insulators conductive and shift the Dirac electrons away from the fermi energy but also affect the mobility of the materials by introducing disorder. By studying a series of Bi_2Se_3 samples that were grown with different conditions with atomic resolving scanning tunneling microscopy, we have successfully identified several types of intrinsic defects, including Se vacancies and Bi-Se antisites. The densities of these different types of defects could be correlated with growth conditions and the total density is related to the band shift measured by tunneling spectroscopy. Our study demonstrates the capability of scanning tunneling microscopy in diagnosing materials like Bi_2Se_3 and similar ones at the atomic level.

5:00pm **MI-MoA10 Probing Topological Crystalline Insulator SnTe (001) Surface States via Energy Resolved Quasiparticle Interference**, ***Duming Zhang***, NIST and University of Maryland, *H. Baek,* NIST and Seoul National University, Korea, *J. Ha, T. Zhang,* NIST and University of Maryland, *J.E. Wyrick, A.V. Davydov,* National Institute of Standards and Technology, *Y. Kuk,* Seoul National University, Korea, *J.A. Stroscio*, National Institute of Standards and Technology

Recently, the topological classification of electronic states has been extended to a new class of matter known as topological crystalline insulators. Similar to topological insulators, topological crystalline insulators also have spin-momentum locked surface states; but they only exist on specific crystal planes that are protected by crystal reflection symmetry. Here, we report an ultra-low temperature scanning tunneling microscopy and spectroscopy study on topological crystalline insulator SnTe nanoplates grown by molecular beam epitaxy. We observed quasiparticle interference patterns on the SnTe (001) surface that can be interpreted in terms of electron scattering from the four Fermi pockets of the topological crystalline insulator surface states in the first surface Brillouin zone. A quantitative analysis of the energy dispersion of the quasiparticle interference intensity shows two high energy features related to the crossing point beyond the Lifshitz transition when the two neighboring low energy surface bands near the X point merge. We present two possible interpretations for the two high energy features due to different scattering vectors along the ΓX and XM line cuts. A comparison between the experimental and computed quasiparticle interference patterns reveals possible spin texture of the surface states.

5:20pm **MI-MoA11 Control of Graphene Nucleation on Magnetic Oxides: Spintronics without Spin Injection**, ***Yuan Cao***, University of North Texas, *P. Kumar,* Indian Institute of Technology-Mandi, India, *I. Tanabe,* University of Nebraska-Lincoln, *J. Beatty, M. Driver,* University of North Texas, *A. Kashyap,* Indian Institute of Technology-Mandi, India, *P.A. Dowben,* University of Nebraska-Lincoln, *J.A. Kelber*, University of North Texas

Graphene direct growth by molecular beam epitaxy (MBE) occurs on a p-type but not n-type oxide, with resulting charge transfer and substrate-induced graphene spin polarization to > 400 K. C MBE on 10 Å p-type $Co_3O_4(111)/Co(0001)$ at ~ 800 K yields layer-by-layer growth of graphene sheets in azimuthal registry. Significant charge transfer -- ~ 0.04 e^-/C atom -- confined to the first 1-2 graphene layers, results in oxide reduction at the oxide/Co(0001) interface. In contrast, MBE on 10 Å n-type $Cr_2O_3(0001)/Co(0001)$ under similar conditions yields only the desorption of C and lattice O, despite similar oxide lattice constants and a stronger Cr-O vs. Co-O bond strength. These results demonstrate that downward band bending at the Co_3O_4/Co interface enhances charge transfer and graphene formation. Upward band bending at the Cr_2O_3/Co interface inhibits such charge transfer. DFT electronic structure calculations show that such charge transfer leads to strong Co(II)/graphene carrier exchange interactions, yielding an enhanced magnetic moment and spin ordering temperature, in excellent agreement with experiment. Such substrate-induced graphene spin polarization makes possible a variety of spintronic devices operating at >> 300 K, without the bottleneck of spin injection, and with predicted magnetoresistance values of ~ 500% or more. The model further predicts such results for other p-type magnetic oxides, making possible high magneto-resistance voltage-switchable devices.

*** Falicov Student Award Finalist**

Actinides and Rare Earths Focus Topic
Room: 301 - Session AC+AS+MI+SA+SS-TuM

Synchrotron Radiation and Laboratory Based Investigations of Actinides and Rare Earths
Moderator: David Geeson, AWE

8:00am **AC+AS+MI+SA+SS-TuM1 The Role of the 5f Band and Partial Occupancy in Actinide L3-edge XANES and RXES Measurements**, ***Corwin Booth***, *S.A. Medling, Y. Jiang,* Lawrence Berkeley National Laboratory*, J.G. Tobin,* Lawrence Livermore National Laboratory*, P.H. Tobash, J.N. Mitchell, D.K. Veirs,* Los Alamos National Laboratory*, M.A. Wall, P.G. Allen,* Lawrence Livermore National Laboratory*, J.J. Kas,* University of Washington*, D. Sokaras, D. Nordlund, T.-C. Weng,* SLAC National Accelerator Laboratory*, E.D. Bauer*, Los Alamos National Laboratory **INVITED**

Although actinide (An) L3-edge x-ray absorption near-edge structure (XANES) spectroscopy has been very effective in determining An oxidation states in insulating, ionically-bonded materials, such as in certain coordination compounds and mineral systems, the technique fails in systems featuring more delocalized 5f orbitals, especially in metals. Recently, actinide L3-edge resonant x-ray emission spectroscopy (RXES) has been shown to be an effective alternative. This technique is further demonstrated here using a parametrized partial unoccupied density of states method to quantify both occupancy and delocalization of the 5f orbital in alpha-Pu, delta-Pu, PuCoGa5, PuCoIn5, and PuSb2. These new results, supported by FEFF calculations, highlight the effects of strong correlations on RXES spectra and the technique's ability to differentiate between f-orbital occupation and delocalization. Potential temperature-dependent spectral changes in the hidden order compound URu2Si2 and the superconductor PuCoGa5 will be discussed.

8:40am **AC+AS+MI+SA+SS-TuM3 Actinide Research with Hard Synchrotron Radiation**, ***Roberto Caciuffo***, European Commission, JRC-ITU, Germany **INVITED**

Advanced x-ray synchrotron radiation techniques, addressing spatial and temporal fluctuations of structural and electronic degrees of freedom, hold outstanding scientific promises for the future of actinide research [1]. Indeed, by probing hidden order parameters and elementary electronic excitations with high sensitivity and resolution, element- and edge-specific (resonant and non-resonant) x-ray scattering experiments provide the bricks for building the novel conceptual frameworks necessary to unravel the complexity of actinides. Here, I will present selected results from these experiments and discuss what they tell us.

Whereas resonant x-ray diffraction (RXD) with photon energies tuned to the $M_{4,5}$ absorption edges of actinide ions are used to study the order of electric quadrupole moments in oxides and intermetallics [2-4], resonant x-ray emission spectroscopy (RXES) and non-resonant inelastic X-ray scattering (NIXS) are applied to study the bulk electronic configuration in solids, liquids and gases [5,6]. In particular, the high penetration depth of hard X-rays employed in NIXS enables flexible containment concepts, facilitating investigations of radioactive materials in the liquid phase or under extreme conditions. Finally, inelastic x-ray scattering (IXS) can be used to map phonon dispersion branches with an energy resolution comparable to the one afforded by inelastic neutron scattering, but using crystal samples with sizes orders of magnitude smaller than those required by neutrons.

In the first example, I will show how a combination of diffraction, RXES, and absorption near-edge spectroscopy experiments at high-pressure can be used to study the correlation between polymorphism, mixing of different electronic configurations, and hybridization effects in elemental americium [7]. The potential of RXD in elucidating the nature of "hidden order" will be illustrated by the examples of the low-temperature phases in NpO_2 [8] and URu_2Si_2 [9]. Then, I will present NIXS results interrogating the $O_{4,5}$ absorption edges of uranium and plutonium materials, and results of IXS studies of the vibrational dynamics in $PuCoGa_5$ and NpO_2.

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9:20am **AC+AS+MI+SA+SS-TuM5 Lumps, Bumps and Pyrophoric Powders - Nuclear Waste Viewed in a New Light**, ***Tom Scott***, University of Bristol, UK, *C.A. Stitt, M. Hart,* Diamond Light Source Ltd., UK, *J. MacFarlane, A. Banos, H. Paraskevoulakos, K. Hallam*, University of Bristol, UK **INVITED**

How do you look inside a nuclear waste package without breaking it open? This question is important when the contained corrosion products are potentially flammable and radioactive. Synchrotron x-rays have been used to perform micro-scale in situ observation and characterisation of uranium entrapped in grout; a simulation for some intermediate level waste. Using specially designed analysis cells X-ray tomography and x-ray diffraction have been used to generate both qualitative and quantitative data from a grout encapsulated uranium sample before, and after, deliberately constrained H_2 corrosion. Tomographic reconstructions determined the extent, rates and mechanisms of the oxidation reaction by assessing the relative densities between the materials and the volume of corrosion products. The oxidation of uranium in grout was shown to follow the anoxic $U + H_2O$ oxidation regime, and the pore network within the grout was observed to influence the induction period for the initiation of uranium hydride formation across the surface of the metal. Powder diffraction analysis identified the corrosion products UO_2 and UH_3, and permitted measurement of corrosion induced stress. Together, x-ray tomography and diffraction provide a means of accurately determining the types and degree of uranium corrosion occurring, thereby offering a future means for studying the reactions occurring in real full-scale waste package systems.

11:00am **AC+AS+MI+SA+SS-TuM10 Isotopic Measurements of Uranium in Particles by SIMS**, ***David Simons***, National Institute of Standards and Technology (NIST) **INVITED**

Secondary ion mass spectrometry (SIMS) has become a primary tool for the International Atomic Energy Agency (IAEA) and its Network of Analytical Laboratories (NWAL) to monitor activities at uranium enrichment sites. IAEA inspectors collect samples by wiping surfaces within facilities with cloth wipes that are later distributed to the NWAL for analysis. At the laboratories particles are extracted from the wipes and searched by various means to find those that contain uranium. The uranium-bearing particles are analyzed by mass spectrometry for their isotopic composition that is the key signature to be compared with the declared use of the facility. Large-geometry (LG) SIMS instruments based on magnetic sector mass spectrometers with multicollector array detectors are used by five members of the NWAL to both search for the uranium particles and analyze those that are found. We have characterized the performance of this type of instrument and found that it can be set up with a mass resolving power that excludes nearly all mass spectral interferences from uranium isotopes while maintaining high instrument transmission and high abundance sensitivity. The total efficiency for uranium detection has been measured with monodisperse microspheres and found to exceed 1 %. Detection of U236 presents a special case because of interference from the U235 hydride ion that is removed by peak-stripping. The effect of the hydride on the uncertainty in the U236 abundance determination has been modeled for different uranium enrichments and hydride-to-parent ratios, and the effect of the particle substrate on hydride production has been investigated. The performance of LG-SIMS instruments for isotopic measurements of uranium in particles was recently demonstrated in the NUSIMEP-7 study organized by the Institute of Reference Materials and Measurements in which these instruments were able to detect and measure all uranium isotopes in particles smaller than 400 nm, including U236 at an isotopic abundance of $8x10^{-6}$.

11:40am **AC+AS+MI+SA+SS-TuM12 X-ray Excited Auger Transitions of Pu Compounds**, ***Art Nelson****, W.K. Grant, J.A. Stanford, W.J. Siekhaus, W. McLean*, Lawrence Livermore National Laboratory

X-ray excited Pu NOO Auger line-shapes were used to characterize differences in the oxidation state of Pu compounds. The Auger line-shapes were combined with the associated chemical shift of the Pu $4f_{7/2}$ photoelectron line, which defines the Auger parameter and results in a reliable method for definitively determining oxidation states independent of binding energy calibration. Results show that PuO_2, Pu_2O_3, $PuH_{2.7}$ and Pu have definitive Auger line-shapes. These data were used to produce a chemical state (Wagner) plot for select plutonium oxides. This Wagner plot allowed us to distinguish between the trivalent hydride and the trivalent oxide, which cannot be differentiated by the Pu $4f_{7/2}$ binding energy alone.

Magnetic Interfaces and Nanostructures
Room: 311 - Session MI+MG-TuM

Advanced Materials Discovery
Moderator: Markus Donath, Muenster University, Germany

8:00am **MI+MG-TuM1 Combinatorial Approach to Novel Functional Materials**, ***Ichiro Takeuchi***, University of Maryland **INVITED**

Throughout the history of mankind, scientists and engineers have relied on the slow and serendipitous trial-and-error approach for materials discovery. In 1990s, the combinatorial approach was pioneered in the pharmaceutical industry in order to dramatically increase the rate at which new chemicals are identified. The high-throughput concept is now widely implemented in a variety of fields in materials science. We have developed combinatorial thin film synthesis and characterization techniques in order to perform rapid survey of previously unexplored materials phase space in search of new inorganic functional materials. Various thin film deposition schemes including pulsed laser deposition, electron-beam deposition, and co-sputtering are implemented for fabricating massive arrays of compositionally varying samples on individual combinatorial libraries. A suite of high-throughput characterization tools are employed to screen the combinatorial libraries and map different physical properties of materials as a function of sweeping composition changes. They include room-temperature scanning SQUID microscopy, microwave microscopy, and micromachined MEMS cantilever arrays. Advanced characterization techniques at synchrotron beam lines are used for rapid diffraction as well as x-ray magnetic circular dichroism measurements.

8:40am **MI+MG-TuM3 Discovery and Design of Two-Dimensional Materials by Data-Mining and Genetic Algorithm Approaches**, ***Richard Hennig***, University of Florida, Gainesville **INVITED**

The rapid rise of novel single-layer materials, presents the exciting opportunity for materials science to explore an entirely new class of materials. This comes at the time when mature computational methods provide the predictive capability to enable the computational discovery, characterization, and design of single-layer materials and provide the needed input and guidance to experimental studies. I will present our data-mining and genetic algorithm approaches to identify novel 2D materials with low formation energies and show how unexpected structures emerge when a material is reduced to sub-nanometers in thickness. We discovered several 2D materials in the families of group III-V compounds and group-II oxides with promising properties for electronic devices and identify suitable metal substrates that can stabilize several of these as-yet hypothetical materials. In the families of group-III monochalcogenides and transition metal dichalcogenides we identify several 2D materials that are suitable for photocatalytic water splitting. We show that these 2D materials in contrast to their 3D counterparts have appropriate bad gaps and alignments with the redox potentials of water, and exhibit high solvation energies, indicating their stability in aqueous environment. We show that strain can be used to tune the electronic and optical properties of these materials. Our results provide guidance for experimental synthesis efforts and future searches of materials suitable for applications in energy technologies.

9:20am **MI+MG-TuM5 Complexities in the Molecular Spin Crossover Transition**, ***Xin Zhang****, *S. Mu,* University of Nebraska-Lincoln*, J. Chen,* Columbia University*, T. Palamarciuc, P. Rosa, J.-F. Létard,* Université de Bordeaux, France*, J. Liu, D. Arena,* Brookhaven National Laboratory*, B. Doudin,* Université de Strasbourg, France*, P.A. Dowben*, University of Nebraska-Lincoln

The electronic structures of three different spin crossover molecules have been obtained by temperature dependent X-ray absorption spectroscopy (XAS). We show compelling evidence that the electronic structure changes associated with the spin crossover transition occur at significantly lower temperature than observed for the change in the molecular spin state. The transition temperatures indicated by XAS is about 20~60 K lower than that given by the magnetic moment switching. The changes in electronic structure are in agreement with density function theory (DFT) results that shows that the molecular electronic structures are different for high spin (HS) and low spin (LS) states. The conclusion that the electronic structure changes occur at significantly lower temperature than observed for the change in the molecular spin state associated with the spin crossover transition are also supported by transport measurements and the temperature dependence of the dielectric properties of SCO molecular system: [Fe(PM-AzA)$_2$(NCS)$_2$].

9:40am **MI+MG-TuM6 Controlling and Imprinting Topological Spin Textures**, *R. Streubel, L. Han,* IFW Dresden, Germany*, M.-Y. Im,* Lawrence Berkeley National Laboratory*, F. Kronast,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany*, U.K. Roessler,* Institute for Theoretical Solid State Physics, IFW Dresden, Germany*, F. Radu, R. Abrudan,* Ruhr-Universitaet Bochum, Germany*, G. Lin, O.G. Schmidt,* IFW Dresden, Germany*, **Peter Fischer**,* Lawrence Berkeley National Laboratory*, D. Makarov*, IFW Dresden, Germany

Topological states in magnetism, such as chiral skyrmions, with an integer topological charge are currently a topic of intensive fundamental research [1-3]. If one was able to control their properties in a digital manner, such as switching their topological charge deliberately in storage devices, a novel path in spintronics would be opened [4]. However, so far, most of these topological spin textures have been only observed in exotic materials with low symmetry and at low temperatures, making them rather impractical for applications. Here, we offer an alternative route by designing synthetic magnetic heterostructures where specific spin textures resembling swirls, vortices or skyrmions with distinct topological charge densities can be tailored at ambient temperatures. This is achieved by vertically stacking two magnetic nanopatterns with in-plane and out-of-plane magnetization and imprinting the in-plane non-collinear spin textures into the out-of-plane magnetized material. Key mechanisms of our concept are demonstrated both by micromagnetic simulations and experimental observations with element-specific magnetic soft x-ray microscopy [6] in a common ferromagnetic thin film element stack, e.g. Co/Pd multilayers coupled to Permalloy. Utilizing the interlayer coupling strength as tuning parameter, a gradual transition in the magnetic pattern of the out-of-plane layer from the decoupled magnetized state to a strongly coupled state with a vortex spin texture is achieved. At an intermediate coupling strength, magnetic spirals with tunable opening angle and in particular donut textures form which can be referred to as skyrmion system with D_n symmetry. Applying a small magnetic field, a controlled and reliable switching between two topologically distinct donut textures is realized.

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11:00am **MI+MG-TuM10 Growth and Properties of Skyrmionic MnSi Nanowires and Thin Film on Silicon**, ***Jieyu Yi***, *S.W. Tang,* University of Tennessee*, I.I. Kravchenko, G.X. Cao,* Oak Ridge National Laboratory*, D.G. Mandrus,* University of Tennessee*, Z. Gai*, Oak Ridge National Laboratory

Magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spin-electronic data storage and other information technology applications . The origin of the magnetic skyrmion phase can be traced to the anti-symmetric Dzyaloshinski-Moriya (DM) interaction that is allowed in space groups lacking inversion symmetry. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. Prototypical materials with the skyrmion ordering are those compounds with B20 structure, like MnSi and FeGe. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the skyrmion phase is much more robust. It is of great interest to determine the properties of the skyrmion phase in quasi-1D nanowires and 2D thin films. If skyrmion ordering can persist in one-dimensional MnSi nanowires and 2D films, then these systems may be very promising for spintronics applications as the magnetic domains and individual skymions could be manipulated with small currents. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in MnSi nanowires.

*** Falicov Student Award Finalist**

The SiO_2 layer pla ys a key role for the high yield, correct stoichiometric and crystalline growth of the B20 MnSi nanowires. A growth phase diagram was constructed. For the thin films, an unique growth receipt was developed for the growth of high quality of thin films. The structure and magnetic properties of the films at different thickness were studied.

11:20am **MI+MG-TuM11 Depth Dependent Mapping of Valence and Other Factors in $LaSrMnO_3$/$PrZrTiO_3$ Magnetoelectric Heterostructures**, ***Mikel Holcomb***, *C.-Y. Huang, R. Trappen, J. Zhou,* West Virginia University, *Y.-H. Chu*, National Chiao Tung University, Taiwan, Republic of China

Our group focuses on the ability to study the unique properties occurring at material surfaces and interfaces. One of the most interesting types of interfaces are magnetoelectric, because they offer the ability to electrically control magnetism or vice versa. This magnetoelectric control offers potential advantages in computing, magnetic sensors, energy scavenging and more. Magnetoelectric interfaces offer advantages over single layer magnetoelectrics as the ordering temperatures can be above room temperature and the coupling can be significantly stronger. Despite these advantages, the mechanism responsible for magnetoelectric coupling is currently unknown, which limits our ability to improve these systems to the parameters required for applications. In order to understand the mechanism for magnetoelectric multilayers, we investigated $LaSrMnO_3$ on $PbZrTiO_3$. By varying the sample thickness and utilizing both surface and bulk sensitive synchrotron radiation techniques, we are able to map out the Mn valence throughout the $LaSrMnO_3$ layer. We have also studied how strain and magnetization change with layer thickness. I will discuss our how results enable us to understand the charge origin of magnetoelectric interfaces.

11:40am **MI+MG-TuM12 Strain Measurements in $LaSrMnO_3$/$PbZrTiO_3$ Magnetoelectric Heterostructures**, ***Chih-Yeh Huang***, *J. Zhou,* West Virginia University, *Y.-H. Chu,* National Chiao Tung University, Taiwan, Republic of China, *M.B. Holcomb*, West Virginia University

LaSrMnO3/PbZrTiO3 (LSMO/PZT) magnetoelectric heterostructures make them attractive not only for data storage applications but also for studying strain measurements. There are many reasons why LSMO/PZT magnetoelectric heterostructures were selected for our studies such as the excellent lattice matching and high ordering temperatures. X-ray micro diffraction technique is used to observe local strain behavior at the interface of LaSrMnO3/PbZrTiO3 magnetoelectric heterostructures. Due to high spatial resolution in X-ray spot size (~1 mm) laterally, the observation of strain measurements in thickness-dependent PbZrTiO3 reveals shiftings of LSMO and PZT peaks, allowing an understanding of the behavior of strain at the interface which can be related to the mechanism of magnetoelectric coupling.

12:00pm **MI+MG-TuM13 Bit-Patterned Media Using Block Copolymer Templating on FePt**, *S. Gupta, H. Su,* ***Allen Owen***, *R. Douglas*, University of Alabama

Block copolymer (BCP) templating has been used to pattern perpendicular magnetic anisotropy media. Large-area arrays of magnetic dots with diameter of ~30nm have been obtained by BCP templating in FePt films. FePt was deposited by dc cosputtering of elemental targets and in situ annealing in the sputtering system at 550°C for 1hr. The polystyrene polyferrocenyldimethylsilane (PS-b-PFS) was spin-coated onto the film and annealed to cause phase separation, followed by oxygen plasma treatment to remove the polystyrene matrix and expose the PFS nanospheres[4]. The FePt films were subsequently etched using an ion mill. Then post-patterning annealing at 600°C was also performed to reverse the ion damage of the film. SEM and XRD were utilized to characterize the morphology and structural properties respectively, while magnetometry was carried out to show the magnetic properties. Response surface methodology was performed to optimize the power, etching time and etching angle of the block copolymer mask and magnetic film. The effects of these patterning parameters on structural and magnetic properties were discussed.

Magnetic Interfaces and Nanostructures
Room: 311 - Session MI+MG-TuA

Development of Multiferroic Materials (2:20- 5:00PM)
MIND Panel Discussion (5:00-6:30 pm)
Moderator: Peter Fischer, Lawrence Berkeley National Laboratory

2:20pm **MI+MG-TuA1 Versatile Abilities of Lattice Instabilities: New Design Strategies for Emergent Ferroics**, ***James Rondinelli***, Drexel University **INVITED**

I describe in this talk the design methodology and theoretical discovery of a new class of "rotation-induced" ferroelectric materials. By tailoring the instabilities of the BO_6 octahedral rotations common to ABO_3 perovskites oxides, I show these lattice distortions provide a new structural "sand box" from which to design and discover such ferroic phases. Bottom-up engineering of the transition metal octahedra at the unit cell level, is applied to realize ferroelectricity in artificial perovskites superlattices formed by interleaving two bulk materials with no tendency to such behavior. This emergent, chemistry-independent, form of ferroelectricity – octahedral rotation-induced ferroelectricity – offers a reliable means to externally address and achieve deterministic electric-field control over magnetism. I discuss the required crystal-chemistry criteria, which are obtained from a combination of group theoretical methods and electronic-structure computations, to select the compositions and stoichiometries giving polarizations comparable to the best known ferroelectric oxides. Much rarer in crystalline materials with an electric polarization, however, is the appearance of a ferri-electric (FiE) state, vis-à-vis ferrimagnetism, where local electric dipoles of different magnitude are anti-aligned to yield a net non-zero electric polarization. The underlying reason is that the long-range Coulomb forces in oxide-based dielectrics favor the cooperative alignment of all electric dipoles in the crystal through cation displacements that occur against an oxygen ligand framework. I conclude by describing our recent discovery of a first-order, isosymmetric, transition between a ferrielectric (FiE) and ferroelectric (FE) state in A-site ordered perovskite superlattices and offering new areas for ferroic discovery

3:00pm **MI+MG-TuA3 Voltage-controlled Exchange Bias and Exchange Bias Training**, ***Christian Binek***, *W. Echtenkamp*, University of Nebraska-Lincoln **INVITED**

Voltage-controlled exchange bias (EB) is a seminal achievement in nanomagnetism. It enables dissipationless electric control of interface magnetic states with major implications for room temperature spintronic applications. Numerous prototypical solid-state spintronic devices rely on switchable interface magnetism, enabling spin-selective transmission or scattering of electrons. Controlling magnetism at thin-film interfaces, preferably by purely electrical means, i.e. in the absence of electric currents, is a key challenge to better spintronics. Currently, most attempts to voltage-control magnetism focus on potentially large magnetoelectric (ME) effects of multiferroics.

Here, we report on the use of antiferromagnetic (AF) ME Cr_2O_3 (chromia) for voltage-controlled magnetism [1,2]. Electrically switchable boundary magnetization (BM) can overcome the weak linear ME susceptibility of room temperature bulk ME antiferromagnets. BM is a roughness insensitive equilibrium property of ME antiferromagnets which is in sharp contrast to the surface magnetic properties of conventional antiferromagnets. Voltage-controlled BM is the key property enabling isothermal voltage-controlled switching of exchange bias (EB) which emerges at the interface of adjacent ferromagnetic (FM) and the ME antiferromagnetic (AF) thin film. The inter-layer exchange alters the magnetization reversal shifting the FM hysteresis loop along the magnetic field axis. In this presentation I introduce voltage-control of EB and EB training [2]. Electric switching between stable EB fields is investigated in heterostructures based on single crystal Cr_2O_3(0001)/PdCo heterostructures and compared with recent results in MBE grown all thin film EB heterostructures. In addition to voltage-switching of EB we electrically and isothermally tune chromia into distinct AF multi-domain states. As a result, EB training, which originates from triggered rearrangements of the AF interface magnetization during consecutively cycled hysteresis loops, is tuned between zero and sizable effects. We quantify and interpret the peculiar voltage-controlled training effect in Cr_2O_3(0001)/PdCo by adapting our recently developed theory which is based on a discretized Landau-Khalatnikov dynamic equation [3].

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4:20pm **MI+MG-TuA7 Multiferroic Z_6 Vortices in Hexagonal $ErMnO_3$**, *Y. Geng, X.-Y. Wang, S.-W. Cheong*, ***Weida Wu***, Rutgers University

Multiferroics are materials with coexisting magnetic and ferroelectric orders, where inversion symmetry is also broken [1-5]. The cross-coupling between two ferroic orders can result in strong magnetoelectric coupling. Therefore, it is of both fundamental and technological interest to visualize cross-coupled topological defects in multiferroics. Indeed, topological defects with six interlocked structural antiphase and ferroelectric domains merging into a vortex core were revealed in multiferroic hexagonal manganites [6, 7]. Numerous Z_6 vortices are found to form an intriguing self-organized network, and may be used to test Kibble-Zurek model of early universe [8, 9]. Many emergent phenomena, such as enhanced conduction and unusual piezoelectric response, were observed in charged ferroelectric domain walls protected by these topological defects [10, 11]. In particular, alternating uncompensated magnetic moments were discovered at coupled structural antiphase and ferroelectric domain walls in hexagonal manganites using cryogenic magnetic force microscopy (MFM) [12], which demonstrates the coupling between ferroelectric and spin orders (B_2 phase). The appearance of correlated net moments at the coupled domain walls is in excellent agreement with a phenomenological Landau theory [13], suggesting that the 120° antiferromagnetic order (B_2 phase) rotates 4pi in each Z_6 vortex. This is further corroborated by the magnetic field dependence of domain wall moments.

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4:40pm **MI+MG-TuA8 Two-Dimensional Manganese Gallium Quantum Height Islands on Wurtzite GaN (000-1)**, ***Jeongihm Pak***, *A. Mandru, A.R. Smith*, Ohio University

We describe the spontaneous formation of five and six-monolayer quantum height manganese gallium islands on gallium-rich, nitrogen polar GaN(000$\underline{1}$). From ex-situ MOKE measurements at room temperature, we expect these MnGa islands to be ferromagnetic. The structural evolution is followed from the beginning of growth using reflection high energy electron diffraction, in which a dotted 2× pattern is observed to form. In-situ scanning tunneling microscopy is also used to investigate the islands' structures with atomic resolution. Based on all the observations, we propose the possible bulk and surface models for the islands. A possible bonding structure at the substrate/island interface is also discussed in which Mn atoms substitute for Ga atoms on the Ga adlayer thus making the MnGa islands bonded to the GaN substrate. Atomic chains are observed only on the six-layer island surface and the model for the chains is also discussed. STM observations of atomic-chain interconnection on the six-layer island surface indicate a dynamic system at room temperature. The models presented here should serve as useful starting points for theoretical calculations.

5:20pm **MI+MG-TuA10 Current Topics in Magnetism: The Importance of Interfaces**, ***Mark Stiles***, National Institute of Standards and Technology

Interfaces play a crucial role in many magnetic systems. As magnetoelectronic devices shrink, this role is becoming more and more important. Unfortunately, many times these interfaces are not well enough characterized to allow measurements to constrain physical models of the behavior in these systems. In this talk, I give several examples from my own experience of systems of both historical and current interest in which the interfaces play a dominant role but for which very little is known. A historical example is exchange bias, the study of systems in which the behavior of a ferromagnetic film is modified by coupling to it to an antiferromagnet. In spite of decades of study on a wide variety of systems, structural characterization of the interfaces has only been done several times on model systems, despite the fact that all of the coupling occurs at this interface. A topic of recent interest is the study of current induced torques in magnetic bilayers consisting of ferromagnetic thin films coupled to non-magnetic materials with strong spin-orbit coupling. The spin orbit coupling dramatically affects the current induced torques in these systems. An outstanding question is what role the interfacial spin-orbit coupling plays. This can be addressed theoretically by first-principles calculations, but these necessarily assume ideal interfaces between perfectly coherent lattices for material pairs with lattice mismatch on the order of ten percent. Without real characterization of the structure of these interfaces, it is almost impossible to definitively determine which parts of the system are playing important roles. Both of these topics are useful or potentially useful for applications, a characteristic that tends to drive research focused on achieving dramatic results rather than doing the time intensive work necessary to characterize the samples adequately to support a deeper understanding of the underlying physics.

5:40pm **MI+MG-TuA11 Optical Spectroscopy of Nanomaterials within Magnetic Fields**, ***Angela Hight Walker***, NIST

Transition-metal dichalcogenides are a new system in which to study the effect of temperature and magnetic field on optical properties. Recent experiments will be discussed from a novel set up which couples a confocal optical microscope into fields up to 9 Tesla and temperatures down to 3.5 K, with several laser sources throughout the visible range. As these dichalengenides or 2D materials are certainly under study for use in nanoelectronic devices they are of general interest to the Magnetic Interfaces and Nanostructures (MIN or MI) Division. Other areas where MIND members see as future foci will be explored. Methods to ensure that the Division draw upon the widest possible spectrum of talented individuals from all segments of society will also be discussed.

Magnetic Interfaces and Nanostructures
Room: Hall D - Session MI-TuP

Magnetic Interfaces Poster Session

MI-TuP3 Fabrication and Magneto-Optical Properties of Co-doped ZnO Hollow Nanospheres, ***Da-Ren Liu***, *C.J. Weng*, ITRC, NARL, Taiwan, Republic of China

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices. ZnCoO is one of the most promising diluted magnetic semiconductors materials due to its room temperature ferromagnetism. In this study, Al_2O_3 layer was conformally deposited on the surface of polystyrene (PS) nanoshpere with different diameter (300nm~800nm) by atomic layer deposition (ALD). After removal of PS nanosphere by heating, Al_2O_3 hollow nanospheres were formed. Then the $Zn_{1-x}Co_xO$ (x=0.03, 0.05, 0.07) coatings were grown on Al_2O_3 hollow nanospheres by pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, Co-doping does not change the wurtzite structure of ZnO and the $Zn_{1-x}Co_xO$ hollow nanospheres are polycrystalline. The surface and cross-section morphologies of the hollow nanospheres were analyzed using a field-emission scanning electron microscope (FE-SEM). Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Co ion concentration. The magneto-optical properties of the nanospheres were measured by micro-MOKE and x-ray magnetic circular dichroism (XMCD) spectroscopy. The results show the magnetic properties of $Zn_{1-x}Co_xO$ hollow nanospheres strongly depend on the Co composition fraction.

MI-TuP4 Study of Structural, Electronic and Magnetic Properties of (Fe2O3)n Clusters Using Density Functional Theory, ***Sholeh Alaei***, *S. Erkoc,* Middle East Technical University, Turkey, *S. Jalili*, Computational Physical Sciences Research Laboratory, School of Nano-Science, Institute for Research in Fundamental Sciences (IPM), Iran (Islamic Republic of)

In this paper, the electronic, magnetic and structural properties of $(Fe_2O_3)_n$ (n = 2-5) clusters were studied using Density Functional Theory. It came out that the most stable structures for n = 2, 3 and n = 4, 5 were ferrimagnetic and antiferromagnetic, respectively. The states with completely geometrical symmetry were spin-symmetric also, i.e. had equal atomic magnetic moments. It was found that by increasing ‘n’, the binding energy (E_b) increased, while such an observation was not seen for n = 4 and n = 5 and the binding energies were equal in these cases. An interesting result was that one of the states for n = 4 (n4-1) was a half-metallic antiferromagnet, which is important in spintronics applications. The most of the considered clusters were semi-metal or half-metal due to presence of Fe atoms.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+EM+MI+MN+NS+TF-WeA

Properties of 2D Materials
Moderator: Guy Le Lay, Aix-Marseille University

2:20pm **2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors**, ***Kirill Bolotin***, Vanderbilt University **INVITED**

Monolayer molybdenum disulfide (MoS2) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS2 differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS2 can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS2. We investigate the transition from direct to indirect band gap in MoS2 under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS2 on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS2 specimens. We use photocurrent spectroscopy to study excitons in pristine suspended MoS2. We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS2.

3:00pm **2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides**, ***Neha Nayyar***, *V. Turkowski, D.T. Le, T.S. Rahman*, University of Central Florida

Single layer MoS$_2$ and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 – 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

3:20pm **2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS$_2$**, ***Michael Watson***, *J.R. Simpson*, Towson University & NIST, *R. Yan, H. Xing*, University of Notre Dame, *S. Bertolazzi, J. Brivio, A. Kis*, EPFL, Switzerland, *A.R. Hight-Walker*, NIST

We report temperature and power dependent photoluminescence (PL) of molybdenum disulphide (MoS$_2$). Mechanical exfoliation of MoS$_2$, from bulk provides single-layer flakes which are then transferred either to sapphire substrates or suspended over holes in Si/Si 3 N 4 . We measure temperature dependence from ≈ 100K to 400K and power dependence from ≈ 6μW to ≈ 7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main exitonic peak(A) at ≈ 1.87eV which consist of both neutral excitons and charged trions (A- or A+) [1]. The A exciton peak and the A- exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE,a broad peak centred at ≈ 1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

[1] KF. Mak et al. Nat. Mat 12,207(2013)

[2] R.Yan and J.R.Simpson, S. Bertolazzi and J. Brivio, M. Watson, X.Wu and A. Kis, T.Luo, H.G.Xing, A.R. Hight Walker, ACS Nano 8,1 (2013)

4:20pm **2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of and TaSe$_2$ and TaS$_2$ Dichalcogenides**, ***Danilo Romero***, University of Maryland, College Park, *M. Watson, J.R. Simpson*, Towson University, *H. Berger*, Ecole Polytechnique Federale de Lausanne, Switzerland, *A.R. Hight Walker*, NIST

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2*H*-TaSe$_2$ and *1T*-TaSe$_2$, and 1*T*-TaS$_2$. In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-density phases, and superconducting ground state as function of temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2*H*-TaSe$_2$ and *1T*-TaSe$_2$, and 1*T*-TaS$_2$, carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:40pm **2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF$_3$Cl Phases on Graphene**, ***Josue Morales-Cifuentes***, *T.L. Einstein, Y. Wang, J. Reutt-Robey*, University of Maryland, College Park

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.[1] Electrical detection of CF3Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.[2] We study the electronic properties of similar phases varying coverage and orientation of CF3Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF1, vdW-DF2).[3] [4] Consistent with a physisorbed phase, binding energies are calculated to be on the order of 280meV, and insensitive to coverage and orientation of the CF3Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sub-lattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

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[2] Yilin Wang et al. , APL **103**, 201606 (2013)

[3] Jiri Klimes et al. , PRB **83**, 195131 (2011)

[4] Kyuho Lee et al. , PRB **82**, 081101(R) (2010)

5:00pm **2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials**, ***Jon Schuller***, UC Santa Barbara **INVITED**

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS$_2$ and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS2 mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental excitonic properties in layered nanomaterials and designing optical systems that efficiently excite and collectlight from exciton species with different orientations.

5:40pm **2D+AS+EM+MI+MN+NS+TF-WeA11 Mechanical Properties of 2D-Materials**, *J.M. Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, ***Ivan Oleynik***, University of South Florida

Graphene and other two-dimensional (2D) materials possess extraordinary mechanical properties, which are currently being explored in various novel applications. Atomic force microscopy (AFM) nanoindentation experiments on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic moduli, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm **2D+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers**, ***Evan Reed***, *K.-A.N. Duerloo, Y. Li*, Stanford University

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer $MoTe_2$ is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform $MoTe_2$ under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

2D Materials Focus Topic
Room: 310 - Session 2D+EM+MI+MN+NS+SS+TF-ThA

Novel Quantum Phenomena in 2D Materials
Moderator: Alexander Sinitskii, University of Nebraska-Lincoln

2:20pm **2D+EM+MI+MN+NS+SS+TF-ThA1 Optoelectronics of Two-Dimensional Semiconductors**, ***Xiaodong Xu***, University of Washington **INVITED**

Two dimensional transition metal dichalcogenides are a recent addition to the 2D electronic materials family. They have shown outstanding electrical and optical properties for new optoelectronic device concepts. In this talk, we will first discuss the unique interplay between spin, valley, and layer pseudospins in bilayer WSe$_2$. Such coupling effects lead to electrical control of spin states and optical generation of valley coherence through interlayer trions, where electrons and holes are localized in different layers. We will then talk about optoelectronic devices based on monolayer WSe$_2$, including p-n junctions as light emitting diodes and hybrid monolayer semiconductor/photonic crystal cavity devices. We will conclude the talk with a discussion of the optoelectronic properties of MoSe$_2$-WSe$_2$ heterostructures.

3:00pm **2D+EM+MI+MN+NS+SS+TF-ThA3 Theory of Graphene Transport Barriers in the Specular Limit**, ***Daniel Gunlycke***, *C.T. White*, Naval Research Laboratory

Offering room-temperature ballistic electron transport well over one micron, while being atomically thin and planar, graphene is undeniably a promising material for future nanoelectronic devices. Presently, however, switchable devices have normally low on-off ratios, a reflection of the challenge of selectively blocking electron and hole carriers from propagating across the graphene surface. This has stimulated a lot of research on different methods for making graphene nanoribbons that exhibit suitable band gaps. An alternative way to obtain a controllable gap takes advantage of resonant tunneling across a pair of transport barriers. For the latter approach, the key is to find a barrier that is fairly reflective but not so much as to effectively cut off all transport across it.

In this presentation, we present a model for straight transport barriers in graphene in the specular limit. Using the Lippmann-Schwinger equation, we obtain the wave function, from which we derive the reflection and transmission probabilities, as well as the local density of itinerant states. This local density of states exhibits fluctuations arising from quantum interference between incoming and outgoing matter waves that allow the transport properties of a barrier to be estimated without explicitly probing the current across the barrier. Our model is tested against exact multi-channel, tight-binding quantum transport calculations for graphene with weak local potentials, local strain, local adsorption, and a locally defective structure. As the model parameters are related to observable quantities, they could be obtained from theory and/or experiment, allowing the model to be adopted even when the precise details of the barrier are unknown.

3:20pm **2D+EM+MI+MN+NS+SS+TF-ThA4 Tip-induced Potential Confinement on Graphene in Scanning Tunneling Microscopy Measurement**, ***Yue Zhao***, *J. Chae, J.E. Wyrick,* NIST/CNST, *F.D. Natterer,* Ecole Polytechnique Fédérale de Lausanne (EPFL), France, *S. Jung,* Korea Research Institute of Standards and Science (KRISS), *A.F. Young, C.R. Dean, L. Wang, Y. Gao,* Columbia University, *J.N. Rodrigues,* Graphene Research Centre, NUS, Singapore, *K. Watanabe, T. Taniguchi,* National Institute for Materials Science (NIMS), Japan, *S. Adam,* Graphene Research Centre, NUS, Singapore, *J.C. Hone, K. Shepard, P. Kim,* Columbia University, *N.B. Zhitenev, J.A. Stroscio*, NIST/CNST

Graphene is a two-dimensional-electron-gas(2DEG) system with exposed surface, which allows scanning tunneling microscopy(STM) to investigate the electron-electron interaction associated with the Dirac nature on a local scale, with a variety of tuning knobs, such as carrier density, spatially varying disorder potential, and applied magnetic field. However, the electron-electron interaction in graphene is sensitive to the disorder details. Moreover, tip induced potential confinement can significantly complicate the interpretation of STM experiment. Utilizing a high mobility graphene device with low residual disorder, we can minimize the effect of local potential fluctuation, to better understand the role tip-induced potential plays in the measurement. We observed the emergency of large spectra gaps, modification to graphene Landau levels (LLs), and quantum dots with changing size due to the spatially inhomogeneous tip gating.

4:00pm **2D+EM+MI+MN+NS+SS+TF-ThA6 Topological Phase Transitions and Spin-orbit Density Waves**, ***Hugo Dil***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

In recent years systems where the spin-orbit interaction (SOI) is not just a perturbation but the main energy scale have received increasing attention. In combination with a broken inversion symmetry in the crystal structure or at interfaces, SOI will lift the spin degeneracy and induce a complex Fermi surfaces and spin textures with spin momentum locking [1,2]. Furthermore, the SOI can drive the system through a phase transition to a so-called topological insulator. Being an insulator in the bulk these systems are characterized by spin-polarized, topologically protected interface states.

After a short introduction to the role of topology in the band structure of solids I will give an overview of our main spin- and angle-resolved photoemission (SARPES) results on a variety of non-interacting topological insulators [3]. One of the questions is how the spin texture evolves around a topological transition. We explored the occurrence of spin polarized states around a SOI driven topological transition [4] and around a structure driven topological transition [5]. In both cases we observe spin-polarized precursor states, which indicate that although the topological transition is sharp, the response of the system is more gradual.

From a fundamental point of view the truly interesting aspect of non-trivial spin textures lies in their combination with other interactions. This can result in a variety of phenomena, cumulating in the creation of the elusive Majorana Fermion. An example of a combination of interactions is our recent verification with SARPES of SmB$_6$ as a topological Kondo insulator [6]. In topologically trivial systems, interactions can lead to the formation of a so-called spin-orbit density wave. I will show how the combination of a large spin-splitting and Fermi nesting leads to the formation of such a state and can explain the anisotropic behavior of Pb nanowires [7]. Furthermore, I will present our recent SARPES results for transition metal oxide surfaces where a subtle interplay between ferroelectricity and magnetic order results in the formation of a single spin-polarized energy contour. The occurrence of superconductivity in such systems could render it a 2D Majorana platform.

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[7] C. Tegenkamp et al. Phys. Rev. Lett. 109, 266401 (2012)

4:40pm **2D+EM+MI+MN+NS+SS+TF-ThA8 The Symmetry Dependent Band Structure of MoS$_2$**, ***Duy Le***, University of Central Florida, *T. Komesu,* University of Nebraska-Lincoln, *Q. Ma,* University of California, Riverside, *E.F. Schwier, H. Iwasawa,* Hiroshima University, Japan, *M. Shimada,* Higashi-Hiroshima, Japan, *T.S. Rahman,* University of Central Florida, *L. Bartles,* University of California, Riverside, *P.A. Dowben*, University of Nebraska-Lincoln

We will present results of density functional theory (DFT) based calculations of symmetry dependent band structures of single crystal MoS$_2$(0001) surface together with symmetry-polarized angle resolved photoemission spectroscopy (ARPES) derived experimental band structure. The good agreement of the DFT band structure with the experimentally derived bands with even and odd symmetries, attests to the reliability of the results. We performed ARPES at the Hiroshima Synchrotron, determining the MoS$_2$ band structure separately for both p-, and s-, polarized to distinguish even and odd symmetry, and the experimentally determined dispersion, in accordance with expectations and experimental confirmation of C$_{3v}$ symmetry, argues in favor of an experimental band structure obtained from single domains. The comparison of theory and experiment provides strong indications that the bands at the top of the valence band are dominated by Mo 4d states. These states and indeed placement of the valence band can be perturbed by adsorbates. Indeed, we find that, under the effect of Na adsorption, the changing placement of the valence band structure of MoS$_2$ clearly indicate the Na atoms donate electrons to MoS$_2$ and that the Fermi energy level shifts as much as 0.5 eV with respect to the top of MoS$_2$'s valance band. Surprisingly, Na adsorption does not perturb the MoS$_2$ band dispersion significantly. We will discuss these results in the light of those obtained for single layer MoS$_2$ for insights and clarity.

5:00pm **2D+EM+MI+MN+NS+SS+TF-ThA9 $CuIn_{III}P_2S_6$ - Room Temperature Layered Ferroelectric**, ***Alex Belianinov***, *P. Maksymovych,* Oak Ridge National Laboratory*, A. Dziaugys,* Vilnius University, Lithuania*, Q. He,* Oak Ridge National Laboratory*, E. Eliseev,* National Academy of Sciences of Ukraine*, A,. Borisevich,* Oak Ridge National Laboratory*, A. Morozovska,* NAS of Ukraine*, J. Banys,* Vilnius University, Lithuania*, Y. Vysochanskii,* Uzhgorod University, Ukraine*, S.V. Kalinin*, Oak Ridge National Laboratory

We have utilized ambient and Ultra High Vacuum Scanning Probe Microscopy tools to explore ferroelectric properties in cleaved 2D flakes of copper indium thiophosphate, $CuIn_{III}P_2S_6$ (CITP), and report on size effect and presently achievable limits of ferroelectric phase stability. CITP is an unusual example of a layered, anti-collinear, uncompensated, two-sublattice ferroelectric system. These are the only materials known to display “2-D” ferroelectric semiconductor behavior in a van-der-Waals crystal. The material exhibits a first-order phase transition of order–disorder type from the paraelectric to the ferrielectric phase at $T_c = 315$ K. Our observations suggest the presence of stable ferroelectric polarization as evidenced by domain structures, rewritable polarization, and hysteresis loops. These observations suggest that flakes above 100 nm have bulk-like polarization and domain structures, whereas below 50 nm polarization disappears. Furthermore, the materials have measurable ionic mobility, as evidenced both by macroscopic measurements and by formation of surface damage above tip bias of 4 V, likely due to copper reduction. We ascribe this behavior to well-known instability of polarization due to depolarization field, along with internal screening by mobile Cu ions, as suggested by their high ionic mobility.

Acknowledgement:

Research for (AB, PM, QH, AB, SVK) was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

5:20pm **2D+EM+MI+MN+NS+SS+TF-ThA10 Doping Efficiency and Mechanisms of Single and Randomly Stacked Bilayer Graphene by Iodine Adsorption**, ***Hokwon Kim***, *A. Tyurnina,* Univ. Grenoble Alpes/ CEA, LETI, France*, J.-F. Guillet, J.-P. Simonato, J. Dijon,* Univ. Grenoble Alpes/ CEA, LITEN, France*, D. Rouchon, D. Mariolle, N. Chevalier, O.J. Renault*, Univ. Grenoble Alpes/ CEA, LETI, France

The precise control of graphene’s conductivity and work function is crucial in developing practical applications of graphene based electronics. In order to enhance the conductivity of graphene, we employed a simple doping method where graphene films produced by chemical vapor deposition and transferred onto SiO_2, Al_2O_3, and WO_3 substrates are p-doped with iodine vapor through physisorption at temperature of ~ 100 °C [1-3]. The work function values and iodine to carbon ratios of the one-layer (1L) and two-layer (2L) folded regions were analyzed by high spatial- and energy resolution X-ray photoelectron emission microscopy (XPEEM) on a *NanoESCA* instrument. After the iodine doping, the work function values were significantly increased up to ~0.4 eV and ~0.5 eV, respectively, for 1L and 2L graphene on SiO_2/Si. This higher degree of doping by iodine was corroborated by I $3d_{5/2}$ core level imaging of the same area where the 2L graphene exhibited significantly larger concentration of iodine (2 at. % versus 1 at. %) likely due to the intercalation of iodine at the inter-layer space.

The main iodine species identified by high resolution core level X-ray photoemission spectroscopy and Raman spectroscopy were I_3^- and I_5^- poly-iodide anionic complexes with slightly higher concentration of I_5^- in 2L than 1L graphene possibly due to different doping mechanisms. Temperature dependent ultra-high-vacuum, in-situ annealing of the doped films has demonstrated that most of iodine is removed above 300 °C for the both 1L and 2L regions, although a significant removal of iodine is observed for 2L graphene at temperature as low as 100 °C. Surprisingly, after the complete removal of iodine by annealing, the work function value did not return to the original one before the doping treatment and remained at a much higher value. This can be ascribed to the residual hydrocarbon contaminations interacting with the atomic defects within the graphene layer that lead to unintentional n-type doping in our samples[4].

Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

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5:40pm **2D+EM+MI+MN+NS+SS+TF-ThA11 Use of XPS for Device Characterization**, *P. Aydogan, E.O. Polat, C. Kocabas,* ***Sefik Suzer***, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is utilized to investigate a number of devices made of graphene. The main objective of the technique is to trace chemical and location specific surface potential variations as shifts of the XPS peak positions under operating conditions. Devices consisting of graphene; (i) acting as a simple resistive element between two gold electrodes, (ii) a semiconducting sheet controlled by a back-gate, and (iii) between the source and the drain metal electrodes in a full transistor geometry, have been analyzed by recording the Au4f of the metal electrodes, the C1s of the graphene layer, and the O1s (or N1s) peaks of the silicon oxide (or nitride) of the substrate. The advantage of this technique is its ability to assess element specific surface electrical potentials of devices under operation based on the deviations of the core level peak positions in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to various stimuli gives unprecedented information about the chemical nature as well as the location of structural and/or other types of defects as a result of doping, oxidation, reduction, etc.

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