Final Report for Period: 09/2009 - 08/2010 **Submitted on:** 08/04/2010

Principal Investigator: Plummer, E. Ward . **Award ID:** 0451163

Organization: U of Tennessee Knoxville

Submitted By:

Plummer, E. Ward - Principal Investigator

Title:

Enhanced Electron-Phonon Coupling at Metal Surfaces

Project Participants

Senior Personnel

Name: Plummer, E. Ward

Worked for more than 160 Hours: Yes

Contribution to Project:

Plummer is the intellectual leader of the program as well as the mentor of the students and postdocs and the cheer leader.

Name: Weitering, Hanno

Worked for more than 160 Hours: No

Contribution to Project:

Professor Weitering agreed to monitor the UTK NSF grant during the last year when Professor Plummer moved to LSU.

Post-doc

Name: Liu, Hong

Worked for more than 160 Hours: Yes

Contribution to Project:

Hong Liu worked on angle-resolved photoemission as a tool to investigate electron-phonon coupling at surfaces of metals. She was involved in most of the early experiments conducted by TeYu Chien and has been the person responsible for the inhouse photoemission system. She is now staying home to raise her two children.

Name: Nascimento, Von Braun

Worked for more than 160 Hours: Yes

Contribution to Project:

Von Braun is the person primarily responsible for the structural analysis using quantitative low-energy electron diffraction. Von Braun is also responsible for the inelastic electron scattering experiments. Von now has an appointment as an Assistant Professor at LSU and is not paid by this grant.

Name: He, Xiaobo

Worked for more than 160 Hours: Yes

Contribution to Project:

Recently Xiaobo has been working on the new STM and using it to study the surfaces of transition metal compounds

Graduate Student

Name: Torija, Maria

Worked for more than 160 Hours: Yes

Contribution to Project:

Maria was a graduate student at UT in the transition period from my previous NSF grant DMR

0105232 and this grant. Here work was on magnitism in arrays of nanodots in collaboration with Jian Shen at ORNL. Maria accepted a postdoc position at the University of Minnesota and now works in the 'Characterization Facility and the nanofabrication center at Univ. of Minnesota.

Name: Moore, Rob

Worked for more than 160 Hours: Yes

Contribution to Project:

Rob Moore did his thesis on electron-electron and electron-phonon coupling in correlated electron systems. The work presented as a highlight was his thesis work. He left UTK to become a postdoc at Stanford with ZX Shin and now is a staff member at SLAC

Name: Chien, TeYu

Worked for more than 160 Hours: Yes

Contribution to Project:

TeYu Chien's thesis was on the experimentally determined electron-phonon coupling at the surface of Be. Most of his work is conducted at synchrotron radiation facilities around the world. His work has been attached as a highlight. He is now working as a postdoc at ANL.

Name: Fuchigami, Kenji

Worked for more than 160 Hours: Yes

Contribution to Project:

Kenji thesis was on dimensional confinement of correlated electron materials, jointly supervised by Plummer and Jian Shen at ORNL. His thesis work showed that you could control the functionality at the surface of La(1-x)Ca(x)MnO(3) by controlling the oxygen concentration. Kenji was and is a researcher at IHI Corporation in Yokohama, Japan. He was sent to the US to complete his Ph.D

Name: Hu, Biao

Worked for more than 160 Hours: Yes

Contribution to Project:

Biao is working jointly with Plummer and Rongying Jin, who is now an Associated Professor at LSU. His thesis will involve the growth and characterization (bulk and surface) of layered transition metal oxides.

Name: Li, Guorong

Worked for more than 160 Hours: Yes

Contribution to Project:

Guorong, is working on the STM/STS characterization of the surface of Transition Metal Compounds. The focus of his thesis will be the geometric and electronic structure of the FeAs based superconductors.

Undergraduate Student

Name: Wiggins, Andr?

Worked for more than 160 Hours: Yes

Contribution to Project:

Andr? is a freshman Chancellor scholar working in our laboratory developing new LEED codes.

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Oak Ridge National Laboratory

Almost all of our correlated electron samples were grown by Rongying Jin when she was at ORNL. The work on dimensional confinement in correlated electron materials is done in collaboration with Jian Shen at ORNL. Now that Rongying Jin is a faculty member at LSU she still works closely with the group at ORNL

We also have a strong partnership with Center for Nanophase Sciences at ORNL.

University of Aarhus

We have worked with Professor Hofmann on the electron phonon coupling at the surfaces of metals using the electron storage ring at Aarhus. TeYu Chien has visted Aarhus several times and Hofmann's students have worked with us at ALS.

Institute of Physics in Beijing

We have had a longstanding collaboration with the Institute of Physics in Beijing. The phonon dispersion data in high-Tc materials reported in 2007 was a collaboration with Jiandon Guo. The theory presented in the recently published Science paper is a result of a long-term collaboration with Zhong Fang. We now have a Dual-Degree program formalized with IOP.

Donostia International Physics Center

We are collaborating with the theory group in San Sabastian on the theory of electron phonon coupling at metal surfaces.

Other Collaborators or Contacts

I have an informal collaboration with Steven Louie at Berkeley on electron phonon coupling.

I am also working with Vidya Madhavan at Boston College on the surface of the new FeAs high-temperature superconductors.

We have worked closely with Professor John Rundgren and the Royal Institute in Stockholm, Sweden to do LEED calculations.

In the recent years we have collaborated with Professor Shuheng Pan from the University of Houston on low temperature STM measurements.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

The Born-Oppenheimer approximation (BOA) decouples electronic from nuclear motion, providing a focal point for most quantum mechanics textbooks. However, a multitude of important chemical, physical and biological phenomena are driven by violations of this approximation. Vibronic interactions are a necessary ingredient in any process that

makes or breaks a covalent bond, for example, conventional catalysis or enzymatically delivered biological reactions. Metastable phenomena associated with defects and dopants in semiconductors, oxides, and glasses entail violation of the BOA. Charge exchange in inorganic polymers, organic slats and biological systems involves charge-induced distortions of the local structure. A classic example is conventional superconductivity, which is driven by the electron-lattice interaction. High-resolution angle-resolved photoemission experiments are yielding new insight into the microscopic origin of electron-phonon coupling (EPC) in anisotropic two-dimensional systems.
Our recent surface phonon measurement on the surface of a high-Tc material clearly indicates an important momentum dependent EPC in these materials.

In the last few years we have shifted our research focus from solely looking at electron phonon coupling to examining the structure/functionality relationship at the surface of complex transition metal compounds. The investigation on electron phonon coupling has allowed us to move to systems where there is coupling between the lattice, the electrons and the spin.

Findings: (See PDF version submitted by PI at the end of the report)

It is becoming increasingly clear that the exotic properties displayed by correlated electronic materials such as high- Tc superconductivity in cuprates, ?colossal? magnetoresistance in manganites, and heavy-fermion compounds are intimately related to the coexistence of competing nearly degenerate states which couple simultaneously active degrees of freedom: charge, lattice, orbital, and spin states. Breaking the symmetry by creating a surface creates an environment for discovery of new Emergent Phenomena and is extremely important to the utilization of artificially layered transition-metal-oxide films for technological applications. We have determined the surface phase diagram of Ca2-xSrxRuO4, revealing quite startling new phases. For $x \sim 0.1$ we see for the first time an inherent purely electronic Mott metal-to-insulator phase with a signature of electron phonon coupling. For $0.2 < x < 0.5$ a new surface phase is found with quite unique properties. The new phases have been explained knowing the change in the structure induced by the creation of the surface and can be transferred to other correlated electron systems. In the last year we have used our capabilities to probe the surface to look at the parent compound BaFe(2)As(2) on the new family of high temperature superconductors as well as the magnetism at the surface of La(2-2x)Sr(1+2x)Mn(2)O(7).

Training and Development:

Six graduate students have been involved in this research; Maria Torija, Rob Moore, TeYu Chien, K. Fuchigami, G. Li and B. Hu. Dane Gillaspie received partial support during the first year. They have learned high vacuum technology, modern computational schemes, and the use of modern surface techniques. Moore and Chien had an opportunity to travel to synchrotron user facilites and to collaborate with scientists abroad. Moore, Torija, Chien, and Fuchigami graduated and have moved on to scientific positions.

We have also had three high school students from Farragut High School working in our laboratory (see attachment). Last year we had a freshman, Andre Wiggings, working with us at LSU in the Chancellors's Future Leaders in Research program. He has returned this year.

Outreach Activities:

The PI is fundamentally an educator so integrating research and education is one of the main objectives, i.e., training the scientific work force needed for research and development in advanced materials. Historically, the students and postdocs trained in this group have found employment in the private sector, in government laboratories, and in academia, with about equal distribution in the three areas. The educational efforts of the PI have expanded in the last several years, aimed at educating the community on the need for advanced materials in the 21st century. These have included a showcase lecture preceding a UTK football game on nanoscience and nanotechonogy and lectures to local business organizations and to high schools in the Knoxville area, stressing the challenges and opportunities in advanced materials. I hosted three Farragut High School students in my laboratory,under the University of Tennessee-Knoxville Pre-CollegiateResearch Scholars Program. We have a LSU freshmen in our laboratory under the Chancellor's scholars program at LSU.

Journal Publications

V. B. Nascimento, R. G. Moore, J. Rundgren, Jiandi Zhang, Lei Cai, R. Jin, D. G. Mandrus, and E.W. Plummer, "A procedure for LEED I-V structural analysis of metal oxide surfaces: Ca1.5Sr0.5RuO4(001)", Phys. Rev, B75, 035408 (2007, p. 035408, vol. 75, (2007). Published,

Jiandi Zhang, Ismail, R. G. Moore, S.-C.. Wang, H. Ding, R. Jin, D.G. Mandrus, and E.W. Plummer, "Dopant-Induced Nanoscale Electronic Inhomogeneity in Ca2-xSrxRuO4", Phys. Rev. Lett., p. 066401, vol. 96, (2006). Published,

M.A. Torija, A.P. Li, C. Guan, E.W. Plummer, and J. Shen, ""Live? Surface Ferromagnetism and Ferromagnetic to Spin-glass Phase Transition in Fe nanodots/Cu Multilayers on Cu(111)", Phys. Rev. Lett., p. 257203, vol. 95, (2005). Published,

J. Zhou, Junren Shi, T. Yoshida, T. Cuk, W. L. Yang, V. Brouet, J. Nakamura, N. Mannella, S. Koviya, Y. Ando, F. Zhou, --- A. Fugimori, Zhenyu Zhang, E. W. Plummer, R. B. Laughlin, Z. Hussain, and Z.-X. Shen, "Multiple Bosonic Mode Coupling in Electron Self-Energy of (La2-xSrx)CuO4", Phys. Rev. Letter, p. 117001, vol. 95, (2005). Published,

R. G. Moore, Jiandi Zhang, V. B. Nascimento, R. Jin, Jiandong Guo, G.T. Wang, Z. Fang, D. Mandrus, and E. W. Plummer, "A Surface-Tailored Purely Electronic Mott Insulator-to-Metal Transition", Science, p. 615, vol. 318, (2007). Published,

R. G. Moore, V. B. Nascimento, Jiandi Zhang, R. Jin, D. Mandrus, and E.W. Plummer, "The Manifestations of Broken Symmetry: Surface Phases of Ca2-xSrxRuO4", Phys. Rev. Lett., p. 066102, vol. 100, (2008). Published,

D. Gillaspie, X. Ma, H.-Y. Zhai, T. Z. Ward, H. M. Christen, E. W. Plummer, and J. Shen, "Influence of Different Substrates on Phase Separation in La1-x-yPryCaxMnO3 Thin Films", J. Appl. Phys., p. 08S901, vol. 99, (2006). Published,

Hong-Ying Zhai, J. X. Ma, D. T. Gillaspie, X. G. Zhang, T. Z. Ward, E. W. Plummer, and J. Shen, "Giant Discrete Steps in Metal-Insulator Transition in Perovskite Manganite Wires", Phys. Rev. Letter, p. , vol. 97, (2006). Published,

R. G. Moore, M.D. Lumsden, M. B. Stone, J. Zhang, Y. Chen,R. Jin, D. G. Mandrus, and E. W. Plummer, "Phonon Softening and Anomalous Mode Near the xc = 0.5 Quantum Critical Point in Ca2-xSrxRuO4", Physical Review B, p. 1723, vol. 79, (2009). Published,

K. Fuchigami, Z. Gai, T. Z. Ward, L. F. Yin, P.C. Snijders, E. W. Plummer, and J. Shen, "Tunable Metalicity at La5/8Ca3/8MnO3(001) Surface by Oxygen Overlayer", Phys. Rev Letters, p. 6610, vol. 102, (2009). Published,

V.B. Nascimento, Ang Li, Dilushan R. Jayasundara, Yi Xuan, Jared O??????Neal, Shuheng, "Surface Geometric and Electronic Structure of BaFe2 As2 (001)", Physical Rev. Letters, p. 07614, vol. 103, (2009). Published,

Te-Yu Chien, Emile Rienks, Maria Fuglsang Jensen, Philip Hofmann, and E. W. Plummer, "Anisotropic Mass Enhancement for the gamma/bar Surface State of Be(0001)", Phys. Rev B, p. 241416, vol. 80, (2009). Published,

V. B. Nascimento, R. G. Moore, D. Mazur, J. W. Freeland, R. Saniz, H. Liu, K. E. Gray, R. A. Rosenbergy, H. Zheng, J. F. Mitchell, A. J. Freeman, J. Rundgren, and E. W. Plummer, "Surface-Stabilized Antiferromagnetism of a Layered Ferromagnetic Manganite", Phys. Rev. letters, p. 227201, vol. 103, (2009). Published, Biao Hu, Gregory T. McCandless, Melissa Menard, V. B. Nascimento, Julia Y. Chan, E. W. Plummer, and R. Jin, "Surface-Stabilized Non-Ferromagnetic Ordering of a Layered Ferromagnetic Manganite", Phys. Rev B, p. 155121, vol. 81, (2010). Published,

T. Z. Ward, S. H. Liang, K. Fuchigami, L. F. Yin, E. Dagotto, E. W. Plummer, and J. Shen, "Reemergent Metal-Insulator Transitions in Manganites Exposed with Spatial Confinement", Phys Rev. Letters, p. 247204, vol. 100, (2008). Published,

Books or Other One-time Publications

Web/Internet Site

URL(s):

http://www.phys.lsu.edu/newwebsite/people/plummer.html

Description:

Other Specific Products

Contributions

Contributions within Discipline:

This work on electron phonon coupling can and will impact many areas such as chemistry and biology. We have made significiant advances in the understanding of the anisotropic nature of the coupling of electrons to vibrational modes in two dimensional systems.

We have lead the way in the last couple years in the characterization of the surface geometric and electronic phases and have pioneered the understanding of the structure/functionality relationship at the surface of complex transition metal compounds

Contributions to Other Disciplines:

My research is basically associated with the properties of surfaces, but this work on complexity at surfaces will impact all aspects of nanoscience and nanotechnology. The surface is the simplest interface and it is now clear that interfaces of complex materials is one path forward in advanced devices.

Contributions to Human Resource Development:

Six graduate students have been involved in this research program, and four have graduated. Only one of them is still in a postdoc position. One works as a staff scientists at SLAC, one works in an industrial laboratory, and the third is working in a characterization laboratory. The remaining two will obtain their Ph.D in a year. One of the graduate students is female.

We have been actively engaged in bringing undergradates into our laboratory to experience first hand discovery based research and at present there is one Chancellor's fellow in the laboratory.

The three high school students who worked in the laboratory are now in college (in the sciences) at Duke, Vanderbilt, and Rice.

Contributions to Resources for Research and Education:

We are developing a new procedure for the analysis of Low energy electron diffraction from surfaces. These codes will be distributed to the scientific community. We are also working with a group from NCS to develop codes for LEEM experiments.

Contributions Beyond Science and Engineering:

Our work on the functionality of complex transitional oxides in an environment of reduced dimensionality (2D or 1D) has created interest in the electronic device community.

Conference Proceedings

Categories for which nothing is reported:

Any Book
Any Product
Any Conference

Results from NSF Support: “Enhanced Electron-Phonon Coupling at Metal Surfaces,” funded jointly by NSF DMR-0451163 and DOE-DMS&E (8/1/05–7/31/09) at $480K.

Publications: There were 14 papers in the last five years, 12 published or accepted and are two submitted. These include 7 *Physical Review Letters* and one *Science* paper. Three papers were about electron-phonon coupling (EPC), two were about magnetism , three were about surface or surface phase transitions, nine were about transition-metal oxides (TMOs), and one PRL on the new FeAs superconductors. Below are a few recent highlights of the research resulting from this NSF funding.

Development of Human Resources in Science and Engineering: The research funded by NSF over the last five years has fully or partially supported the Ph.D. thesis work of (1) Maria Torija (magnetism), now on the staff at University of Minnesota; (2) Dane Gillaspie (TMOs), postdoc at NREL; (3) Rob Moore (TMOs), postdoc at Stanford; (4) TeYu Chien (EPC) now a postdoc at ANL, (5) Kenji Fuchigami (TMO surfaces), now back at IHI Corporation in Japan; (6) Biao Hu, working of layered TMOs, and Guorong Li working on the new FeAs superconductors. There were three Farragut High School Students working in the laboratory in 2007-2008.

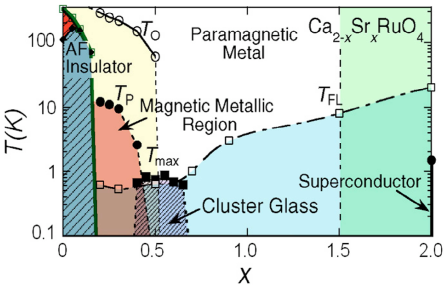

Fig. 1. *Rich phase diagram for* $\mathrm{Ca}_{2-x}\mathrm{Sr}_x\mathrm{RuO}_4$ *[1].* T_0 *and* T_P *are the structural transition temperature and the peak temperature in the magnetic susceptibility. A magnetic cluster glass forms below* T_{max}*, and heavy mass Fermi-liquid behavior is observed below* T_{FL} *(*T^2*dependence of specific heat).*

Selected Research Highlights:

1. Structure and Dynamics of the Layered Perovskite $\mathrm{Ca}_{2-x}\mathrm{Sr}_x\mathrm{RuO}_4$.

Nakatsuji and coworkers [1] have shown that the phase diagram for this material is very rich, as can be seen in **Fig. 1**. The pure Ca samples are a Mott insulator with antiferromagnetic ordering, and the pure Sr compound is a *p*-wave superconductor [2]. There is a first-order metal-insulator transition, second-order structural and magnetic transitions, and a signature of a *quantum critical point* (QCP) at $x_c \sim 0.5$. This compound offers an ideal platform for a study of the manifestations of broken symmetry on the functionality of a layered TMO.

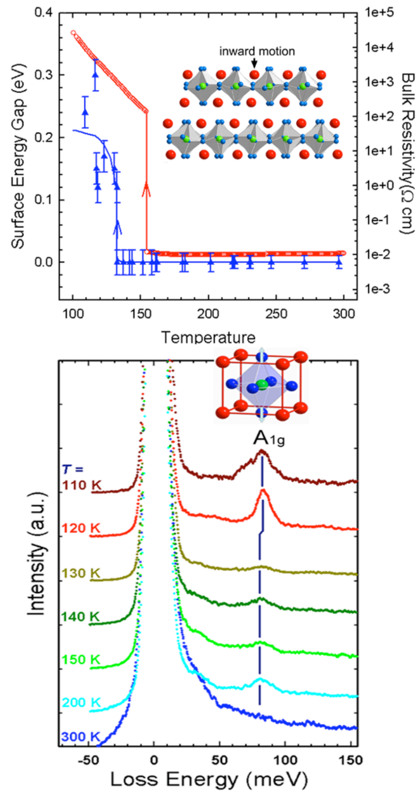

Fig. 2. *Top, comparison of resistivity measurements (red) and STS gap (blue) as a function of T [3]. Insert is marble model of surface structure. Bottom, electron loss spectra as a function of T [3, 4].*

2. Surface-Tailored, Purely Electronic Mott Metal-to-Insulator Transition (MIT):

Rob Moore’s thesis. A Mott transition, which is a MIT driven by electron-electron interactions, is usually accompanied in bulk by structural phase transitions. In the layered perovskite $\mathrm{Ca}_{1.9}\mathrm{Sr}_{0.1}\mathrm{RuO}_4$, such first-order Mott MIT occurs in the bulk at a temperature of T_c = 154 K on cooling. In contrast, at the surface, an unusual, inherent Mott MIT is observed at $T_{c,s}$ = 130 K, also on cooling but without a simultaneous lattice distortion. The broken translational symmetry at the surface causes a compressional stress that results in a 150% increase in the buckling of the Ca/Sr-O surface plane compared with the bulk (see insert top of **Fig. 2**). The Ca/Sr ions are pulled toward the bulk, which stabilizes a phase more amenable to a Mott-insulator ground state than does the bulk structure ($>T_c$) and also energetically prohibits the structural transition that accompanies the bulk MIT [3].

Figure 2 (top) shows a comparison of the bulk resistivity (red) and the surface gap seen with scanning tunneling spectroscopy (STS) [3] upon cooling the same sample. The bulk Mott MIT is accompanied by a structural distortion, but the surface MIT, which occurs at ~25 K lower, is a purely electronic transition, i.e., an *inherent* Mott MIT. The keys to this observation were (1) our ability to synthesize samples; (2) surface structural measurements using quantitative low-energy electron diffraction (LEED) *I-V* (Intensity-Voltage) [5] (insert at top of **Fig. 2**); (3) measurements of several spectroscopic features such as the phonon mode energy, width and intensity, Drude tail, and STS gap to determine the surface transition temperature [3, 4]; and (4) the close coupling with theory to explain why the observed surface structure stabilizes the surface against the bulk distortion (collaboration with Zhong Fang, IOP, China).

The bottom panel of **Fig. 2** shows the electron loss spectra from this sample as a function of temperature. The asymmetric tail on the elastic peak (zero energy) is the Drude tail due to electron-hole pair creations in the metallic state, and the peak at ~80 meV is from the apical oxygen vibration at the surface (see insert). The dramatic change in intensity and position of this mode with temperature indicates strong electron-phonon coupling associated with the MIT.

3. The Surface Phases of $Ca_{2-x}Sr_xRuO_4$. Determination of the structure at the surface is an essential first step in understanding the physical and chemical properties. We, in collaboration with John Rundgren (Sweden), have recently developed a new theoretical approach for the surface structure determination of complex TMOs using LEED *I-V* [5]. LEED *I-V* has been utilized to map out the surface phase diagram of $Ca_{2-x}Sr_xRuO_4$ [6]. For the pure Sr case ($x = 2$), the surface is reconstructed, driven by the surface stress freezing in a soft phonon mode in the bulk [7]. The surface analog of the *I4/mmm* bulk symmetry, which exists for $1.5 < x < 2$, never exists at the surface due to a $\sqrt{2}x\sqrt{2}$ reconstruction. For $x < 0.5$, the downward movement of the Ca/Sr plane is what stabilizes the surface against the bulk tilt distortion (see insert top of **Fig. 2**) which accompanies the Mott MIT in the bulk, creating the situation described above of an *inherently electronic Mott MIT at the surface* [3].

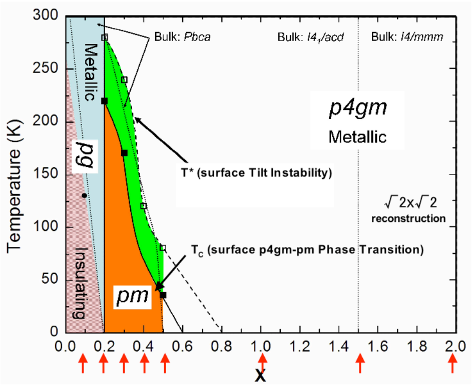

***Fig. 3**. Surface phase diagram for $Ca_{2-x}Sr_xRuO_4$ [6]. The red arrows indicate the different concentrations investigated.*

The surface phase diagram generated from our LEED *I-V* analysis is shown in **Fig. 3**. In general, we find that the *broken symmetry* at the surface enhances the structural instability against the RuO_6 rotation, while it diminishes the instability against the RuO_6 tilt. This leads to some interesting and unique surface properties, shown in **Fig. 3**. The dashed line marked T^* is the temperature where a tilt instability at the surface is revealed by weak diffuse LEED reflections. T_c is the line marking the *p4gm to pm* structural phase boundary. The two dotted lines mark the bulk structural phase transitions [1]. There are clear signs in our data that the bulk second-order phase transition exhibits hysteresis at the surface, a signature of some first-order character ($x = 0.3$). We have speculated from these data that the *broken symmetry* at the surface will most likely displace or even destroy the quantum critical point at $x_c = 0.5$.

4. Phonon Softening and Anomalous Mode Near the Quantum Critical Point $x = 0.5$. One of the attractive features of this type of research program is that the students become actively involved in bulk measurements such as inelastic neutron scattering. This is in many cases driven by the desire to understand the surface phase and the lack of appropriate bulk data. The surface phase diagram shown in **Fig. 3** exhibited such strange behavior near the QCP at $x_c = 0.5$ that it seemed imperative to determine the nature of the bulk phase transition for the high-temperature tetragonal (HTT) structure to the low-temperature orthorhombic (LTO). Given the observation that the surface reconstruction for $1.5 < x < 2$ is caused by a soft Σ_3 phonon (in-plane rotation of the octahedra), we assumed that the HTT to LTO transition would be involved with a Σ_4 (tilt) phonon going soft, the same as what was observed for the parent compound of the high-temperature superconductor, $La_{2-x}Sr_xCuO_4$ [8]. Inelastic neutron scattering was used to measure the temperature dependence of the phonon dispersion for two samples ($x = 0.4$ and $x = 0.6$). The results are shown in **Fig. 4**. The in-plane Σ_4 tilt mode softens significantly at the zone boundary in both samples as the temperature decreases, but for $x = 0.6$, the mode never softens below ~2 meV because there is not a structural transition in the bulk. For the $x = 0.4$ sample, the mode goes to zero at the zone boundary at the transition temperature for the HTT to LTO transition, as expected.

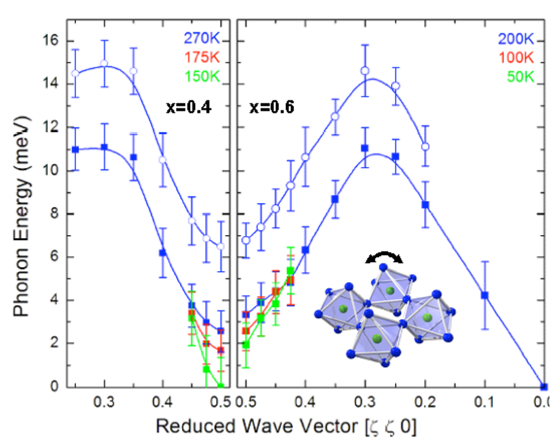

Fig. 4. *Dispersion of the Σ_4 (filled symbols) and anomalous (open) phonon modes for both x = 0.4 and x = 0.6. The Σ_4 mode shows typical soft mode behavior, and the anomalous mode mimics the Σ_4 dispersion. Lines are added as guides to the eye [9].*

Figure 4 shows an anomalous phonon mode in both samples that seems to track the Σ_4 mode but at higher energy, and even the x = 0.6 sample never softens below ~6 meV, even at temperatures below the HTT-LTO transition temperature [9]. This mode is attributed to the presence of intrinsic structural disorder within the HTT structure of the doped ruthenate. The unresolved question is does this intrinsic bulk structural disorder manifest itself at the surface?

5. Anisotropic Electron-Phonon Coupling (EPC) on the Be(0001) Surface: TeYu Chien's thesis. (Thesis work of Te-Yu Chien done in collaboration with P. Hofmann's group at Aarhus, Denmark). The first paper published in 2005 on EPF (PRL, **95**, 117001) has be cited ~60 times.

The quantity used for characterizing the EPC is the mass enhancement factor, λ, defined as $\lambda = m_{eff}/m_0 - 1$, which is the fractional increase in the effective mass relative to the bare-particle mass induced by the electron-phonon interaction. The value of λ of the bulk Be is only 0.24 [10]; while the reported values of λ range from 0.6 to 1.1 for different angle-resolved photoemission experiments [11]. One question arises: Why is there such a large spread in the published findings?

This experiment was performed at the ASTRID facility, Aarhus, Denmark. **Figure 5(a)** shows the Fermi energy mapping at a photon energy of 60 eV. Two surfaces states are easily seen—one is circular shaped centered at $\overline{\Gamma}$, and the other is ellipse shaped centered at $\overline{M}$. We focused on the isotropic surface state centered at $\overline{\Gamma}$ using a photon energy of 30 eV to maximize the signal. The red line in **Fig. 5(a)** shows one of the 16 measurement cuts in momentum space [12]. By fitting the momentum distribution curves (MDCs) with the Lorentzian function, the dispersion relation can be extracted. λ was determined in several ways. The first was to use the maximum entropy method, and the second was to use the slope of the real part of the self energy. The results from both procedures are plotted in **Fig. 5(b)** and compared to previously published values (blue circles). Obviously, λ has a local maximum around the $\overline{\Gamma}-\overline{M}$ and $\overline{\Gamma}-\overline{K}$ directions. The local minimum appears about 10 degrees away from the $\overline{\Gamma}-\overline{K}$ direction.

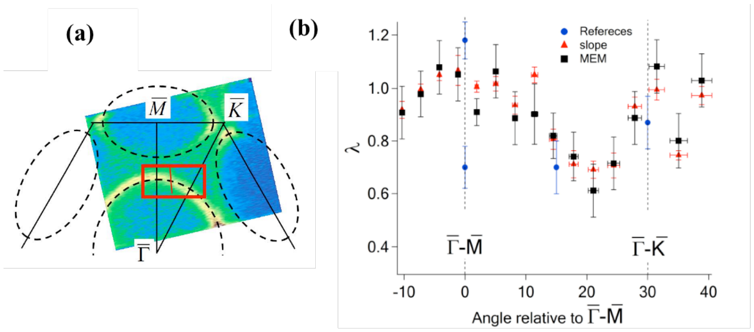

Fig. 5. *(a) The Fermi surface mapping and (b) the corresponding extracted values of the mass enhancement factors [12].*

The two different methods used here produce the same trend in the momentum dependence of the mass enhancement λ, confirming the anisotropic EPC scenario. Because the electronic surface is isotropic in k-space, the anisotropic EPC must be driven by the anisotropic phonon dispersion.

This work has resulted in a robust, dependable procedure for systematically extracting the mass enhancement factor from angle-resolved photoemission spectroscopy (ARPES) data. We can and will use this for new materials being investigated in this proposal. It is also straightforward to use this maximum entropy method to extract the value of ω_{log}, a qualitative measure of the average phonon energy involved in the EPC.

7. Surface-Stabilized Antiferromagnetism of a Layered Ferromagnetic Manganite. (Collaboration with J. F. Mitchell and J. W. Freeland at Argonne National Laboratory and A. J. Freeman's group at Northwestern).

The bulk phase of the colossal magnetoresistive [13] $La_{2-2x}Sr_{1+2x}Mn_2O_7$ manganites display a variety of both magnetic and electronic states [14]. In the range $0.3 < x < 0.4$, the low-temperature bulk phase exhibits metallic ferromagnetic (FM) properties. Characterization of the (001) surface magnetic properties for x from 0.36 to 0.4 reveals the presence of a non-FM phase in the top bilayer [15, 16]. Recently, electronic and magnetic characterization has been performed for in-situ cleaved (001) surfaces of the bilayered manganites by the use of x-ray resonant magnetic scattering (XRMS) [17, 18] and x-ray magnetic circular dichroism (XMCD) [19] techniques. The results indicate that the nonmagnetic surface layer is an inherent property of this material and not a result of surface contamination [15, 16].

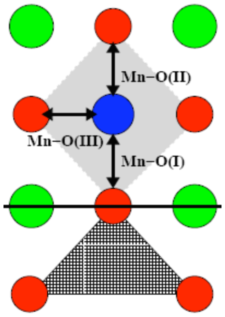

Fig. 6. *Top half of the first bilayer, showing the three distinct manganese-oxygen distances: (1) Mn-O(I), distance between manganese and oxygen in the center of the bilayer; (2) Mn-O(II), distance between manganese and top/bottom oxygen; and (3) Mn-O(III), distance between manganese and in-plane oxygen [20].*

We performed a LEED *I-V* analysis of the surface structure [20] and compared the findings with first-principles calculations by Freeman's group. The structural changes are much more subtle than those reported for $Ca_{2-x}Sr_xRuO_4$ because there is no rotation or tilt of the octahedra, but the change in functionality at the surface is dramatic. The results indicate no reconstruction but that the change in magnetic ordering at the surface is intimately coupled to the structure of the surface, a collapse of the c-axis lattice parameter in the outermost bilayer [20]. **Figure 6** shows that there are three different Mn-O distances of these La/Sr manganites. At the surface, the Mn-O(II) distance is reduced (c-axis collapse), while Mn-O(I) and Mn-O(III) remain basically at their bulk values. A Jahn-Teller distortion (Δ_{JT}) can be defined as the ratio of the averaged apical Mn-O distances [Mn-O(I) and Mn-O(II)] to the equatorial Mn-O distance [Mn-O(III)]. According to experimental results from the bulk structure [21, 22], Δ_{JT} ranges from ≈1.034 for $x = 0.30$ (FM) to ≈1.011 for $x = 0.50$ (antiferromagnetic). The change in magnetic order with increasing hole concentration (x) results from the depopulation of the $3z^2 - r^2$ orbitals and, consequently, a decrease in Δ_{JT} [23]. This weakens the ferromagnetic double exchange between the two layers in favor of the t_{2g} antiferromagnetic super-exchange, resulting in an A-type state with moments aligned ferromagnetically within the layer and antiparallel between the double layers. When a comparison of our surface data ($\Delta_{JT} = 1.00$) is made with the bulk, it can be inferred that the surface should exhibit antiferromagnetic order.

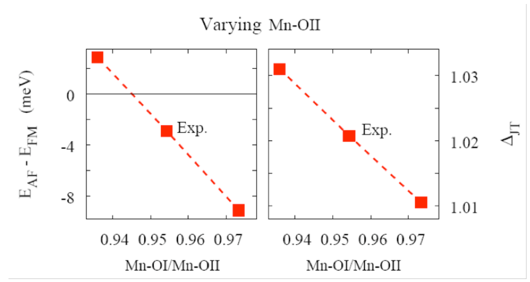

Fig. 7. *FLAPW results for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ [26]. The difference in energy between antiferromagnetic and FM configurations ($\Delta E = E_{AF} - E_{FM}$) is presented in the following situation: (left) the Mn-O(I)/Mn-O(II) ratio is varied by changing the Mn-O(II) distance. The associated Jahn-Teller distortion (Δ_{JT}) is also presented (right). The surface values for Mn-O(I)/Mn-O(II) and Δ_{JT}, respectively equal to 1.01 and 1.00, indicate an antiferromagnetic state as the most stable one.*

This speculation can be justified using theory. Results of theoretical calculations, performed within the full-potential linearized augmented plane-wave (FLAPW) [24] theoretical approach, are presented in **Fig. 7**. As can be seen, a comparison of the experimental values for surface Mn-O(I)/Mn-O(II) and Δ_{JT} with the theoretical predictions corroborates the existence of an antiferromagnetic state at the surface.

8. Surface Geometric and Electronic Structure of $BaFe_2As_2$: Beginning of Guorong Li's thesis. This work was done in collaboration with Shuheng Pan at the University of Houston. $BaFe_2As_2$, the parent compound of one of the newly discovered non-cuprate high-T_c superconductors, presents very interesting physical properties such as a structural transition occurring prior (140K) to the formation of a spin density wave (135K) with antiferromagnetic order (AFM) [25]. Scanning tunneling microscopy (STM) and quantitative Low Energy Electron Diffraction (LEED) have been utilized to explore the structural and electronic properties of a single crystal of $BaFe_2As_2$ cleaved in vacuum exposing a (001) surface (See **Figure 8**). LEED shows a clear (1 × 1) periodicity with an As-terminated surface structure slightly different from the bulk while STM images reveal a disordered Ba atoms on the surface [26]. However STM reveals a weak (√2x√2)R45^0 periodicity, consistent with the low temperature bulk phase of $BaFe_2As_2$. This apparent contradiction can be explained by small in-plane atomic displacements in the bulk (~0.02 Å). The (√2x√2)R45^0 periodicity seen with STM is inherently structural, a manifestation of the small Fe displacements on the surface second atomic layer, present in the low temperature orthorhombic phase.

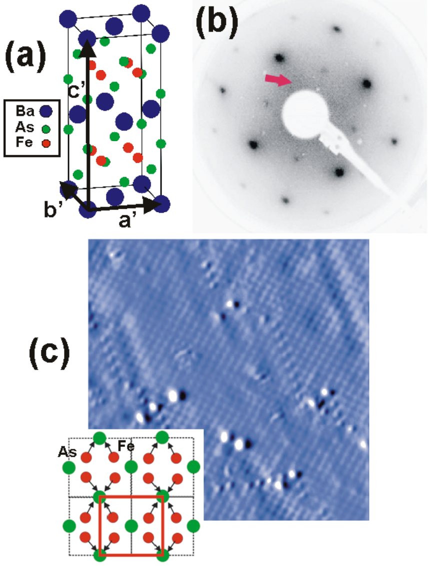

Fig. 8 (a) Low temperature AFM bulk structure of $BaFe_2As_2$. (b) LEED diffraction patter of $BaFe_2As_2$(001) at 122 eV. (c) 200 x 200 Å STM image, showing the orthorhombic symmetry. Only one type of As atom is imaged, as schematically shown in the inset [26].

9. Tunable Surface Metallicity: Extrinsic Oxygen Doping: $La_{1-x}Ca_xMNO_3$: Thesis work of Kenji Fujchigami in collaboration with Jian Shen (ORNL).

Perovskite manganites are complex systems in which the structural, electronic, and magnetic properties are strongly coupled. Creating a surface provides a controlled way to disturb the coupled system by breaking the symmetry without changing the stoichiometry, which may lead to completely new physical properties. We have demonstrated that oxygen adsorption / desorption can change a surface structure of $LaCaMnO_3$ (LCMO) back and forth between (1×1) (metallic) and (√2×√2)R45° (insulating) [26]. **Figure 9** shows the flowchart at the top using an STM to probe the structure. The films were grown using laser MBE and the characterization done *insitu.* Interestingly, the conductivity of the surface is also strongly influenced by existence of oxygen in the surface. Tunable metallicity of LCMO surface is clearly demonstrated in this study as can be seen in the bottom panel of Fig. 9 using STS/ I/V curves.

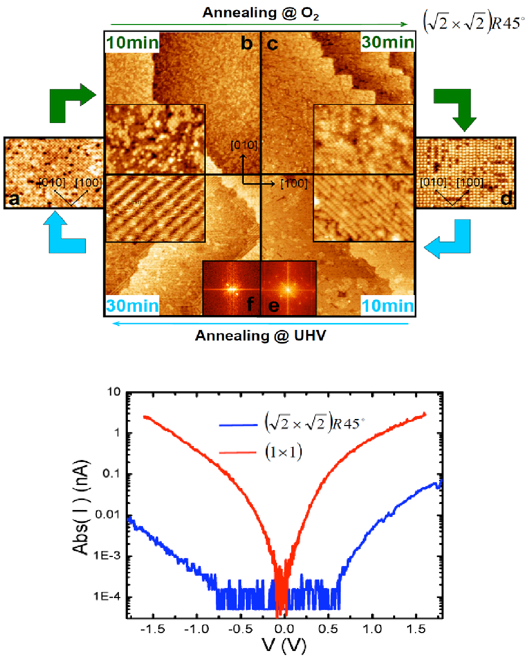

Fig. 9. Flow chart (top) of the structure evolution between the (1x1) and a (√2x√2)R45° surface. Below the STS I/V curves shown that (1x1) is metallic and a (√2x√2)R45° is insulating, induced by oxygen adsorption [26].

Kenji Fuchigami, a researcher at IHI Corporation (Yokohama, Japan) has been on leave from his company from 2005 to 2008 to complete his Ph.D degree in our group. At IHI, he has engaged in many research and development projects regarding novel surface treatment and functionalization techniques. It became clear that understanding and controlling a surface is important to achieve significant advances in product performance. The purpose of the stay in Tennessee was to obtain a high level of knowledge and experience with techniques used by surface sciencients in order to open up an opportunity to apply it to the industrial field. The international contacts he made at UTK and ORNL will also be very valuable assets for him with anticipating future collaboration.

10. Outreach at Local High Schools

UT launched the Pre-Collegiate Research Scholars Program in the Summer of 2007, a program where top scientists from UTK mentored exceptional students from Farragut High School in Knox County. In 2007–2008, there were three Farragut High School students working in Plummer’s laboratory (**Fig. 10**). Their project was a LEED analysis of the structure of carbon films on Ni. Three new students from Farragut High will be in the laboratory this fall.

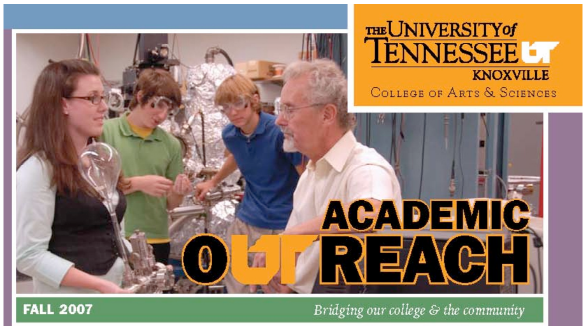

Fig. 9. *Three Farragut High School students, Emma Stockdale, Kyle Peterson, and Michael McCormick, working in Plummer’s laboratory.*

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Findings:

There were many scientific highlights originating from this research program which have reported in the previous years. The thesis work of Rob Moore of the surface phase diagram for the **layered perovskite $Ca_{2-x}Sr_xRuO_4$** was featured in the 2007, 2008 and 2009 annual reports. Dr. Te Yu Chien's study of the anisotropic electron phonon coupling on Be surfaces is contained in the 2009 report. The work of Dr. Von Braun Nascimento (postdoc) on the surface-stabilized Antiferromagnetism on a layered ferromagnetic manganite was also reported in 2009. In the same report the thesis work of Kenji Fuchigami on *tunable* metalicity at the surface of a transition metal oxide was described. Here we report the findings of the two students presently working on the NSF grant, Guorong Li and Biao Hu.

Biao Hu's thesis involves the determination of the bulk and surface phases of the double-layered doped ruthenate system **$Sr_3(Ru_{1-x}Mn_x)_2O_7$**. The structural results for the parent compound $Sr_3Ru_2O_7$ have been published and demonstrate that the surface structure of $Sr_3Ru_2O_7$ is quite distinct from the bulk [1]. The octahedra RuO_6 at the surface are not only rotated with a higher angle than in the bulk but also tilted, which is not seen in the bulk. In this system lattice distortions are strongly coupled with the orbital and spin degrees of freedom so the structural difference likely leads to different physical properties at the surface compared to the bulk. What has motivated this work is that the $Sr_3Ru_2O_7$ paramagnetic metallic ground state can be driven into an antiferromagnetic insulator with a partial substitution of Ru by Mn [2]. An electronic phase diagram in $Sr_3(Ru_{1-x}Mn_x)_2O_7$ ($0.0 \leq x \leq 0.2$) has revealed a single boundary line separating paramagnetic metallic regions from antiferromagnetic insulator regions [2]. But the preliminary results by Biao Hu show that the temperature T_M separating magnetic/nonmagnetic phase is different from the temperature T_{MIT} separating metallic/insulating phase in the $Sr_3(Ru_{1-x}Mn_x)_2O_7$ system. T_M corresponds to a true phase transition while T_{MIT} just corresponds to a crossover. The difference between T_M and T_{MIT} ($T_M<T_{MIT}$) increases with increasing doping level x. In $Sr_3(Ru_{0.8}Mn_{0.2})_2O_7$, three regions with different features have been characterized by using both scanning electron microscope (SEM) and scanning tunneling microscopy/spectroscopy (STM/STS) [3].

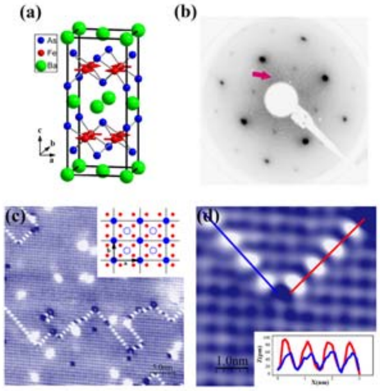

***Fig. 1**. a) Low temperature bulk and spin structure of $BaFe_2As_2$. (b) LEED diffraction pattern of $BaFe_2As_2(001)$ at 122 eV. The red arrow indicates where the weak diffraction spot should appear with the orthorhombic surface structure. (c) 355 x 355 Å STM image, showing the orthorhombic symmetry. Only one type of As atom is imaged, as schematically shown in the inset.(d) Two types of boundaries indicated the C_2 symmetry of spin structure. The right boundary has elongated spots and higher line profile shown in the inset.*

The thesis project of Guorong Li will be the determination of the **surface geometric and electronic structure of $Ba(Fe_{2-x}Co_x)As_2$ (001).** This is one of the new Fe based superconductors. At present we have investigated the properties of the parent compound (x=0) [4, 5] $BaFe_2As_2$ which exhibits properties that are characteristic of the parent compounds of the newly discovered iron (Fe)-based high-T_C superconductors. By combining real-space imaging of scanning tunneling microscopy and spectroscopy (STM and STS) with momentum-space quantitative low-energy electron diffraction (LEED *I-V*), we have identified the surface plane of cleaved $BaFe_2As_2$ single crystals as the As terminated Fe-As layer (see Fig. 1)—the plane where superconductivity occurs [4].

The structure at the surface is what would have been expected for the bulk orthorhombic crystal structure with no reconstruction or any appreciable lattice distortion. **Fig. 1** shows (a) the structure of the bulk, (b) the LEED pattern on the surface of $BaFe_2As_2(001)$, and (c) the STM topographical image of the ordered As surface with the structure expected for a (001) surface of the bulk orthorhombic bulk structure (a≠b). The orthorhombicity (a≠b) is enhanced at the surface. There are two surprises, first the STM images only show one As bright spot per unit cell where the marble model indicates two As atoms in each cell and LEED *I-V* indicates no rumpling of the surface, and the symmetry is C_2 not C_{2V} expected from the geometric structure [5]. This is evident at the boundary showing in Fig. 1c. Evidently the STM is imaging Fe-As orbitals, which are different for the two As atoms. We have shown that the electron topography mirrors the spin structure at the surface presumably due to strong orbital/spin coupling. The two As sites in the surface plane are not identical if one includes the spin structure in the Fe layer below.

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Educational Activities: The research activities are described in detail in this report with the findings highlighted in a separate attachment. I am an educator and my legacy will be the minds I molded, not the papers I wrote or the prizes I won. My record over the years mentoring graduate students (~50) and postdoctoral fellows (~30) speaks for itself. But it is imperative that we reach out to high school and undergraduates to show them the thrill of *discovery*. It is important to keep our best minds in in the *Science, Technology, Engineering, and Mathematics* (STEM) pipeline. At UTK, the "UTK Pre-Collegiate Research Scholars Program" has been very successful and productive for both the faculty and high school students involved. This program, initiated in the summer of 2007 with one high school in Knoxville, brought high school students into the research environment at the university. Three Farragut High School students worked in Plummer's laboratory during their senior year (see **Fig. 1**). All of these students are now enrolled in science and or engineering—Emma Stockdale at Rice, Michael McCormick at Duke, and Kyle Peterson at Vanderbilt. The first "Distinguished Faculty Lecture Series" was given by Plummer in the Fall of 2007 at Farragut High attracting an audience of nearly 150 students, teachers, and parents. The second lecture was given at Fulton High School. This lecture, which has now been presented at high schools in the Knoxville area, to local business and professional organizations, the LSU foundation, the dean's circle, and internationally, is titled *Materials for the 21st Century:A revolutionary—not an evolutionary—approach.* It focuses on discovery-based science needed in response to global competitiveness and the need to assure a secure energy future, which is environmental friendly for the United States of America.

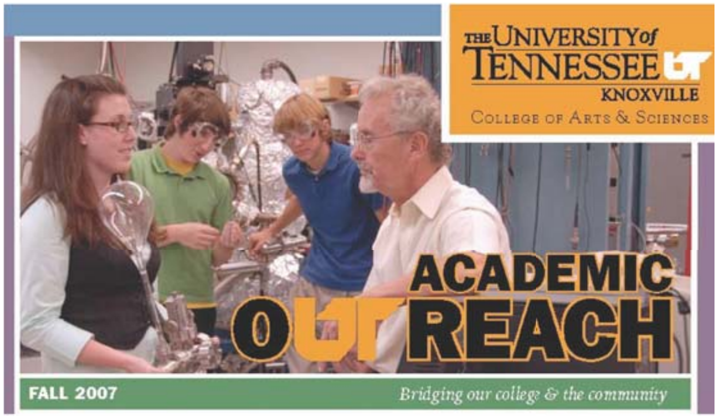

Fig. 1: *Three Farragut High School students, Emma Stockdale, Kyle Peterson, and Michael McCormick, working in Plummer's laboratory.*

***Fig. 2**: "Chancellor's Future Leaders in Research": Donovan Myers, Aliesa Warwick and André Wiggins in the laboratory at LSU with Jin and Plummer.*

At LSU I am also participating in the "Chancellor's Future Leaders in Research" program. We have three outstanding young freshmen working in our laboratory, André Wiggins, Donovan Myers, and Aliesa Warwick. All of these students are natives of Louisiana and are pictured in **Fig. 2** in the laboratory of my colleague Rongying Jin. At the present time the closely interacting groups of Professors Jin, Plummer and Zhang contains four undergraduates, four women and one Hispanic. All three of us moved to LSU in a state sponsored multidisciplinary hiring iniative aimed at building a world renowned research and education program in materials.

Strong **International Collaboration** is essential in today's globalization of science and technology. We have had a very effective and long-term collaboration with the *Institute of Physics,* Chinese Academy of Sciences in Beijing. Last summer, we signed an agreement with IOP establishing formal agreements with universities and institutes that will result in the exchange of students in a **dual degree. Fig 3** is the official picture of the signing with Dean Kevan Carman signing for the chancellor of LSU. We have now set up a similar program with Nanjing University. The first Dual Degree student from Beijing is now doing his thesis work at LSU.

Fig. 3*: On July 3, 2009, PIs signed the formal agreement with Institute of Physics (Chinese Academy of Sciences) for training Ph.D. students with dual degrees.*