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NSSEFF - DESIGNING NEW HIGHER TEMPERATURE
SUPERCONDUCTORS

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14. ABSTRACT We propose here a new methodology where electronic structure calculations are integrated with the synthesis of new superconducting materials, with the aim of providing a rigorous test of the apparent association of high temperature superconductivity with electron delocalization transitions occurring at quantum critical points. We will use realistic electronic structure calculations to assess which transition metal monpnictides are closest to electron delocalization, and hence optimal for superconductivity. The functional layer will be matched with a layered host taken from an extensive library of known framework structures, and then single crystals of the desired compound will be synthesized. Rapid turnaround characterization will determine the basic properties of these new materials, identifying the most promising candidates.					
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Final Report

Scientific and Technical Activities and Findings

Designing New Higher Temperature Superconductors

PI: Meigan Aronson Stony Brook University

We propose here a new methodology where electronic structure calculations are integrated with the synthesis of new superconducting materials, with the aim of providing a rigorous test of the apparent association of high temperature superconductivity with electron delocalization transitions occurring at quantum critical points. We will use realistic electronic structure calculations to assess which transition metal monpnictides are closest to electron delocalization, and hence optimal for superconductivity. The functional layer will be matched with a layered host taken from an extensive library of known framework structures, and then single crystals of the desired compound will be synthesized. Rapid turnaround characterization will determine the basic properties of these new materials, identifying the most promising candidates. Optical conductivity and angle resolved photoemission measurements will be used to compare the actual electronic structure with theoretical results, providing feedback to the initial choices of functional and charge reservoir layers.

The members of this collaboration are Meigan Aronson (Stony Brook University), Dimitri Basov (University of California, San Diego), Gabriel Kotliar (Rutgers University), James Allen (University of Michigan), Liu Hao Tjeng (Max Planck Institut for Chemical Physics, Dresden), Stephen Julian (U. Toronto), and Liling Sun (Chinese Academy of Sciences, Institute of Physics).

The objective of this project is to implement and test a new methodology 'Theory – Assisted Synthesis' as a means to design and then synthesize new materials with higher superconducting transition temperatures than are currently known. A collaborative approach is required to carry out this project, where the group of PI Meigan Aronson is responsible for synthesizing new materials and assessing their basic properties. Prof. Gabriel Kotliar's group carries out dynamical mean field theory (DMFT) calculations of the electronic structure, providing not only accurate determinations of the electronic structure in these inherently highly correlated materials, but also explicit results for the photoemission and optical conductivity that can be directly compared to experimental results. The group of Prof

. Dimitri Basov (University of California San Diego) performs optical spectroscopy experiments, ideal for distinguishing between metals and insulators, and in combination with DMFT can determine the overall strength of the electronic correlations. Prof. Hao Tjeng's group (Max Planck Institute for Chemical Physics, Dresden) provides information about the transition metal valence state via x-ray absorption, and as well photoemission measurements that can be directly compared to theoretical results from Kotliar's group. In our original proposal, Prof. James Allen (University of Michigan) was responsible for the electron spectroscopy part of this collaboration, but he was forced to withdraw due to illness. He will now be participating in a

more limited capacity as a consultant to the group of Prof. Hao Tjeng, with whom he has a long history of collaboration. We have two different partner groups that address different aspects of high pressure measurements. The group of Dr. Liling Sun (Chinese Academy of Sciences, Institute of Physics, National Laboratory on Superconductivity) carry out x-ray diffraction measurements and x-ray absorption measurements under high pressures, needed input for the DMFT to calculate idealized lattice constants for transforming insulators to metals. The group of Stephen Julian (U. Toronto) will carry out high pressure resistance measurements at low temperatures, to seek evidence for incipient order and to determine temperature power laws with the intent to provide insight into the nature of the quasiparticles present near collapsing order.

Our hypothesis is that superconductivity is a potential attribute of metals with strong electronic correlations, provided other sorts of order do not intervene first. In particular, we believe that the combination of ground state entropy and reduced kinetic energy from strong correlations enable superconductivity when the system is close to an electronic delocalization transition (EDT), for instance a Mott-like transition. Unlike the cuprates, where the metallic compositions that support superconductivity are derived by doping strongly correlated Mott insulators, the iron pnictide superconductors are all derived from metals, and –with the exception of the as-yet incompletely understood but nonstoichiometric $K_{1-x}Fe_2Se_2$ family- there are no known manganese based -pnictide superconductors. The focus of our project is to find more highly correlated Fe-based metals that may be closer to electronic delocalization than the heavily studied iron-pnictides, possibly superconducting with higher transition temperatures. The second objective is to start with insulating and antiferromagnetic LaMnPO, and to use pressure and charge doping to drive it metallic- and thus potentially superconducting.

In the first year of this project, we focused on Mn-based insulators, primarily LaMnPO. The first step was to make the 'handshake' with theory, where DMFT calculations were found to be in excellent agreement with the antiferromagnetic moment of 3.2 mB/Mn that was found in neutron diffraction measurements, and with the insulating gap of 1 eV that was found in optical transmission experiments. Evidence for strong charge fluctuations was found in x-ray absorption measurements as well as DMFT, signaling proximity to electronic delocalization. We began with electron (LaMnPO $_{1-x}Fx$) and hole (La $_{1-x}Ca_x$ MnPO) doping measurements, but found that neither substantially modified the magnitude of the charge gap, Neel temperature, or ordered moment, and that LaMnPO remained stubbornly insulating even at high doping levels (30% or more). More recent efforts to hydrogen dope LaMnPO at high pressures reduced the electrical resistivity more substantially, but not to the point that truly metallic behavior was found. These results were published in Physical Review B ("Gap states in insulating LaMnPO $_{1-x}Fx$ ($x=0 - 0.3$)", J. W. Simonson, K. Post, C. Marques, G. Smith, O. Khatib, D. N. Basov, and M. C. Aronson, Phys. Rev. B **84**, 165129 (2011).

Our next step was to use high pressures, and here we had success. Dr. Liling Sun initially carried out x-ray diffraction measurements in a diamond anvil cell using the Beijing Synchrotron Center. She found that the tetragonal structure that is stable at 1 bar is destabilized at ~16 GPa, where it becomes orthorhombic. There is a further isostructural volume collapse at 30 GPa. These data allowed the Aronson group to carry out full structural refinements over the full range of pressures, and this information was used by our theory team to determine that the insulating gap is expected to close at ~8 GPa, and the Mn moment itself is suppressed by the volume collapse at 30 GPa. This work was published in the Proceedings of the National Academy of

Sciences ("From antiferromagnetic insulator to correlated metal in pressurized and doped LaMnPO", J. W. Simonson, Z. P. Yin, M. Pezzoli, J. Guo, J. Liu, K. Post, A. Efimenko, N. Hollmann, Z. Hu, H.-J. Lin, C. T. Chen, C. Marques, V. Leyva, G. Smith, J. W. Lynn, L. L. Sun, G. Kotliar, D. N. Basov, L. H. Tjeng, and M. C. Aronson, Proceedings of the National Academy of Sciences **109**, E1815-E1819 (2012).

The next step was to actually demonstrate that the charge gap collapse results in a insulator-metal transition, followed by an intermediate metallic phase that is still magnetically ordered, and finally a T=0 first order transition where magnetic order finally vanishes. This evidence has come only in the past year. First, K. Post and D. Basov carried out an experimental tour de force, using optical techniques to demonstrate that the charge gaps in LaMnPO and CaMn₂Sb₂ collapse under pressures. These experiments were performed in collaboration with G. Goncharev (Carnegie Institute of Geophysics). The critical pressures from high pressure optical and resistivity experiments are in good agreement with the DMFT results, showing that the collapse of the charge gap is not mediated by in-gap impurity states in LaMnPO. Recently, our Beijing collaborators have used a combination of resistivity and ac susceptibility measurements to confirm the theoretically predicted scenario of a double transition, and LSDA calculations further support the likelihood that electronic delocalization in LaMnPO is via an orbitally selective Mott transition. It would be the first demonstration of this elusive instability, much conjectured for the iron-pnictide compounds. This work has appeared in "Observation of antiferromagnetic order collapse in pressurized LaMnPO insulator", Jing Guo, J. W. Simonson, Liling Sun, Qi Wu, Peiwen Gao, Chao Zhang, Dachun Gu, Gabriel Kotliar, Meigan Aronson, and Zhongxian Zhao, Scientific Reports **3**, 2555 (2013).¹²

Despite the rather complete experimental description that we have developed in the past two years regarding electronic delocalization in LaMnPO, the origin of the gap itself was unclear. One possibility is that the antiferromagnetic order plays a part in stabilizing the gap, as in a Slater insulator. Graduate student Kirk Post in the Basov group carried out optical transmission measurements to temperatures as high as 725 K, showing that there is only a ~10% reduction in the gap from its room temperature value of 1 eV, and that there were no particular features near the 375 K Neel temperature. This work was reported in "Electronic correlations and pressure induced metallicity in LaMnPO revealed via infrared spectroscopy", K. W. Post, A. F. Goncharov, Z. P. Yin, J. W. Simonson, J. Guo, L. L. Sun, S. Zellman, M. D. Goldflam, H. T. Stinson, B. C. Chapler, D. E. McNally, Z. Zhao, G. Kotliar, M. C. Aronson, and D. N. Basov, Phys. Rev. B **94**, 045115 (2016).

Graduate student Daniel McNally carried out inelastic neutron scattering measurements on powdered LaMnPO to show that the antiferromagnetic spin waves are well described by the Heisenberg model, with a near neighbor exchange $J_1 \sim 39$ meV. This exchange suggests that the mean field antiferromagnetic transition would occur between 700-800 K, and so the quasi-two dimensional character is responsible for the artificially low Neel temperature. Short-ranged antiferromagnetic correlations are enough to inhibit electron hopping, so it is plausible that the exchange could contribute to gap stabilization even up to the mean field transition temperature. However, the optical measurements prove that they are only a contributing factor, and since the exchange energy is only ~10% of the charge gap magnitude, we must look elsewhere to explain the correlations that are responsible for gap formation in LaMnPO. Electronic structure calculations have been performed to show that the combination of Coulomb correlations with a Hubbard $U=8$ eV as well as a Hund's interaction $J_H=0.9$ eV are both required

to reproduce the observed gap in LaMnPO, even in the absence of antiferromagnetic order. This work, including inelastic neutron scattering, optical transmission measurements, and DFT+DMFT calculations appeared in "Origin of the charge gap in the Hund's insulator LaMnPO", D. E. McNally, J. W. Simonson, K. S. Post, Z. P. Yin, M. Pezzoli, G. J. Smith, Y. Zhao, J. W. Lynn, A. I. Kolesnikov, L. DeBeer-Schmidt, D. N. Basov, G. Kotliar, and M. C. Aronson, Phys. Rev. B **90**, 180-403(R) (2015). We corrected a longstanding error in the literature regarding the charge gap in the related compound BaMn₂As₂ ("From Hund's insulator to Fermi liquid: Optical spectroscopy study of K-doping in BaMn₂As₂", D. E. McNally, S. Zellman, Z. P. Yin, K. Hao, D. N. Basov, G. Kotliar, C. Homes, and M. C. Aronson, Phys. Rev. B **92**, 115142 (2015).)

We have investigated several other Mn-based compounds, in order to determine whether it might be possible to find an experimental condition where the charge gap and magnetic order collapse together. We were originally attracted to CaMn₂Sb₂ and SrMn₂Sb₂ for their unusual metallic character and high Mn moment, which seemed to deviate from our understanding of the systematics of Mn-square net compounds. We grew large and high quality single crystals of both compounds. Electrical resistivity and optical transmission experiments showed unambiguously that both are intrinsic insulators, in agreement with electronic structure calculations carried out using LSDA. We believe that the previous reports that these compounds are metallic were likely based on samples that were contaminated with metallic flux. Extensive experimentation using neutron and xray diffraction, electrical transport, specific heat, and full magnetic characterization was carried out, showing that neither compound can become metallic, either under modest pressure (<2 GPa) or by doping. Instead, we found evidence for magnetic polaron formation, subsequently destroyed by the onset of antiferromagnetic order. This work appeared in "The magnetic and structural phase diagram in CaMn₂Sb₂", J. W. Simonson, G. Smith, K. Post, M. Pezzoli, D. E. McNally, C. S. Nelson, G. Kotliar, D. N. Basov, and M. C. Aronson, Phys. Rev. B **86**, 220401 (2012). Subsequent Raman scattering measurements ("Singlet pairing on an antiferromagnetic background in CaMn₂Sb₂", V. K. Thorsmølle, A. Ignatov, M. E. Pezzoli, K. Haule, D. Kolchmeyer, J. W. Simonson, M. C. Aronson, and G. Blumberg, Phys. Rev. Lett. (submitted).

Daniel McNally of our group has used the Sequoia time of flight spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory to measure the inelastic neutron scattering. Analysis of these results in terms of spin waves using a Heisenberg model was carried out to determine the exchange constants. Interestingly, CaMn₂Sb₂ is one of the first examples of the geometrically frustrated honeycomb lattice, similar to some of the new iridate compounds. By combining new computational results with the measured values of the exchange constants, we have shown that CaMn₂Sb₂ is apparently quite close to a tricritical point where the antiferromagnetic order collapses in favor of a spin liquid phase. The relative weakness of antiferromagnetic order would be a good harbinger for superconductivity, however all indications are that the electronic charge remains strongly localized, given the persistence of the polaronic behavior. We now believe that superconductivity is unlikely in CaMn₂Sb₂. This work appeared in "CaMn₂Sb₂: Spin Waves on a Frustrated Antiferromagnetic Honeycomb Lattice", D.E. McNally, J.W. Simonson, J.J. Kistner-Morris, G.J. Smith, J.E. Hassinger, A.I. Kolesnikov, L. DeBeer-Schmidt, I. A. Zaliznyak, and M.C. Aronson, Phys.Rev. B (Rapid Communications) **91**, 180407 (2015).

clear that there are compounds where the Mn is strongly hybridized, becoming so itinerant that correlations are very weak. DFT calculations were used as the basis of a heuristic phase diagram that shows that the square planar motif does not permit the Mn-Mn spacings that would be for this, at least for the pnictogens. We have discovered several new systems where Mn-Mn spacings are very small, or where direct Mn-Mn hybridization is replaced by indirect Mn-X hybridization. The challenge is to minimize magnetic order in these new compounds, and this seems to be possible in low dimensional compounds and on geometrically frustrated lattices. Our first results on itinerant Mn in the Kagome lattice appeared in "New Kagome Metal $\text{Sc}_3\text{Mn}_3\text{Al}_7\text{Si}_5$ and its Gallium-doped analogues: Synthesis Crystal Structure, and Physical Properties", H. He, W. Müller, and M. C. Aronson, *Inorganic Chemistry* **53(17)**, 9115 (2014). $\text{CaMn}_2\text{Al}_{10}$ is a nonordering compound, based on square plaquettes, which is also a candidate for a spin liquid (" $\text{CaMn}_2\text{Al}_{10}$: Itinerant Mn magnetism on the verge of magnetic order", L. Steinke, J. W. Simonson, W-G. Yin, G. J. Smith, J. J. Kistner-Morris, S. Zellman, A. Puri, and M. C. Aronson, *Phys. Rev. B (Rapid Communications)* **92**, 020413 (R) (2015). Editor's Suggestion.)

We have worked hard to assemble a top-notch synthesis team, so that we can not only service our many measurement collaborators, but also to have sufficient capacity to have a vigorous materials exploration effort as well. We are focusing on the layered motif, involving square nets of transition metals, covalently bonded to anions from the telluride and pnictide elements. In the past year we have completed work on several different iron-silicides. In $\alpha\text{-FeSi}_2$, we reported the first measurements of this metastable compound where the d-electron count is locked to 6 by the composition, even under Mn and Co doping. DMFT calculations show that this is not due to a breakdown of the 'self-doping' paradigm ("Protected Iron Valence in pure and charge doped $\alpha\text{-Fe}_{1-x}\text{Si}_2$ ($x=0.17$)", W. Müller, J. M. Tomczak, J. W. Simonson, G. Smith, G. Kotliar, and M. C. Aronson, *J. Phys.: Cond. Matter* **27**, 175601 (2015)).

We have also discovered a new Fe-Si based superconductor, $\text{Zr}_{2-x}\text{Fe}_4\text{Si}_{14-y}$ ($x=0.82$, $y=0.41$). Here, the superconductivity occupies a substantial part of the sample volume, but does not form a continuous superconducting pathway for conduction. Instead, we believe that the SC is confined to the boundaries between intrinsic nanoscaled domains that are induced by local variations in composition ("Intrinsic nanostructure in $\text{Zr}_{2-x}\text{Fe}_4\text{Si}_{14-y}$ ($x=0.816$, $y=0.412$)", G. J. Smith, J. W. Simonson, T. Orvis, C. Marques, J. E. Grose, J. J. Kistner-Morris, L. Wu, K. Cho, H. Kim, M. A. Tanatar, V. O. Garlea, R. Prozorov, Y. Zhu, and M. C. Aronson, *J. Phys. : Condensed Matter* **26**, 376002 (2014).)

At present, we are working to develop new Mn-based compounds that are metallic, but close to the magnetic quantum critical point. We are deploying the full methodology of "Theory Assisted Synthesis" for the first time, where we used LSDA calculations to estimate the locus of Mn-Mn spacings and Mn-anion angle where this transition can be expected to occur, and then examine the crystal structure data base to identify test compounds that are expected to be close to these conditions. Finally, we have taken up a proposal from Kotliar that charge reservoirs with metallic compositions may optimize superconductivity in square planar systems. We have successfully grown the layered compounds LaTSb_2 ($T=\text{Mn, Fe, Co, Ni}$) that were proposed in this theoretical work. Postdoc Jennifer Misuraca and graduate student Daniel McNally carried out a complete characterization of these compounds, finding that LaMnSb_2 does order antiferromagnetically near 500 K, but that LaFeSb_2 and LaCoSb_2 do not order at all, and LaNiSb_2 is superconducting below 2 K. The entire doping series $\text{LaFeSb}_2 - \text{LaNiSb}_2$ is

possible, and we find that the enhanced Sommerfeld coefficient remains unaffected by doping, right up to the collapse of the LaFeSb₂ structure itself at 10% Fe doped LaNiSb₂. Our experiments indicate that replacing Ni for Fe in LaFeSb₂-xNiSb₂ is clearly isovalent doping, with the result that the excess d-electrons remain localized on the Ni sites, and do not contribute to the itinerant electrons contained by the Fermi surface. This is a stark demonstration of what is only suspected in the Fe-pnictides, which is that there is no real doping effect beyond the suppression of magnetic order via disorder from introducing the dopants themselves. Accordingly, we find that Fe ions in LaNiSb₂ are magnetic and thus pairbreaking, although Cu dopants are not. Unfortunately, the intrinsic lack of dopability in these compounds means that we were not able to increase the superconducting onset temperature of LaNiSb₂. Part of this work is submitted to Physical Review B ("Physical and Magnetic Properties of Layered LaFe_{0.62}Sb₂", J. E. Grose, J. W. Simonson, C. Marques, J. Liu, G. Smith, and M. C. Aronson, Phys. Rev. B (submitted)).

Our synthesis is carried out by a team of undergraduates (Shelby Zellman, Thomas Ciavatti, Jed Kistner-Morris, Julian Hassinger, Akshat Puri, and Tom Orvis), supervised by postdocs Jack Simonson and Hua He. We are experimenting with a new team structure where two postdocs are paired for each project: one with major responsibility for synthesis and one for measurement. They are separately supported by rotating groups of undergrads. In this way, we hope to maximize our throughput and also make the dissemination of both synthetic and measurement skills most effective.

Personnel

The following junior personnel were supported during this project:

Graduate students: Mr. Kirk Post (University of California, San Diego). Mr. Post is mentored by Prof. Dmitri Basov. He is carrying out measurements of the optical conductivity, while working closely with Dr. Pezzoli to test the comparable theoretical results. Stony Brook graduate student Mr. Daniel McNally was involved in sample synthesis and characterization, neutron scattering and photoemission measurements. He was mentored by Prof. Meigan Aronson. After receiving his PhD in 2015, he took a postdoc at PSI.

Postdocs: Dr. Jack Simonson (Stony Brook University), Dr. Maria Pezzoli (Rutgers University), Dr. Zhiping Yin (Rutgers University), Dr. Wojciech Miiller (Stony Brook), Dr. Hua He (Stony Brook University), Dr. Jennifer Misuraca (Stony Brook, joint with Prof. Laura Greene University of Illinois) have all been supported by this project.

Undergraduate students: Stony Brook undergraduate students Shelby Zellman, Ashley Zenbo, Plamen Kamenov, Thomas Ciavatti, Jed Kistner-Morris, Julian Hassinger, Akshat Puri, and Tom Orvis, as well as Hofstra undergraduate Claire Weaver have all been members of our synthesis team. They work on an hourly basis during the academic year (full time in the summer) to prepare new growths, to analyze new products, and carry out crystal structure determinations using x-ray diffraction.

Publications:

“Gap states in insulating $\text{LaMnPO}_{1-x}\text{F}_x$ ($x=0 - 0.3$)”, J. W. Simonson, K. Post, C. Marques, G. Smith, O. Khatib, D. N. Basov, and M. C. Aronson, *Phys. Rev. B* **84**, 165129 (2011).

“From antiferromagnetic insulator to correlated metal in pressurized and doped LaMnPO ”, J. W. Simonson, Z. P. Yin, M. Pezzoli, J. Guo, J. Liu, K. Post, A. Efimenko, N. Hollmann, Z. Hu, H.-J. Lin, C. T. Chen, C. Marques, V. Leyva, G. Smith, J. W. Lynn, L. L. Sun, G. Kotliar, D. N. Basov, L. H. Tjeng, and M. C. Aronson, *Proceedings of the National Academy of Sciences* **109**, E1815-E1819 (2012).

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“Strong Correlations and Antiferromagnetic Order in $\text{Zr}_4\text{Fe}_4\text{Si}_7$ ”, J. Simonson, M. E. Pezzoli, G. J. Smith, J. Misuraca, G. Kotliar, and M. C. Aronson, *Phys. Rev. B (Rapid Communications)* **88**, 081107 (2013).

“Observation of antiferromagnetic order collapse in pressurized LaMnPO insulator”, Jing Guo, J. W. Simonson, Liling Sun, Qi Wu, Peiwen Gao, Chao Zhang, Dachun Gu, Gabriel Kotliar, Meigan Aronson, and Zhongxian Zhao, *Scientific Reports* **3**, 2555 (2013).

“Synthesis and properties of the theoretically predicted mixed-valent perovskite superconductors: CsTlX_3 ($X=\text{F}, \text{Cl}$)”, M. Retuerto, T. Emge, M. R. Li, Z. P. Yin, M. Croft, A. Ignatov, J. W. Simonson, M. C. Aronson, P. Stephens, J. Hadermann, A. Pan, D. N. Basov, G. Kotliar, M. Greenblatt, *Chem. Materials* **25**, 4071 (2013).

“Magnetic and transport properties of the novel layered transition metal pnictides $\text{R}_3\text{T}_4\text{As}_4\text{O}_{2-\delta}$ ($\text{R}=\text{La}, \text{Ce}, \text{Pr}, \text{Nd}$, and Sm , $\text{T}=\text{Ni}, \text{Cu}$)”, J. K. Wang, A. Marcinkova, C.-W. Chen, H. He, M. Aronson, and E. Morosan, *Phys. Rev. B* **89**, 094405 (2014).

“Magnetic and transport properties of the novel layered transition metal pnictides $\text{R}_3\text{T}_4\text{As}_4\text{O}_{2-\delta}$ ($\text{R}=\text{La}, \text{Ce}, \text{Pr}, \text{Nd}$, and Sm , $\text{T}=\text{Ni}, \text{Cu}$)”, J. K. Wang, A. Marcinkova, C.-W. Chen, H. He, M. Aronson, and E. Morosan, *Phys. Rev. B* **89**, 094405 (2014).

“New Kagome Metal $\text{Sc}_3\text{Mn}_3\text{Al}_7\text{Si}_5$ and its Gallium-doped analogues: Synthesis Crystal Structure, and Physical Properties”, H. He, W. Müller, and M. C. Aronson, *Inorganic Chemistry* **53(17)**, 9115 (2014).

“Intrinsic nanostructure in $\text{Zr}_{2-x}\text{Fe}_4\text{Si}_{14-y}$ ($x=0.816$, $y=0.412$)”, G. J. Smith, J. W. Simonson, T. Orvis, C. Marques, J. E. Grose, J. J. Kistner-Morris, L. Wu, K. Cho, H. Kim, M. A. Tanatar, V. O. Garlea, R. Prozorov, Y. Zhu, and M. C. Aronson, *J. Phys. : Condensed Matter* **26**, 376002 (2014).
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“CaMn₂Sb₂: Spin Waves on a Frustrated Antiferromagnetic Honeycomb Lattice”, D.E. McNally, J.W. Simonson, J.J. Kistner-Morris, G.J. Smith, J.E. Hassinger, A.I. Kolesnikov, L. DeBeer-Schmidt, I. A. Zaliznyak, and M.C. Aronson, Phys.Rev. B (Rapid Communications) **91**, 180407 (2015).

“Protected Iron Valence in pure and charge doped α -Fe_{1-x}Si₂ (x=0.17)”, W. Miiller, J. M. Tomczak, J. W. Simonson, G. Smith, G. Kotliar, and M. C. Aronson, J. Phys.: Cond. Matter **27**, 175601 (2015).

“CaMn₂Al₁₀: Itinerant Mn magnetism on the verge of magnetic order”, L. Steinke, J. W. Simonson, W-G. Yin, G. J. Smith, J. J. Kistner-Morris, S. Zellman, A. Puri, and M. C. Aronson, Phys. Rev. B (Rapid Communications) **92**, 020413 (R) (2015). Editor's Suggestion.

“From Hund's insulator to Fermi liquid: Optical spectroscopy study of K-doping in BaMn₂As₂”, D. E. McNally, S. Zellman, Z. P. Yin, K. Hao, D. N. Basov, G. Kotliar, C. Homes, and M. C. Aronson, Phys. Rev. B **92**, 115142 (2015).

“Electronic correlations and pressure induced metallicity in LaMnPO_{1-x}F_x revealed via infrared spectroscopy”, K. W. Post, A. F. Goncharov, Z. P. Yin, J. W. Simonson, J. Guo, L. L. Sun, S. Zellman, M. D. Goldflam, H. T. Stinson, B. C. Chapler, D. E. McNally, Z. Zhao, G. Kotliar, M. C. Aronson, and D. N. Basov, Phys. Rev. B **94**, 045115 (2016).

Conference Proceedings None.

Presentations

“Towards New and Higher Temperature Superconductors via Theory Assisted Synthesis”, Air Force Institute of Technology, Columbus OH. May 2011. Presented by M. Aronson.

“Quantum Criticality: an Organizing Principle for Strongly Correlated Electron Systems?”, Physics Colloquium, Ohio State University. May 2011. Presented by M. Aronson.

“High spin-low spin transition in insulating CaMn_2Sb_2 ”, 2012 March Meeting of the American Physical Society. Presented by J. Simonson.

“Synthesis of Large Single Crystals Within the Zr - Fe - Si System”. March Meeting of the American Physical Society. Presented by G. Smith.

“An infrared study of electron delocalization in Mn-based relatives of the pnictides”, March Meeting of the American Physical Society. Presented by K. Post.

“Theoretical insight on layered Mn-compounds under pressure”, March Meeting of the American Physical Society. Presented by M. Pezzoli.

“Strong Electronic Correlations in YMn_2Ge_2 ”, March Meeting of the American Physical Society. Presented by D. McNally.

“Electronic Delocalization in Mn-based Compounds: Prospects for New Superconductors”, International Workshop on Dynamical Mean-Field Approach for Strongly Correlated Materials. Dresden Germany. September 2012.

“Quantum Criticality and Superconductivity”, International Winter School on Superconductivity, Hong Kong, China. January 2013.

``Towards higher temperature superconductors'', International Workshop on Superconductivity. Hong Kong, China. January 2013.

``Implementing Theory-Assisted Synthesis'', International Workshop on Realistic Electronic Structure Calculations'', Bariloche Argentina. February 2013. Presented by postdoc Jack Simonson.

``Electronic Delocalization in LaMnPO'', Tokyo Institute of Technology. August 2013.

``Implementing Theory-Assisted Synthesis'', ICAM Workshop on Digital Design of New Materials, Boston University. September 2013.

``Electronic Delocalization in LaMnPO: Implementing Theory Assisted Synthesis'', Max Planck Institut for Chemical Physics of Solids. September 2013

``Superconductivity and electronic delocalization in Mn-based systems'', Workshop on Novel Superconductivity (Rick Greene Festschrift), University of Maryland, College Park MD. November 2013.

``Implementing Theory-Assisted Synthesis'', Colloquium, Department of Physics, Boston University. November 2013.

``1+1=3: Emergent Criticality from Correlated Electrons'', CuWiP 2014 East Coast Conference for Undergraduate Women in Physics. Stony Brook NY January 2014.

``Introduction to Quantum Criticality: a Perspective from Experimental Condensed Matter'', Workshop on Strongly Coupled Systems Away From Equilibrium, Simons Center for Geometry and Physics, Stony Brook University. February 2014.

``Electronic Localization and Magnetic Order: transition metal-based heavy fermions'', Condensed Matter Physics seminar, Rutgers University. February 2014.

``Search for New Superconductors in New Mn and Fe-based Layered Compounds'', Beijing International Workshop on Iron-Based Superconductivity. Beijing China. August 2014.

``Superconductivity September: Finding new higher temperature superconductors'', Society of Physics Students, Stony Brook University. September 2014.

``Future Experimental Prospects'', Strongly Correlated Electron Matter at 60. Urbana IL. October 2014.

``Towards Higher Temperature Superconductivity: Materials by Design'', La Jolla Workshop on Big Ideas in Quantum Materials, December 2015.

``Towards Higher Temperature Superconductivity: Materials by Design'', Colloquium, Department of Materials Science and Engineering, Texas A+M University. February 2016.

``Towards Higher Temperature Superconductivity: Materials by Design'', 4th Chinese Academy of Sciences - Department of Energy-Basic Energy Sciences collaboration workshop on novel superconductors'', Shanghai China. May 2016.

``Articulated Synthesis: Towards a better union of theory and synthesis of correlated electron compounds", Center for Computational Materials Synthesis Fall Workshop. Stony Brook NY. November 2016.

``Articulated Synthesis: Towards a better union of theory and synthesis of correlated electron compounds", National High Magnetic Field Laboratory Winter School for Theory, Tallahassee FL. January 2017.

} \$ ``Articulated Synthesis: Towards a better union of theory and synthesis of correlated electron compounds", University of Maryland Winter School on the Fundamentals of Quantum Materials. College Park. MD. January 2017.

Inventions or Patent Disclosures (if none, report none) **None.**

Sabbatical or other professional development

None.

Awards and Honors (including Team Members) Prof. Meigan Aronson was awarded a two year ICAM Postdoctoral Fellowship, jointly with Prof. Laura Greene (University of Illinois). We intend to collaborate on developing new superconductors, and to carry out point contact spectroscopy measurements on these materials.

Prof. Aronson has been appointed Qiushi Visiting Professor, Zhejiang University, Hangzhou China. She currently serves as the chair of the Neutron Advisory Board (Oak Ridge) and of the External Advisory Board (National High Magnetic Field Laboratory), while serving on the Advisory Boards of Oak Ridge National Laboratory, Max Planck Institut for Solid State Research (Stuttgart), the University of Illinois Department of Physics, and a number of international conferences (M2S 2015, LT-27, SCES 2010-2014). She is a member of the Board of Trustees of the Gordon Research Conferences, and the Editorial Board of the Annual Reviews of Condensed Matter Physics.

Accomplishments

- Established that LaMnPO is a correlation gap insulator, with robust magnetic moments that don't couple to magnetic fields in the antiferromagnetic or paramagnetic phases. LaMnPO is effectively undopable, since the insulating gap, magnetic moment, and Neel temperature are little affected, even when ~40% of the O ions are replaced with F. Electron doping induces correlated gap states with the full Mn moment, which are always localized.
- Showed that the insulating state of LaMnPO can be suppressed with ~12 GPa of pressure, although 30 GPa is required to destroy the Mn moments.
- Synthesized more than 20 new Fe and Mn based compounds, including compounds that had never been synthesized previously and several forming in crystal structure types that have not been previously reports.
- Identified new structure types that are likely closer than LaMnPO to metallization.

International Collaborations We have enjoyed and profited from our collaboration with Dr. Liling Sun of the National Laboratory of Superconductivity, Institute of Physics, Chinese Academy of Sciences. Dr. Sun performed x-ray diffraction and absorption measurements at high pressures, which will be a crucial complement to the DMFT calculations carried out by G.

Kotliar's group in identifying the lattice constants needed to metallize the strongly correlated insulators that we've been focusing on. A new collaboration began in 2013 with Prof. Stephen Julian (Toronto) who is a leading expert in low temperature / high measurement measurements on quantum critical materials. In addition, we have started a new collaboration with the group of Prof. Hao Tjeng (Max Planck Institute for Chemical Physics, Dresden). Prof. Tjeng's group has carried out x-ray absorption and photoemission measurements on our new materials, providing important information about the transition metal valence states, and as well photoemission data that can be directly compared to the DMFT results.

Interactions with DoD (service on boards or panels, visits to laboratories, etc.) Prof. Meigan Aronson visited the Air Force Institute of Technology and presented a talk on the project in May 2011. She has participated in the annual reviews of the Superconductivity MURI programs during the first four years of the NSSEFF project, as well as the joint US-China Collaboration meetings.

Other contributions

Prof. Aronson is active in the Institute for Complex and Adaptive Matter (ICAM), serving on the Board of Governors. She was recently involved starting a new ICAM branch at Stony Brook/Brookhaven. She serves on the ICAM working group for superconductivity and is involved in developing a display on superconductivity that is being constructed for the on-line museum 'Emergent Universe'.

Change in AFOSR program manager, if any. None

Extensions granted or milestones slipped, if any. A 6-month no-cost extension has been granted in July 2014, extending the end date of this project to 10/31/2015.

