Pre-Application to Stewardship Science Academic Alliances Program

High Pressure Thermodynamic Properties of f–electron Metals, Transition Metal Oxides, and Half-Metallic Magnets

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Scope Areas:
Properties of Materials under Extreme Conditions and Hydrodynamics

Proposed project is a Research Grant

1. Description of Proposed Research

Overview: The DOE/NNSA laboratories have a long standing interest in the behavior of f-electron metals under pressure and the critical underlying scientific issue of electron correlation and its impact on material properties. Generally speaking the effects of electron correlation diminish with pressure, yet there are a host of unanswered scientific questions. Why do some of these metals undergo unique correlation-driven phase transitions with huge 9-20% volume changes (Pu and Am among the actinides; Ce, Pr, and Gd among the lanthanides), yet others (Nd) do not? If these large "volume collapse" transitions are of predominant electronic origin, is long-range crystalline order critical, or could remnant anomalies persist into the liquid as if an extension of the phase boundary? What is the role of magnetic moments or magnetic order, whose loss often coincides with these transitions? These and other questions may be addressed not only to actinide and lanthanide metals, but also to their compounds, and to transition metal compounds, where the relevant f or d orbitals may be pushed into the strongly correlated regime by the associated increase in their interatomic separation, then be brought closer again by the application of pressure.

Three experimental groups at LLNL are probing these questions with entirely different diagnostics. C.-S. Yoo's group has recently studied the Pr volume collapse as a function of temperature, and would like to explore possible residue anomalies in the liquid using the structure factor obtained from inelastic x-ray scattering now possible at third generation light sources. S. Weir and J. Akella are collaborating with Y. Vohra at the U. Alabama in a "designer diamond anvil" program, and plan to measure changes in magnetic susceptibility (and thus magnetic moment) across the collapse in Gd and other rare earths. P. Springer's group is collaborating with SNL to use their Z machine to launch isentropic compression waves into Pr, with the potential to cross the collapse boundary in the solid and then move to the adjacent liquid, using VISAR wave profiles as the initial diagnostic.

This proposal suggests two complementary thrusts coupled to this wide ranging experimental attack. First, we propose to use the unique DOE/NNSA laboratories to study correlation driven changes in transition metal oxides (TMOs) and half-metal magnets (HMMs). The physical phenomena in these systems are closely related to those in rare earth materials already being studied. Indeed, in some cases the simpler physics in the TMOs and HMMs might provide very useful guidance to the rare earth experiments. A U.C.D. graduate student, resident primarily at LLNL in the group of C.-S. Yoo, will carry out this work under the joint guidance of Yoo and the U.C.D. PIs.

Second, we propose the application of recently developed theoretical methodologies to provide a unified understanding for all three classes of materials. Here, theory can also play a crucial role in iterating with the experimentalists as to the best choice of material, regimes, and diagnostics. Theoretical work will be conducted by a post-doctoral researcher and the PIs. The post-doc and one of the PIs will spend substantial portions of the summer resident at LLNL, where the PI already has an office at the Materials Research Institute.

Volume Collapse Transitions in the Lanthanides and Actinides: A number of Actinides and Lanthanides exhibit phase transitions under pressure characterized by abnormally large volume changes and usually also accompanied by loss of the magnetic moment. A quantitative description of the phenomenon is lacking, and even the underlying physical mechanisms are unsettled. Quantitative data for these systems is important: Defense Programs maintains a

strong interest in the Actinides, and the Lanthanides provide an unclassified analog. The two main conjectures for the origin of the volume collapse are a "Mott" transition in which high pressure causes an increased overlap between initially localized f orbitals and a resulting change to a metallic phase. This band–widening also causes the destruction of local magnetic moments. The competing "Kondo volume collapse" mechanism suggests instead that the important pressure–induced change is in localized–valence electron coupling. An abrupt reduction in volume occurs as the moments are screened by the increased hybridization.

Diamond anvil efforts at LLNL are poised to make definitive contributions to these issues. The group headed by Yoo can measure the volume change as a function of temperature and also get related spectroscopic data. The group of Weir and Akella has begun measurements of the temperature dependence of the magnetic susceptibility in Gd and Pr from which detailed information about the moment and its screening can be extracted.

The integrated theory effort proposed here couples tightly with these experiments. Measurements of the slope of the transition curve and the volume change directly yield the change in the entropy which we have extracted from Quantum Monte Carlo and Dynamical Mean Field studies of Ce. At the same time, our theoretical work has focussed on the existence and screening of the moments, and on antiferromagnetic order, which can now be measured for the first time. Finally, the appearence of a Kondo resonance in the electronic density of states is closely associated with the magnetic properties and volume collapse. In short, this new capability offers a unique opportunity to put together theory and experiment to get a complete picture of the volume collapse.

Mott Transitions in Transition Metal Oxides: The f-electron phenomenon described above have closely related parallels in transition metal oxides (TMOs) like FeO and MnO, materials which have important geophysical implications for the earth's structure. MnO, for example, transforms from the antiferromagnetic insulating phase at ambient conditions directly to a metallic phase, at 70–100 GPa. The fundamental causes of this behavior are likely closely related to the Lanthanides and Actinides, since the TMOs appear to have the same strong on–site Coulomb repulsion. Hence our theoretical tools for exploring strong correlation effects will be vital here. As with the volume collapse transitions, spectroscopy and susceptibility measurements will provide a key experimental diagnostic. But the metal–insulator character of the TMO phase transitions offers a very interesting complement to the rare earth work, since conductivity is likely to provide a cleaner probe of the transition than ones which look solely at the magnetism. The experimental work on the TMOs which will be undertaken in this proposal thus has the potential to provide a simpler route to the first observation of pressure induced paramagnetic–antiferromagnetic transitions, one of the long-term objectives of the Weir group.

Half-Metallic Magnetism: To date, there has been virtually no use of pressure to study the half metallic ferromagnetic state, in which electrons with one spin direction are metallic while those for the other direction are gapped. The position of the Fermi level of the metallic channel within the gap of the non-metallic channel will vary with pressure, allowing one to probe the half metal-to-normal metal transition. Prime candidates are Fe_3O_4 and CrO_2, for which the ambient pressure characteristics are relatively well studied. For Fe_3O_4, at least, strong electron correlations are present, and spectroscopy under pressure provides an ideal means to observe the transition. The specific experimental measurements here will be to

study both the change in the high-pressure electrical conductivity and the change in the high-pressure magnetic susceptibility as one or more of the two different band gaps close.

We plan a novel procedure to *create* a half metallic ferromagnet with the use of pressure. A ferromagnetic insulator has, in general, a different band gap for up and down spin directions. Under the application of pressure, one spin direction will metallize due to gap closure before the other, resulting in the half metallic state. Although ferromagnetic insulators are not common, several are known, and candidates include EuO and EuS, which are structurally simple but involve a lanthanide atom, or Cr compounds such as the Cr trihalides, which are structurally more involved but may metallize more readily under pressure.

2. Importance to Relevant Area of Technical Scope/ Overall Scientific Vitality

The work described falls under the SSAAP category of "Properties of Materials under Extreme Conditions and Hydrodynamics" in a clear way. Indeed, we believe the project addresses some of the most exciting current experimental and theoretical work in this area. The three classes of materials are individually of central importance. The TMO's have long occupied a paradigmatic place in attempts to understand metal-insulator and magnetic phase transitions. Volume collapse transitions in the lanthanides and actinides are similarly the focus of considerable interest. Half-metallic magnets, if observed, would constitute discovery of materials which have truly unique properties. The parallel study of these systems promises to yield insight into their behavior beyond that possible in isolation. At the same time, the theoretical methodologies are at the forefront of the condensed matter physics communities efforts to develop *ab initio* approaches to solids in which electron interactions play an important role.

3. Scientific Approach/Equipment Needed

It is not anticipated that major equipment needs will arise for the experiments proposed, which will use existing LLNL facilities. Likewise, computational aspects of the theoretical efforts will be supported through existing machines and supercomputer grants available to the PIs. We focus here on describing the theoretical approach.

It is generally acknowledged that understanding volume collapse, TMO, and HMM systems will require both an accurate treatment of the electronic band structure and the strong correlations among the electrons. The theoretical work to be undertaken in this project begins with the full band structure, but then employs three levels of treatment of the electron-electron interactions. First, density functional calculations will be done in which the local density energy functional is augmented by a Hubbard-like term:

$$E_{LDA+U} = E_{LDA}[n] - \frac{1}{2}U\sum_i \sum_{ms\neq m's'} n_{ims}n_{ims} + \frac{1}{2}\sum_i \sum_{ms\neq m's'} U_{m,m'}\hat{n}_{ims}\hat{n}_{im's'}, \qquad (1)$$

where i denotes the lattice site, and n_{ims} is the site charge for orbital m and spin s. This functional is minimized by iteratively adjusting the spin and orbital occupations as well as the itinerant states. For a number of magnetic insulators, this LDA+U method has produced remarkable improvements in the description of the electronic state, and therefore will provide a good starting point for our theoretical work.

Next, we will combine LDA treatment of the band structure with a dynamical mean field theory (DMFT) of the correlations which improves upon LDA+U by allowing particle densities to vary in time (but still not spatially). More specifically, one treats Hamiltonians,

$$H = \sum_{\mathbf{k},lm,l'm',\sigma} (H^0_{\rm LDA}(\mathbf{k}))_{lm,l'm'}\, \hat{c}^\dagger_{\mathbf{k}lm\sigma}\hat{c}_{\mathbf{k}l'm'\sigma} + \frac{1}{2}U_f \sum_{i,m\sigma,m'\sigma'}{}' \hat{n}_{ifm\sigma}\,\hat{n}_{ifm'\sigma'}\,, \qquad (2)$$

where $\mathbf{k}$ are Brillouin zone vectors, i are lattice sites, lm denote the angular momentum, σ is the spin quantum number, $\hat{n}_{ifm\sigma} \equiv \hat{c}^\dagger_{ifm\sigma}\hat{c}_{ifm\sigma}$, The matrices $H^0_{\rm LDA}(\mathbf{k})$ denote the matrix elements of the LDA Hamiltonian w.r.t. the full many-orbital problem for the material in question, and the interactions are treated by replacing the momentum- and frequency-dependent Green's function by one integrated over momentum. The resulting single site problem is then solved with QMC. Algorithms our group has already successfully applied to Cerium will be extended to more general forms of the Coulomb operator to include Hund's rule and spin-orbit terms before application to the full set of rare earths can be fully undertaken.

Finally, multi-orbital determinant QMC calculations which include the full momentum and frequency dependence of the self-energy will be undertaken. So far, such studies have been completed only for model Hamiltonians with between one and three orbitals. We hope to extend them to the more complex volume collape, TMO, and HMM systems. This approach is the most difficult computationally, but yields, finally, an exact treatment of the interactions. Careful comparisons of the results of the three methodologies will help determine the range of validity of the faster, but approximate approaches.

4. Mechanism of Interaction with NNSA/DP Laboratory Personnel

The PI's already have close ties with LLNL staff scientists, including an ongoing collaboration on a smaller aspect of this project. Geographic proximity allows frequent visits. The graduate student will be doing experimental work and will therefore be in residence at the LLNL experimental facilities for extended periods. The senior UCD and LLNL investigators will have a monthly meeting to maintain close contact. One UCD PI (Scalettar) will spend one month in the summer at LLNL where he has an office in the Material Research Institute.

5. Anticipated Results

The overall objective of this project is a quantitative description of the correlation-driven phase transitions in the Lanthanides, transition metal oxides, and half-metallic magnets. The centerpiece is a combination of new experimental diamond anvil results for $V(P,T)$, the magnetic susceptibility, and spectroscopy, with theoretical calculations from which these same quantities can be obtained. Theoretical work will model Lanthanide experiments currently underway in the Yoo/Weir/Springer groups, and also new, closely related experiments which are proposed on TMOs and HMMs. The success of the theoretical work rests on improvements in DFT and QMC methods and in techniques for putting them together, which have recently been pioneered and which we have applied successfully to Ce. Detailed milestones are presented below.

6. Project Schedule and Milestones

YEAR ONE:

- Baseline LDA+U calculations for TMOs and HMMs to determine best candidate materials.
- Initial experiments on most promising TMO and HMM systems determined above.
- Continue DMFT studies of Ce and make quantitative contact with diamond anvil studies of spectroscopy and magnetic susceptibility currently under way in Yoo/Weir groups.

• Extend DMFT algorithms to include full complexity of Coulomb operator (Hund's rule and spin-orbit coupling) in preparation for application to full set of volume collapse systems.
• Development of full multi-orbital determinant QMC code.

YEAR TWO:
• Continue experimental work on TMOs and HMMs. Measure conductivity and ac susceptibility to provide two independent diagnostics of transition.
• DMFT studies of TMO and HMM systems to validate and extend results of LDA+U.
• Begin DMFT studies of complete set of lanthanide systems (Gd, Ds, Tb) using generalized DMFT codes. Initial comparison to equation of state and magnetic susceptibility measurements.
• Begin detailed comparisons of full determinant QMC and DMFT codes.

YEAR THREE:
• Continue detailed comparison of theoretical DMFT studies to rare earth equation of state and magnetic susceptibility measurements.
• Continue detailed comparison of theoretical DMFT studies to TMO and HMM equation of state and magnetic susceptibility measurements.
• Full determinant QMC calculations for representative volume collapse, TMO, or HMM system. Evaluate effect of LDA+U and DMFT approximations.

7. Budget

Funding is requested for three years, with the same budget items each year. The year one budget is adjusted up by two percent for inflation in years two and three.

Summer Salaries Scalettar/Pickett (0.5 month each)	$ 11,730
Post-Graduate Researcher	$ 32,000
Graduate Research Assistant	$ 19,023
Benefits	$ 7,594
Total Salaries, Wages, and Benefits	$ 70,347
Travel (domestic)	$ 2,000
Fee Remission	$ 5,026
Total Direct Costs	$ 77,373
Indirect Costs (48.5%)	$ 37,526
Total Request, Year One	$ 100,279
Total Request, Year Two	$ 102,285
Total Request, Year Three	$ 104,330
Cumulative Request, Years One-Three	$ 306,853