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

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A. SUMMARY OF PROJECT GOALS

This project involves research into the thermodynamic properties of f -electron metals, transition metal oxides, and half-metallic magnets at high pressure. These materials are ones in which the changing importance of electron-electron interactions as the distance between atoms is varied can tune the system through phase transitions from localized to delocalized electrons, from screened to unscreened magnetic moments, and from normal metal to one in which only a single spin specie can conduct. Three main thrusts are being pursued: (i) Mott transitions in transition metal oxides, (ii) magnetism in half-metallic compounds, and (iii) large volume-collapse transitions in f -band metals.

B. DETAILED TECHNICAL REPORT OF ACCOMPLISHMENTS

(i) Mott transitions in transition metal oxides:

The Mott insulator-metal transition of MnO at 110 GPa

Magnetic $3d$ transition metal monoxides (MnO, FeO, CoO and NiO) are typical Mott insulators at ambient conditions and have been predicted to transform into metals with large 10-20% volume collapses above 100 GPa.[1] These volume collapse transitions are also predicted to be associated with a loss of magnetic moment, although such a ‘magnetic collapse’ has never been detected in any of these $3d$ transition metal monoxides. In fact, the previous results on FeO are highly controversial in this regard: is FeO is a low-spin metal above 90 GPa[2] or a Mott insulator even at 140 GPa [3]? To help understand this issue, we have determined the change in magnetic moment in MnO across the volume collapse transition by using high-resolution x-ray emission spectroscopy (XES) and angle-dispersive x-ray diffraction (ADXRD) at the Advanced Photon Source (APS). The experimental work was complemented by LDA+U studies of the moment and volume collapse in MnO, and ongoing work using dynamical mean field theory (DMFT).[4]

Our key experimental accomplishment this year was the completion of high-resolution x-ray emission spectroscopy and angle-resolved x-ray diffraction studies of highly compressed MnO, and the presentation of strong evidence for an isostructural, first-order Mott transition in MnO at 105 ± 5 GPa.[5] The pressure-induced structural/spectral changes provide a coherent picture of MnO phase transitions from paramagnetic B1 to antiferromagnetic distorted B1 at 30 GPa, to paramagnetic B8 at 90 GPa, and to diamagnetic B8 at 105 ± 5 GPa. The last is the Mott transition, accompanied by a complete loss of magnetic moment, a 6.6% volume collapse and a visual appearance change to metallic luster consistent with recent resistivity measurements. Figure 1 illustrates the MnO P-T phase diagram based on this project’s high pressure experiments. This will be one of the central parts of the doctoral thesis of UCD graduate student Brian Maddox.

Figure 1. The conceptual phase diagram of MnO based on this project’s static high pressure data (open circles), previous shock data (star), and the ambient-pressure Néel temperature. The thick phase line signifies the first-order isostructural Mott transition which simultaneously accompanies loss of magnetic moment, a large volume collapse and metallization. This transition line should end in a critical point (solid circle). The gray fan above the critical point represents a region of smooth crossover to metallic behavior at high temperature.

The theoretical focus for this year (an intermediate step on the way to carrying out full dynamical mean field theory (DMFT) calculations) has been to study the behavior of MnO under pressure with the LDA+U correlated band approach.[6, 7] We have in addition chosen MnO as the prototype of a study supported by DOE’s Computational Materials Science Network (CMSN) to compare different methodological approaches of “correlated band theory.” The methods being compared are: (1) LDA+U (results reported below),

(2) the “hybrid functional” method in which $\sim 25\%$ Hartree-Fock exchange is used with $\sim 75\%$ local density exchange in an otherwise local density functional procedure, and (3) the pseudopotential-based self-interaction correction (pSIC) approach. Each method in fact obtains a high-spin to low-spin transition under pressure; we concentrate here only on our LDA+U results.

It has been known for several years that LDA is seriously in error in describing the pressure evolution of MnO: the gap closes much too soon as the volume is decreased, incorrect occupation of states results, and the moment decreases at too low a pressure, and finally vanishes continuously.[8] Our recent LDA+U predictions are very encouraging and also quite surprising: (a) a volume collapse transition within the rocksalt phase is obtained, at about the same volume ($V/V_0 \sim 0.7$) as the volume collapse observed experimentally (under this project), and (b) the collapse from the low pressure $S=\frac{5}{2}$ insulating phase is to an $S=\frac{1}{2}$ insulating phase rather than to a nonmagnetic metallic phase as might have been expected. Within these antiferromagnetic (AFM) LDA+U studies, the local site symmetry of the Mn ion is found to be important. The e_g, t_{2g} crystal field splitting is disrupted already by AFM ordering, which changes the symmetry to rhombohedral. The crystal field splittings are now $e_g, t_{2g} \rightarrow e_g, a_g, e'_g$, and in addition the e_g and e'_g representations mix (they have identical symmetry, the prime merely distinguishes the two). This work will comprise one of the central parts of the doctoral thesis of UCD graduate student Deepa Kasinathan.

Figure 2. Calculated LDA+U volume-collapse and moment-collapse transition within the rocksalt phase of MnO, which occurs at $a/a_0 = 0.89$ ($V/V_0 = 0.70$). Note that the moment collapse is from $S=\frac{5}{2}$ to $S=\frac{1}{2}$ rather than to nonmagnetic. The volume collapse calculated from the two equation of state curves is about 7%.

While this mixing is interesting and rather nontrivial to sort out, the main physics is in the a_g orbital space; this orbital is the rhombohedral d_{3z^2-1} orbital, equivalent to the rocksalt t_{2g} linear combination $(d_{xy} + d_{yz} + d_{zx})/\sqrt{3}$. It is this orbital that remains spin polarized in the high pressure phase. The transition is $d_{\uparrow}^5 : t_{2g\uparrow} + e_{g\uparrow} \rightarrow d_{\uparrow}^3 d_{\downarrow}^2 : e_{g\uparrow}^* + e_{g\downarrow}^* + a_{g\uparrow}$. Here e_g^* denotes some combination of the two e_g doublets, determined by the interactions in the system. Work on this topic has now turned to a more serious addressing of the experimental data, which indicate there is a rocksalt (B1) $\rightarrow$ NiAs (B8) transition, and only then a volume collapse and moment drop within the NiAs-structure phase. Calculations so far indicate a strong dependence on the energy of MnO around 100 GPa on the magnetic order: in the inverse-NiAs structure *ferromagnetism* is favored, while in the NiAs structure AFM is favored. The AFM NiAs structure has the lower energy, however, in apparent agreement with experimental findings so far.

These results are proving an important guide in the DMFT calculations on MnO that are now underway, and form the primary objective of our project for the transition metal oxides.

Not only is the inclusion of uncorrelated orbitals (O 2p) with the correlated ones (Mn 3d) crucial as the volume is decreased, but the site symmetry – cubic versus rhombohedral – is going to be essential, at least when the question of magnetic order is addressed. The DMFT calculations underway utilize both the full quantum Monte Carlo correlated-shell solution as well as the simpler, more transparent, but approximate Hubbard I solution.

(ii) Magnetism in Half-Metallic Compounds:

Pressure Driven Structural Transformation in Half Metallic CrO₂

The allure of the half metallic state is strong both for spintronic applications and for fundamental understanding of this unique form of matter. A half metallic ferromagnet is magnetically ordered, but with carriers of one spin direction being metallic while those of the other direction are gapped (“insulating”) the half metal lies in a state that is intermediate between magnetic insulators and conventional metallic magnetic alloys. The half metal to normal ferromagnet (HM-NFM) transition pressure has yet to be studied carefully in any half metal, but CrO₂ with its relatively simple crystal structure provides one of the more promising possibilities. Pressures available in diamond anvil cells are likely to shift bands substantially, with the possibility of a HM-NFM transition.

UCD graduate student Brian Maddox has investigated CrO₂, a half metallic transition metal oxide to high pressures (up to 60 GPa) and low temperatures (down to 10 K) using both x-ray diffraction and Raman spectroscopy. It is found that CrO₂ undergoes a structural phase transition from a half-metallic *rutile* structure to a (possibly normally) metallic CaCl₂ structure at about 12±3 GPa. The system shows an unusual *increase in compressibility* in the high pressure phase. Raman spectroscopy shows evidence of soft-mode behavior, as well as the possibility of a second transition at 30 GPa leading to a new Raman peak.

Band structure calculations by student Deepa Kasinathan performed in conjunction with these experiments are assessing the likelihood that the electronic half-metal to normal-metal transition also occurs at this phase change. The possibility that movement of the Fermi level across the minority conduction band edge can provide the driving force for the transition is being pursued. Calculations and preliminary analysis suggests that CrO₂ (ambient pressure) is truly half metallic only below $T^* \approx 150$ K, so experiments below T^* will be crucial for observing the HM-NFM crossover.

(iii) Large volume-collapse transitions in *f*-band metals

Dynamical Mean Field Theory calculations for compressed Ce, Pr, and Nd

The behavior of *f*-electron metals under pressure offers many problems of long-standing interest concerning the effects of electron correlation on materials properties. 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?[9–11] 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?

During this year we have refined calculations for compressed Ce (4f¹) and extended this study to Pr (4f²) and Nd (4f³) using a combination of the local-density approximation (LDA)

and dynamical mean field theory (DMFT), or LDA+DMFT.[12] This work extended significantly earlier work on Ce alone.[13, 14] The 4f moment, spectra, and the total energy among other properties were examined as functions of volume and atomic number for an assumed face-centered cubic (fcc) structure. These materials were seen to be strongly localized at ambient pressure and for compressions up through the experimentally observed fcc phases (γ phase for Ce), in the sense of having fully formed Hund's rules moments and little 4f spectral weight at the Fermi level.

Figure 3. Evolution of the Pr 4f density of states under pressure (the volumes are noted); dashed and shaded lines denotes the $j = \frac{5}{2}$ states, solid lines denote the $j = \frac{7}{2}$ states. The Abrikosov-Suhl resonance at the chemical potential (μ) grows quickly for volumes below $25 \text{ \AA}^2$. These LDA+DMFT calculations were carried out at 632 K.

Subsequent compression for all three lanthanides was found to bring about significant deviation of the moments from their Hund's rules values, a growing Kondo resonance at the Fermi level, an associated softening in the total energy, and quenching of the spin-orbit splitting since the Kondo resonance is of mixed spin-orbit character while the lower Hubbard band is predominantly $j = 5/2$. The calculated spectrum under pressure for Pr is shown in Fig. 3, where the degradation of spin-orbit splitting and growth of the Fermi level resonance can be followed. While the most dramatic changes for Ce occur within the two-phase region of the γ - α volume collapse transition, as found in earlier work, those for Pr and Nd occur within the volume range of the experimentally observed distorted fcc (dfcc) phase, which is therefore seen here as transitional and not part of the localized trivalent lanthanide sequence. The experimentally observed collapse to the α -U structure in Pr occurs only on further compression, and no such collapse is found in Nd. These lanthanides start closer to the localized limit for increasing atomic number, and so the theoretical signatures noted above are also offset to smaller volume as well, which is possibly related to the measured systematics of the size of the volume collapse being 15%, 9%, and none for Ce, Pr, and Nd, respectively.

The f -band electronic structure of Gd at high pressures

We have investigated the electronic structure change of Gd to 113 GPa in a diamond anvil cell, by using resonant inelastic x-ray scattering (RIXS) at HPCAT/APS.[15] Utilizing the resonance at the LIII-absorption edge of Gd, we were able to probe the dipole allowed $3d - 5d$ transition as well as the quadrupole $3d - 4f$ transition as a function of pressure. The degree of 4f electron correlation should manifest as a change in relative intensity of 4f and 5d transition peaks.

Magnetic correlations in “nonmagnetic” Eu^{3+} : EuN and EuP

The nominally nonmagnetic Eu^{3+} ion ($4f^6$, $S=3$, $L=3$, $J=0$) is enigmatic for theorists trying to calculate its electronic structure and its implications. It is “nonmagnetic” because its $J=0$ Hilbert space is too poor to describe any vector (*i.e.* any direction). Its magnetic moment $\vec{M} = \mu_B(\vec{L} + g_s\vec{S})$ is actually large in magnitude; more particularly for theory, its spin polarization $\vec{S}^2 = 3 \times 4 \mu_B^2$ is very large, and it cannot be ignored in an electronic structure calculation. Once it is included, it is natural to consider exchange coupling between the spins. In fact, it is our contention that not only is there such an exchange coupling in spite of the $J=0$ Hilbert space, but that the way to probe this spin-spin coupling is to use pressure.

We are pursuing the many questions this raises within the context of the rocksalt structure compounds EuN and EuP . Both compounds are ionic [$\text{Eu}^{3+}\text{Pn}^{3-}$, Pn denotes pnictide] semimetals or narrow-gap semiconductors similar to isovalent GdN . The valence bands derive from Pn $2p$ states and conduction states from Eu $5d$ states primarily. We requested and obtained EuN powders from Frank DiSalvo’s group at Cornell, with C. S. Yoo and Brian Maddox carrying out pressure studies. Note that Eu metal is of strong interest in itself for this program: pressure provides the opportunity to observe and analyze a $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ valence transition.

Experimental characterization (Cornell group) on the powder EuN samples showed them to have metallic-like temperature dependence, so this compound is semimetallic like several other trivalent mononitrides. The susceptibility has the van Vleck increase below room temperature similar to other Eu^{3+} materials. Pressure studies by Maddox and Yoo reveal Raman peaks detected at 13 GPa and above (the B1 phase has no Raman-active modes), and a $\text{B1} \rightarrow$ tetragonal transition at 700 GPa. Analysis of compressed EuN is ongoing.

Figure 4. The magnetic susceptibility of the two-site model with various strengths of spin-spin interaction K . The curve resembles a Van Vleck paramagnetic susceptibility for small K and smoothly evolves to an AFM-like susceptibility curve when K dominates.

On the theoretical side, the calculated Eu-Eu exchange coupling using the LDA+U functional is found to be ferromagnetic at ambient pressure, increasing slowly in magnitude with compression. On the other hand, the exchange coupling in EuP is AFM in sign and a factor of ~ 5 larger at ambient pressure, decreasing somewhat with compression. Using a two-site model

$$H = K\mathbf{S}_1 \cdot \mathbf{S}_2 + \lambda \sum_i \mathbf{L}_i \cdot \mathbf{S}_i - \sum_i \mathbf{M}_i \cdot \mathbf{B} + \sum_i (\mathbf{D} \cdot \mathbf{L}_i)^2$$

with exchange coupling constant K , spin-orbit coupling λ , single-ion anisotropy $\vec{D}$ and magnetic field $\vec{B}$, we have studied the dependence of the spin-spin and moment-moment correlation functions, the magnetization, and the susceptibility on the relative magnitudes of K , λ , and D . The behavior of the susceptibility with strength of the exchange coupling (which varies with pressure) is shown in Fig. 4. The sensitivity of this Van Vleck susceptibility provides one means of detecting variation of the exchange coupling with pressure.[16]

(iv) Other Related Work

Pressure-driven nonmagnetic $\rightarrow$ ferromagnetic transition in CoN at 43 GPa

Although transition metal nitrides might be expected to retain several chemical and physical similarities to the oxides, they have been studied far less. The mononitrides show structural similarities to the monoxides (B1 rocksalt structure being common in both), but their physical properties differ considerably. The main sources of these differences are the electronegativity (less for N than for O) and the fact that nitrogen requires three extra electrons to form a closed shell whereas oxygen requires only two. The N^{3-} ion should be highly polarizable. In fact mononitrides differ strongly from monoxides: insulating behavior, magnetic transitions under doping, temperature, and pressure, and strongly correlated behavior are the norm in the monoxides, but mononitrides typically are metallic and weakly correlated.

Figure 5. Left: The calculated moment versus volume for rocksalt CoN; note the apparent first order transition is verified by the fixed spin moment calculations in the right panel. Right: The energy versus fixed (imposed) spin moment for rocksalt CoN at $1.2V_0$. The double minimum structure reveals the cause of the moment collapse in the left panel: as the volume changes, the positions of the minima remain fixed but the energies at the minima change, and the volume at which the minima are degenerate marks the critical volume. Note the very small energy scale, which accounts for the calculated values not lying on a completely smooth curve.

Thin films of CoN_x were reported some time ago by Matsuoka, Ono, and Inukai.[17] Unlike the bulk materials of Suzuki *et al.*[18] their films were ferromagnetic (they reported hysteresis curves and coercive fields). Very interestingly, the magnetic moment showed a strong perpendicular anisotropy, a property that has long been of great interest to the

magnetic recording industry and is receiving renewed attention due to possible spintronics applications. The source of the magnetism, whether intrinsic, induced by strain, or induced by N vacancies, was not determined, partially due to the multiphase nature of the films.

In last year's report we noted that zincblende structure CoN is strongly favored energetically[19] over the B1 structure at ambient pressure, and a nonmagnetic-to-ferromagnetic transition (a very unusual occurrence) is predicted at 43 GPa. In Fig. 5 the evolution of the moment with pressure within the B1 phase is shown; there is a rapid drop initially and then a moment collapse (to a smaller but nonzero value) around 4% compression. The explanation of the collapse is also shown in Fig. 5, where the energy versus (fixed) moment in the region of the moment collapse (calculated by Deepa Kasinathan) shows a double-minimum shape. The moment collapse corresponds to a first-order transition between these two minima. The maximum of energy between the two minima has been traced to the energetically unfavorable positioning of the Fermi energy in a narrow peak in the minority density of states. A report of this study has been submitted for publication.

Figure 6. X-ray Raman spectra of α , β , and γ phases of Li_3N shown in black, with statistical uncertainties denoted by bars. Nitrogen $2p$ projected densities of states (solid red curve) are shown beneath the experimental curves, offset by 394.2 eV; occupied valence states (in the calculation) are shown as dashed lines, and the vertical line indicates the Fermi energy. The changes in spectra from $\alpha \rightarrow \beta \rightarrow \gamma$ phases are reproduced remarkably well by the calculations, providing detailed understanding of the structure of each phase.

High pressure structural phase transition in Li_3N

Using diamond anvil cell technology UCD graduate student Amy Lazicki discovered a new cubic (Fm3m) γ phase of Li_3N at 40 GPa while carrying out a study of the structure and XRS spectra up to 200 GPa using synchrotron x-ray diffraction and inelastic x-ray Raman scattering techniques. Lazicki has also carried out first principles calculations that predict a factor-of-five widening of the bandgap at the $\beta - \gamma$ transition that is consistent with the observed color change, and the agreement of the x-ray Raman spectra with Lazicki's calculated density of states of each phase, shown in Fig. 6, is spectacular. The calculations further predict that metallization of this highly ionic compound will not occur until ~ 8 TPa. The high structural stability, wide bandgap, and simple electronic structure of γ - Li_3N are analogous to those of lower valence closed-shell solids such as Ne (neutral atoms), NaCl (monovalent ions), and MgO (divalent), meriting its use as a low-Z internal pressure standard. This work has been submitted to *Physical Review Letters*.

High pressure structural phase transition in Lithium Oxide Li_2O

Our mapping of the pressure phase diagram of Li_3N is being followed by study of the

related ionic low-Z system Li_2O , which is one of the simplest oxides and is of interest partially because of its superionic character above 1300 K. An angular dispersive x-ray diffraction study, accompanied by laser heating up to ~ 2000 K, has been carried out by Amy Lazicki. This work has provided the equation of state in the low pressure antiferroite phase, and identified structural transitions at 20 GPa and around 48 GPa. The first transition is probably antiferroite-to-antiferroite as reported previously for Li_2S ; this phase has six Raman-active modes (ferroite has only one). The higher pressure phase seems to be complex, and has ten Raman modes. The feasibility of probing the superionic transition around 1300-1400 K is being pursued.

Charge disproportionation and spin differentiation in Na_xCoO_2 .

Takada and coworkers reported[20] two years ago a remarkable finding: they took as-made (using common ceramic methods) Na_xCoO_2 , $0.65 < x < 0.85$, chemically de-intercalated the Na content down to $x \approx 0.3$, and then washed the sample in water and dried it. The result was a superconductor at 4.5 K. It is not a superconductor without the H_2O , which insinuates itself into the lattice to form $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3 \text{H}_2\text{O}$. Similarities to the high T_c cuprates were striking: the superconducting layer is a 2D transition metal oxide layer; carrier concentration is variable and the right concentration is essential to the superconductivity; in both systems the transition metal is near its upper limit of oxidation state. Distinctions between the systems are also clear: the transition metal lies on a triangular lattice (frustrated for near neighbor antiferromagnetic coupling) rather than a square lattice (bipartite, which strongly encourages AFM), and the $3d$ bands are much narrower in the cobaltate.

In our 2004 report we related several aspects of our theoretical work on this system, most notably the discovery that charge disproportionation ($2\text{Co}^{3.5+} \rightarrow \text{Co}^{3+} + \text{Co}^{4+}$) as the Coulomb repulsion U is varied.[21] This disproportionation is observed for $\text{Na}_{0.5}\text{CoO}_2$,[22] accompanied by antiferromagnetic ordering and the open of a small gap. The result is particularly relevant to this project: variation of U is one way to adjust the ratio the interaction strength to the bandwidth, but this ratio can equally well be changed using pressure. We are advocating such experiments in specific ranges of the Na_xCoO_2 phase diagram. This theoretical development, and close comparison to experimental data, has allowed us (1) to determine that U depends on the carrier density (concentration x of Co), and (2) to obtain an upper bound on $U(x)$ and thereby a reasonable estimate of $U(x)$. Briefly, our more recent contributions also include:

- our early contention was that the regime $s \sim \frac{1}{3}$ is not strongly correlated and that there was no reason for a “superconducting dome” in the phase diagram in that region. Several studies have now confirmed that some of the intercalated water undergoes a chemical reaction, releasing $(\text{H}_3\text{O})^+$ which dopes the system just as Na^+ does. These studies all suggest the Co oxidation state is in the range corresponding $x_{\text{eff}} = 0.55\text{-}0.60$, *i.e.* somewhat electron-doped from the $x = \frac{1}{2}$ antiferromagnetic insulating phase.
- we have found that our LDA+ U calculations reproduce the AFM insulating phase at $x = \frac{1}{2}$ as seen experimentally; analysis of this result is ongoing.
- armed with the experimental information that the $x \rightarrow 0$ compound is a nonmagnetic metal (not a magnetic insulator that had been guessed by many), we have concluded from our computational study of CoO_2 that the system is most likely in a *three-band* regime and hence only weakly correlated.

C. PROGRESS TOWARDS TECHNICAL MILESTONES

Project is on track to meet technical milestones:

Task i: Mott Transitions in Transition Metal Oxides: The correlated band approach (LDA+U) is leading to very encouraging results for the representative Mott insulator MnO: a first order volume collapse transition at the observed volume, accompanied by a collapse in the moment from $S=5/2$ to $S=1/2$. This work is however in the rocksalt structure, and calculations will in the third year be extended to the NiAs structure which is where the volume collapse transition actually occurs. Collaboration and detailed comparison with two groups using other correlated band approaches (pSIC and hybrid functional) on this same system (MnO) is allowing us to identify the more promising aspects of each method. Two different but related dynamical mean field theory codes have been written, tested, and applied to MnO. Unexpected results necessitated going back to model systems, where important results were obtained for Mott transitions for systems containing both correlated and uncorrelated states (this is after all the most common, practically ubiquitous, situation). The codes are now being applied to the systems of interest for this grant: initially MnO (following our LDA+U study), followed by another $3d$ transition metal monoxide. One of these codes will also be applied to the layered superconductor Li_xNbO_2 to assess the extent of correlation effects in this little studied (so far) layered metal oxide superconductor.

Task ii: Half-Metallic Magnetism: Student Brian Maddox has investigated CrO_2 , a half metallic transition metal oxide to high pressures (up to 60 GPa) and low temperatures (down to 10K) using both x-ray diffraction and Raman spectroscopy. It is found that CrO_2 undergoes a structural phase transition from a half-metallic *rutile* structure to a (possibly normally) metallic CaCl_2 structure at about 12 ± 3 GPa. The system shows an unusual *increase in compressibility* in the high pressure phase. Raman spectroscopy shows evidence of soft-mode behavior, as well as the possibility of a second transition at 30 GPa leading to a new Raman peak. Band structure calculations by student Deepa Kasinathan were performed in conjunction with these experiments to assess the likelihood that the electronic half-metal to normal-metal transition also occurs at this phase change. The possibility that movement of the Fermi level across the minority conduction band edge can provide the driving force for the transition is being pursued. A manuscript is nearing completion.

Task iii: Volume Collapse Transitions in the Lanthanides: The pre-grant calculations [10, 13, 14] of the volume-collapse transition in compressed Ce ($4f^1$) has been followed by analogous studies of Pr ($4f^2$), and Nd ($4f^3$) to assess trends and identify separate issues in these heavier rare earth metals. In this LDA+DMFT method, the $4f$ moment, spectra, and the total energy (and microscopic properties) are examined as functions of volume and atomic number for an assumed face-centered cubic (fcc) structure. These materials are localized at ambient pressure and remain so for compressions up through the experimentally observed fcc phases (γ phase for Ce), in the sense of having fully formed Hund's rules moments and little $4f$ spectral weight at the Fermi level. Subsequent compression for all three lanthanides leads to a localized $\rightarrow$ delocalized crossover, based on their Hund's rules values, a growing Kondo resonance at the Fermi level, an associated softening in the total energy, and quenching of the spin-orbit splitting. This work represents a significant landmark in the progression of our project, and it is the leading work of its kind.

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PROJECT PARTICIPANTS/BREAKDOWN OF TIME DEVOTED TO THE PROJECT

Project Participant	Affiliation/Position	Percent SSAAP time
Amy Lazicki	Graduate Student, Physics, UCD	100%
Brian Maddox	Graduate Student, Physics, UCD	100%
Deepa Kasinathan	Graduate Student, Physics, UCD	50%
Karan Aryanpour	Postdoctoral Researcher, UCD	100%
Jan Kuneš	Postdoctoral Researcher, UCD	†
Andy McMahan	LLNL Staff Scientist	‡
Warren Pickett	Professor, Physics, UCD	15%
Richard Scalettar	Professor, Physics, UCD	20%
Choong-Shik Yoo	LLNL Staff Scientist	‡

† Collaborator funded by other DOE sources.

‡ NNSA/DOE Collaborators funded by other sources.

D. PUBLICATIONS/PRESENTATIONS

Publications

- [1] C. S. Yoo, B. Maddox, J.-H. P. Klepeis, V. Iota, W. Evans, A. McMahan, M. Hu, P. Chou, M. Somayazulu, D. Hausermann, R. T. Scalettar, and W. E. Pickett, *First-order Isostructural Mott Transition in Highly Compressed MnO*. Phys. Rev. Lett. **94**, 115502 (2005); http://yclept.ucdavis.edu/Publ/MnO_PRL.pdf
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- [4] K.-W. Lee and W. E. Pickett, *Na_xCoO_2 in the $x \rightarrow 0$ Regime: Coupling of Structure and Correlation Effects*. Submitted to Phys. Rev. B (2005); arXiv:cond-mat/0505606
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- [7] B. Maddox, C. S. Yoo, D. Kasinathan, W. E. Pickett, and R. T. Scalettar, *Metallization and Second-Order Rutile-to- CaCl_2 Phase Transition in Half Metallic CrO_2 at High Pressure*. In preparation.
- [8] M. D. Johannes and W. E. Pickett, *Magnetic Coupling Between Non-Magnetic Ions: Eu^{3+} in EuN and EuP* , In preparation.

Presentations

- [1] A. Lazicki, *High Pressure Phase Transitions in Li_3N* , technical review for the Physics and Advanced Technology Directorate, LLNL (2005).
- [2] A. Lazicki, *High Pressure Phase Transitions in Li_3N* , HPCAT (high pressure collaborative access team) sector review, Advanced Photon Source, Argonne National Laboratory (2005).
- [3] D. Kasinathan, *Structural and Magnetic transitions in CoN under pressure*, 2004 American Physical Society March Meeting, Toronto. (contributed)
- [4] D. Kasinathan, *MnO Moment collapse : LDA+U study*, DOE Computational Materials Science Network Coordination Meeting, Oak Ridge, TN (2004). (contributed)
- [5] W. E. Pickett, *Charge Disproportionation and Spin Ordering in Na_xCoO_2* . 2004 American Physical Society March Meeting, Los Angeles. (invited)

- [6] D. Kasinathan, J. Kuneš, W. E. Pickett, R. T. Scalettar, B. Maddox, C.S. Yoo, A.K. McMahan, *LDA+U Picture of the Moment Collapse under Pressure in MnO*. 2005 American Physical Society March Meeting, Los Angeles. (contributed)
- [7] B. Maddox, W. E. Pickett, R. T. Scalettar, C. S. Yoo, A. K. McMahan, Paul Chou, and M. Hu, *RIXS across the volume collapse transition in Gd metal at high pressures*. 2005 American Physical Society March Meeting, Los Angeles. (contributed)
- [8] A. Lazicki, C. S. Yoo, W. E. Pickett, R. T. Scalettar, M. Somayazulu, and D. Hausermann, *High Pressure Structural Phase Transitions in Lithium Nitride*. 2005 American Physical Society March Meeting, Los Angeles. (contributed)
- [9] W. E. Pickett, *Correlation, Disproportionation, and Phase Diagram of Na_xCoO_2* . UC/LANL Workshop on “Complex Functional Oxides,” UCSB, May 2005. (invited)
- [10] W. E. Pickett, *Correlation Effects and Disproportionation in Na_xCoO_2 and Related 2D Oxides*. Conference on “Collective Quantum States in Low-Dimensional Transition Metal Oxides,” Dresden, February 2005. (invited)
- [11] W. E. Pickett, *Correlation and Disproportionation in Na_xCoO_2 and its Phase Diagram*. Uppsala University, April 2005. (seminar)
- [12] W. E. Pickett, *Advances in the Theory of Charge Disproportionation And Applications to Na_xCoO_2* . “New Materials Science: Kyoto/UCSB Workshop,” April 2005. (invited)
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- [14] W. E. Pickett, *Charge Disproportionation in Na_xCoO_2* . Workshop on “Inorganic Materials Chemistry in the UC System,” UCSB, August 2004. (invited)
- [15] K.W. Lee and W.E. Pickett, *Disproportionation Followed by Metal-Insulator Transition at Critical Interaction Strength in $\text{Na}_{0.5}\text{Co}_2$* . “12th Workshop on Computational Physics and Materials Science: Total Energy and Force Methods”, Trieste, Italy (2005). (poster)

E. FINANCIAL STATUS

Grant is on track financially. A financial status report (Form SF269) is being sent separately.