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. These volume collapse transitions are also predicted to be associated with a loss of magnetic moment, although such a ‘magnetic collapse’ has never been seen in any of these 3d transition metal monoxides. In fact, the previous results of FeO are highly controversial in this regard: is FeO a low-spin metal above 90 GPa[1] or a Mott insulator even at 140 GPa[2]? To help understand this issue, we have determined the change in magnetic moment in MnO across the volume collapse transition[3] by using high-resolution x-ray emission spectroscopy (XES) and angle-dispersive x-ray diffraction (ADXRD) at the Advanced Photon Source (APS).

Figure 1 illustrates the pressure-induced changes in the $K\beta$ emission spectra of MnO. The spectra can be classified into three groups depending on pressure: the first group below 30 GPa with the most dominant $K\beta'$ intensity (bottom), the second between 40 and 98 GPa where the $K\beta'$ intensity is substantially reduced yet still apparent (middle), and the third above 108 GPa where the $K\beta'$ lines nearly disappear (top). It is well known in many

FIG. 1: X-ray emission spectra of MnO in the $K\beta$ region obtained from the paramagnetic B1 phase at 11 GPa, antiferromagnetic distorted-B1 phase at 56 GPa, and diamagnetic B8 phase at 108 GPa. The $K\beta$ emission represents the core-hole decay from $1s$ to $3p$ in Mn^{+2} , which splits into two branches, $K\beta_{1,3}$ (7P) and $K\beta'$ (5P), as a result of $3p$ - $3d$ electron exchange interaction. While data for only three pressures are shown, in fact the spectra at many pressures have been obtained and all fall on top of one of the three shown. That is, the spectra remain relatively unchanged for a range of pressures, and then evolve suddenly between the different phases.

magnetic 3d transition metal oxides that the intensity the $K\beta'$ intensity is sensitive to the local magnetic moment. Therefore, the complete loss of the $K\beta'$ intensity above 108 GPa indicates a complete loss of magnetic moment in MnO. A small (≈ 1 eV) shift of the $K\beta_{1,3}$ band is also evident as the pressure increases from one to the other group. It is important to note that the pressure-induced spectral changes are subtle but occur abruptly at around 30 GPa and 108 GPa.

In our x-ray diffraction studies, we have further found structural phase transitions from cubic-B1 (NaCl-like) to rhombohedral-distorted-B1 at 30 GPa, to a mixture of distorted-B1 and hexagonal-B8 (NiAs) at 90 GPa, and finally to isostructural B8 at 110 GPa. The isostructural phase transition at 110 GPa is based on the observed discontinuous changes in both specific volumes and c/a ratio. The remnant of distorted-B1 phase, on the other hand, was observed well above 90 GPa to about 120-130 GPa. In contrast, the previous diffraction study suggested an “intermediate” phase in the pressure region between 90 and 120 GPa, without the characterization of crystal structure[4].

Together, these pressure-induced structural and spectral changes of MnO observed in this SSAAP project provide a coherent picture of a sequence of phase transitions from paramagnetic B1 to antiferromagnetic distorted-B1 at 30 GPa, to paramagnetic B8 at 90 GPa, and to diamagnetic B8 at 110 GPa. The 110 GPa transition is accompanied by a complete loss of magnetic moment, $\approx 7\%$ drop in specific volume, and a visual change to metallic luster. A complete discussion of this work has been submitted for publication.[3]

FIG. 2: Raman spectrum of CrO_2 -I at 4.2 GPa. The inset represents four Raman-active vibrational modes of this phase ($P42/mnm$), as looking down the c -axis. The low frequency shear-type B_{1g} libration mode is not apparent in the figure. The tetragonal-to-orthorhombic phase transition at 12 GPa is accompanied by the splitting of the E_g mode into B_{2g} and B_{3g} .

(ii) Magnetism in Half-Metallic Compounds:

Pressure Driven Structural Transformation in Half Metallic CrO_2

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”). Thus the half metal lies in a state that is intermediate between magnetic insulators and conventional metallic magnetic alloys. The half metal – to – normal metal (HM-NM) transition has yet to be studied carefully in any material, but CrO_2 with its relatively simple crystal structure and simple band 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-NM transition.

We have studied CrO_2 , a prototypical half-metallic system at ambient conditions, to 60 GPa by using Raman spectroscopy and angle-resolved x-ray diffraction at the HPCAT (16ID-B) at the APS. The Rietveld-refined x-ray diffraction data indicate that CrO_2 -I (Rutile, $P42/mnm$) transforms into CrO_2 -II (CaCl_2 , $Pnma$) at 12 GPa. Raman data also exhibit a splitting of the E_g mode at 12 GPa, which can be assigned to the B_{2g} and B_{3g} modes based on a factor group analysis of the CaCl_2 structure (Fig. 2). This structural phase transition is accompanied by a minor modification in crystal structure without any apparent discontinuity in specific volume: less than 1% difference in the a - and b -axis, while the c -axis remains unchanged. This distortion is most likely caused by the close contact distance in the $a - b$ plane of CrO_2 -I, resulting in mechanical instability of the lattice. Such a mechanical instability is often reflected in the softening of the low-frequency shear-type B_{1g} libration

mode (see the inset in Fig. 2) in many isostructural systems such as stishovite[5]. However, we were not able to probe the B_{1g} mode, because of its diminishingly weak Raman intensity near the Rayleigh line of near metallic CrO_2 at high pressures.

Subsequent band structure calculations indicate that half metallic character is lost in the high-pressure CaCl_2 phase. Therefore, we have conjectured that the movement of the Fermi level across the minority conduction band edge can provide the driving mechanism for the transformation. To confirm this possibility, we are also currently determining the conductivity of CrO_2 at high pressures.

(ii) large volume-collapse transitions in f -band metals

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

The merger of Local-Density Approximation (LDA) techniques with all of their numerical specificity and material realism and Dynamical Mean Field Theory (DMFT) has created an exciting new technique (LDA+DMFT) for the treatment of strong correlation in real materials[6]. We have previously used such calculations to investigate successfully the volume collapse transition in Ce [7]; and are presently extending this effort in two ways, first by including the spin-orbit interaction, and secondly by the examination of Pr and Nd in addition to Ce. As in our earlier work, these calculations still assume a scalar Coulomb interaction, the Hubbard U_f , although ultimately we seek to include all rotationally-invariant intra-atomic exchange terms. One of the most striking aspects of the new results is a quenching of the spin-orbit under compression, that is the $4f$ electrons change from being predominantly in the $j=5/2$ sub-shell at large volume to being roughly equally distributed among the $j=5/2$ and $7/2$ states at smaller volume. This change is fairly dramatic, and coincides with the on-site $4f$ moment $\langle J^2 \rangle$ decreasing from a large-volume constant value, characteristic of the local moment, as it approaches the value anticipated for uncorrelated f electrons at small volume. These changes begin in the vicinity of the collapse transitions in Ce and Pr, however, the detailed association with the volume collapse is still under investigation. While adding spin-orbit has in fact sharpened up somewhat our calculated isostructural collapse transition in Ce, the change in crystal structure across the Pr collapse, and the absence altogether of a collapse transition in the Nd data, both complicate matters and make the physics more interesting.

b. The f -band electronic structure of Gd at high pressures

The goal of this study is to develop an experimental technique to probe the f -band electronic structure in $4f$ rare-earth metals at high pressures. The information most relevant to electron correlation effects is contained in the M band (corresponding to the $3d - 4f$ transition in rare-earths) at approximately 1 keV. However, high-pressure investigation of such a low energy transition is not feasible by using a conventional x-ray absorption technique, because of strong x-ray absorption by the diamond and/or metal gasket. In fact, such low energy x-rays do not even penetrate through the bulk of f -electron metal samples, thus the studies have remained largely dominated by surface effects at ambient conditions.

In this study, utilizing an intense third-generation synchrotron x-ray, we have been able to resolve the low-lying x-ray band of Gd, for the first time, at high pressures (see Fig. 3). In this experiment, we used a high-energy (≈ 7 keV) incident x-ray beam near the LIII edge ($2p - 5d$ or quadrupole allowed $2p - 4f$ transitions) through an x-ray transparent Be gasket, and measured inelastically scattered x-ray photons at the resonance with the

FIG. 3: Resonance Inelastic X-ray Scattering (RIXS) of Gd at 8 GPa, plotted as a function of energy transfer ΔE between the incident x-ray energy W (marked on each spectrum) and the fluorescence x-ray fluorescence w . At each incident x-ray energy in the vicinity of LIII edge (corresponding to the quadrupole allowed $2p - 4f$ transition at 7.241 keV and the dipole allowed $2p - 5d$ transition at 7.247 keV) of Gd, the inelastically scattered x-ray photons were scanned in the vicinity of the La emission line (corresponding to the $2p - 3d$ core-hole decay at around 6.05 keV).

$3d - 4f$ transition. Figure 3 shows the $3d - 4f$ resonance at 7.241 keV nicely resolved from the $3d - 4d$ transition at 7.247 keV. Note that the dipole forbidden band can be observed in this way. More importantly, these bands are relatively sharp, because their band widths are dependent on life-time of the final state $3d$ core-hole, which is substantially longer than that of the $2p$. The spectral details, on the other hand, provide the fundamental information of crystal field splitting, spin-orbit coupling, and electron-electron exchange interaction and, thus, can be compared with theoretical results of electronic structure calculations.

The present measurements have been made up to 48 GPa, which will be continued to higher pressures above the volume collapse transition at 60 GPa in the next year. These experiments, particularly with an improved energy resolution 0.1 eV (compared to the present resolution of about 0.5 eV), should be able to probe the growing f character near the Fermi level, as Gd becomes itinerant above 60 GPa. The importance of such data is paramount to evaluate different mechanisms, Mott transition vs. Kondo volume collapse, presently proposed to explain these unusual electronic transitions in f -metals[8]. Therefore, we are planning to carry out high-resolution RIXS experiments during the next reporting period.

c. Effective Hamiltonians for MnO

The analogy between the correlation-driven transitions in the $3d$ transition metal monox-

ides and the volume collapse transitions in the rare earth metals was stressed years ago by Johansson [9]. New resistivity [10] and moment-sensitive x-ray spectroscopy measurements [11] for MnO, the latter described previously in this report, corroborate this view. To push the analogy further, one would expect the metallic B8 phase of MnO to be still strongly correlated near but on the high-pressure side of the transition, with its metallic character caused by 3d spectral weight at the Fermi level coexisting with still significant Hubbard side bands. A *static* mean-field treatment of such a correlated phase would be expected to yield a polarized or magnetic solution, as is indeed found in the local-density approximation (LDA) calculations of Fang *et al.*[12]. Such solutions can give good low-temperature energies, but are incorrect in regard to the magnetism, as indicated by the spectroscopic measurements showing the absence or screening away of any moment in the B8 phase.

It would therefore be very interesting to carry out a truly correlated calculation for the B8 phase, using the recently successful combination of LDA and correlated DMFT, or so called LDA+DMFT [6]. We found that our usual “atomic-sphere” approximation LDA technique is not fully adequate for the very open MnO structure to carry out the LDA part, and therefore have switched to a more rigorous “full potential” counterpart (FPLO). In a significant effort, we first verified that the FPLO results were in reasonable agreement with Fang *et al.* [12] including the importance of using the Generalized Gradient Approximation for exchange and correlation, and then created add-on’s to the FPLMTO package to generate the requisite orthogonal all-valence electron effective Hamiltonians. Because the full-potential basis is comparatively large, the appropriate symmetry operators were also developed to allow storing these matrices only for the irreducible wedge. We have generated these effective Hamiltonians for B8 MnO at selected volumes, and will shortly test them with Hartree-Fock calculations before moving on to the DMFT.

(iv) Other Related Work

(a) Prediction of pressure-driven nonmagnetic→ ferromagnetic transition in CoN at 43 GPa

Transition metal oxides (examples discussed above) comprise perhaps the most thoroughly studied class of solids. Transition metal nitrides, which might be expected to retain several chemical and physical similarities to the oxides, have been studied far less. Although the mononitrides do show substantial structural similarities to the monoxides (B1 rocksalt structure being common in both), their physical properties differ considerably. The main sources of these differences are the electronegativity (which is less for nitrogen than for oxygen) and the resulting ionic character, and the fact that nitrogen requires three extra electrons to form a closed shell whereas oxygen requires only two. The N^{3-} ion, if real, should be an extremely highly polarizable ion. However, while insulating behavior, magnetic transitions under doping, temperature, and pressure, and strongly correlated behavior are the norm in the monoxides, the mononitrides typically are metallic and at most weakly correlated.

Thin films of CoN_x were reported some time ago by Matsuoka, Ono, and Inukai.[13] Unlike the bulk materials of Suzuki *et al.*[14] their films were ferromagnetic and 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.

FIG. 4: Calculated equation of state of CoN for non-magnetic ZB structure and both nonmagnetic and ferromagnetic B1 structure. ZB-CoN is stable at ambient pressure and temperature, where above $P_c=43$ GPa the ferromagnetic B1 structure becomes the stable one. The critical pressure P_c is determined by the common tangent (not shown) or, as we did, by equating the enthalpies $E+PV$ of the two phases.

The combination of (a) the structural ambiguity of CoN, (b) the report of ferromagnetism, (c) the connection to zincblende (ZB) structure transition metal nitrides that suggest spintronics applications, and (d) the desire to compare and contrast a transition metal mononitride to the monoxides that we are studying has led us to make a detailed first principles study of the energetics and magnetism of CoN. In both structures at all volumes studied, CoN is metallic and the ionic $\text{Co}^{3+}\text{N}^{3-}$ picture makes no sense. We find[15] that ZB CoN is strongly favored energetically over the B1 structure at ambient pressure (Fig. 4). At 43 GPa pressure we predict a pressure driven structural transition, which is unusual because it is a nonmagnetic-to-ferromagnetic transition. Magnetic to nonmagnetic transitions under pressure are common, but it is quite unusual to encounter the opposite type. Separately, we discovered and studied using fixed spin moment methods a magnetic moment collapse transition within the B1 structure (within its region of instability). This (experimentally inaccessible) first order moment-collapse transition was found to be the result of the avoidance by the system of placement of the Fermi level in a sharp and narrow peak in the density of states (a well known unstable situation).

Evaluation of the possibility of experimental study of this transition within this collaboration is underway.

(b) High pressure structural phase transition in Lithium Nitride Li_3N

Li_3N is a very interesting material with extremely high ionic character, largely arising from the alternating layer structure of N^{3-} and Li^+ of the ambient pressure a phase (P6/mmm). Because of the superionic conductivity, open layer structure, and its light weight, Li_3N has been an important system in the studies of lattice dynamics and electronic structure calculations[16] as well as to technological applications for an electrolyte in Li batteries and a hydrogen storage[17]. It also exhibits certain behavior under pressure, including strong

FIG. 5: The pressure-volume relationship of Li_3N to 65 GPa at ambient temperature. A first-order structural phase transition from hexagonal β - to cubic γ -phase at 35 GPa is evident. This transition is accompanied by a large volume change, owing to the 3 fold-to-4 fold nitrogen coordination change. Another phase transition at low pressure is not shown in the figure.

modifications of electronic structure and a change in coordination, which make it relevant to study for this SSAAP project.

In this study, we explore the high-pressure behavior of Li_3N by using *in situ* angle-resolved synchrotron x-ray diffraction up to 62 GPa in a diamond anvil cell. At room temperature, α - Li_3N is known to undergo a structural phase transition to a second layered hexagonal β -phase (P63/mmc) at very low pressure (≈ 1 GPa). Following this transition, we found a second structural phase transition from β - Li_3N to a close-packed cubic γ -phase (Fm-3m) in the pressure range of 35-40 GPa. This transition is accompanied by a relatively large 7.5% drop in specific volume as shown in Fig. 5. The data has been fit to the three-parameter Birch-Murnaghan equation, yielding the equation of state for the two high-pressure phases (solid lines). We found that the resulting values for bulk modulus, pressure derivative, and equilibrium volume agree very well with the previous theoretical predictions.

The β – γ transition in Li_3N is in many ways analogous to the graphite-diamond transition in carbon, converting the three-fold coordinated nitrogen atoms into four-fold coordination accompanied by a large volume collapse. It is, therefore, expected that this transition be associated with a substantial change in chemical bonding and ionicity (or covalency). The transition is also accompanied by an interesting color change from nearly black β -phase to nearly transparent γ -phase, reflecting a strong modification of electronic structure again analogous to the graphite $\rightarrow$ diamond transition. To further validate these conjectures, we plan to determine directly the electric conductivity of Li_3N in a diamond anvil cell as well as chemical bonding characteristics of N atoms by using inelastic x-ray Raman spectroscopy

FIG. 6: Effect of the on-site repulsion U on the magnetic moments for FM ordering; decreasing U is analogous to applying pressure. The change shows a first-order transition (and accompanying hysteresis) in the critical region (3.1 eV to 3.6 eV). Gap opening (metal-insulator transition) simultaneously occurs with charge disproportionation (CD) due to the first-order nature. Dashed and solid lines represent the CD and the CUD state, respectively. *Inset*: Change of the magnetic moments for the O ions: O1 (with 2n site symmetry) is shared by two Co1 and one Co2, while O2 (with 2m site symmetry) is shared by one Co1 and two Co2.

at the APS. In parallel, we are also calculating the electronic band structure of both β - and γ -phases of Li_3N to understand the observed color change and to quantify the ionicity change across the phase transition.

(c) Charge disproportionation and spin differentiation in Na_xCoO_2 .

In early 2003 Takada and coworkers reported[18] 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 $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3 \text{H}_2\text{O}$. The similarities to the high T_c cuprates are quite 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.

Our work to date (begun under separate DOE funding) has focused on the question of charge disproportionation (CD) and spin formation on the Co ions. For $x > \frac{1}{2}$, a Curie-Weiss susceptibility $\chi(T)$ is observed, completely in line with the number of Co^{4+} ions with $S=\frac{1}{2}$ that is expected from the carrier concentration (the remaining Co^{3+} ions have $S=0$). Hence the charge is disproportionated even though the system is a good conductor. For $x < \frac{1}{2}$, no Curie-Weiss $\chi(T)$ is seen indicating there are no local moments. Precisely at $x = \frac{1}{2}$,

the charges order (doubling the unit cell) and the spins order antiferromagnetically (further doubling the unit cell).[19]

We have found that the LDA+U method applied to this system gives a microscopic (self-consistent but still mean field at this level) window into the charge disproportionation of this system. By varying the on-site Coulomb repulsion U (there is no agreement on the best value) we obtain a first order transition[20] in the critical range $U=3.2-3.5$ eV. This is of particular interest to our high pressure work because varying U (more specifically, the U to bandwidth ratio) is analogous to applying pressure. The charge/spin disproportionation transition is presented in Fig. 6 for our $x = \frac{1}{2}$ calculations. Briefly stated, our results indicate that while at x concentrations closer to one (few holes in NaCoO_2) a single a_g -band model might carry much of the physics, for $x = \frac{1}{2}$ this is an intrinsically multiband (three, in this case) system: the spin development involves full polarization of the a_g orbital on the Co^{4+} ion, and the reason the ion charge difference is only ~ 0.2 electrons is that there is a compensating change of charge in the other two t_{2g} orbitals. We can anticipate that such behavior may also arise in the pressure-driven transitions in the oxides (discussed above) that comprise one of the primary thrusts of this collaboration.

The finding with electronic structure methods of possible charge disproportionation at $x = \frac{1}{3}$, followed by ordering of the spins onto a honeycomb lattice, stimulated some more general study of this problem. The calculations involved determinant quantum Monte Carlo simulations of the Hubbard model on triangular and honeycomb lattices. Initial results on the paramagnetic-antiferromagnetic transition on the honeycomb lattice are being reported by Paiva *et al.*[21] A particular focus in this work was understanding the behavior of the specific heat as one changes the on-site repulsion through the critical point.

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C. 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%
Karan Aryanpour	Postdoctoral Researcher	100%
Andy McMahan	LLNL Staff Scientist	†
Warren Pickett	Professor, Physics, UCD	15%
Richard Scalettar	Professor, Physics, UCD	20%
Choong-Shik Yoo	LLNL Staff Scientist	†

† NNSA/DOE Collaborators funded by other sources.

D. PUBLICATIONS/PRESENTATIONS

- [1] “Charge- and Spin-Ordering Tendencies in Na_xCoO_2 at $x=1/3$,” K.-W. Lee, invited talk at Fall 2003 *Predictive Capabilities for Strongly Correlated Systems* workshop, Knoxville, TN.
- [2] “Pressure Induced Phase Transitions in Half-Metallic CrO_2 ,” Brian Maddox, C.-S. Yoo, V. Iota, D. Kasinathan, W.E. Pickett, and R.T. Scalettar, contributed talk, 2004 American Physical Society March Meeting, Montreal.
- [3] “Correlation Between T_c and t'/t : Perspective from First-Principle Wannier Functions,” Wei Ku, D. Kasinathan, W.E. Pickett, and R.T. Scalettar, contributed talk, 2004 American Physical Society March Meeting, Montreal.
- [4] “Ab Initio Calculation of Charge Disproportionation in Na_xCoO_2 ,” K.-W. Lee, J. Kunes, and W.E. Pickett, contributed talk, 2004 American Physical Society March Meeting, Montreal.
- [5] “Metal-Insulator Transitions in the Two Band Hubbard Model,” K. Aryanpour, W. E. Pickett, and R. T. Scalettar, contributed talk, 2004 American Physical Society March Meeting, Montreal.
- [6] “Charge- and Spin-Ordering Tendencies in Na_xCoO_2 at $x=1/3$,” invited talk at NATO Advanced Research Workshop on *New Challenges in Superconductivity*, W.E. Pickett, University of Miami, January 2004.
- [7] “Dynamical Mean Field Theory: What is it and what does it tell us about the volume collapse transition in Cerium?” seminar, Institute Non-Lineaire de Nice, March 2003, R.T. Scalettar.
- [8] “Dynamical Mean Field Theory of the Cerium Volume Collapse Transition,” seminar, University of California, Santa Cruz, May 2003, R.T. Scalettar.
- [9] “Charge Disproportionation and Spin Ordering Tendencies in the Superconducting Layered Cobaltates,” seminar, University of Washington, Seattle, May 2004, W. E. Pickett.
- [10] K.-W. Lee, J. Kunes and W. E. Pickett, *Charge disproportionation and spin ordering tendencies in Na_xCoO_2* . Phys. Rev. B **70**, 045104 (2004).

- [11] “First-order Isostructural Mott transition in highly-compressed MnO,” C.S. Yoo, B. Maddox, J.H.P. Klepeis, V. Iota, W. Evans, A. McMahan, M. Hu, P. Chow, M. Somayazulu, D. Hausermann, R.T. Scalettar, and W.E. Pickett, submitted to *Physical Review Letters*.
- [12] “Ground state and finite temperature signatures of quantum criticality in the Half-filled Hubbard Model on a Honeycomb Lattice,” Thereza Paiva, R.T. Scalettar, W. Zheng, R.R.P. Singh, and J. Oitmaa, cond-mat/0406535, submitted to *Phys. Rev. B*.
- [13] “Pressure Driven Nonmagnetic to Ferromagnetic Transition in CoN,” D. Kasinathan and W. E. Pickett, in preparation.
- [14] “Microscopic Study of Charge Disproportionation: $\text{Na}_{1/2}\text{CoO}_2$,” K.-W. Lee, J. Kuneš, P. Novak, and W. E. Pickett, in preparation.