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14. ABSTRACT

The broad goal of the project is the identification of the factors controlling the nontrivial many-body physics in artificially nanostructured materials based on transition metal oxides, thereby enabling the design of materials with desired correlated electron properties. The means of achieving this goal is the implementation and development of the hybrid methodology of density functional theory and dynamical mean-field theory (DFT+DMFT). We achieved a vastly improved understanding of the physics of the correlation-driven metal-insulator transition in real materials based on the identification of the d-valence as a critical parameter controlling the transition, and

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Report Title

Electronic Structure at Oxide Interfaces

ABSTRACT

The broad goal of the project is the identification of the factors controlling the nontrivial many-body physics in artificially nanostructured materials based on transition metal oxides, thereby enabling the design of materials with desired correlated electron properties. The means of achieving this goal is the implementation and development of the hybrid methodology of density functional theory and dynamical mean-field theory (DFT+DMFT). We achieved a vastly improved understanding of the physics of the correlation-driven metal-insulator transition in real materials based on the identification of the d-valence as a critical parameter controlling the transition, and identifying that this finding is insensitive to the choice of orbital provided it is well localized. Secondly, we discovered a new mechanism for correlation-driven metal-insulator transitions (the site-selective Mott transition) and demonstrated that this mechanism accounts for the main features of the previously mysterious metal-insulator phase diagram of the rare-earth nickelates. Thirdly, we demonstrated the ability to design new Mott insulators via heterostructuring. Finally, we developed a fully charge self-consistent implementation of DFT+DMFT, which allows us to compute total energies. This major technical development allowed us to compute the pressure vs. rare earth phase diagram in the nickelates.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
08/31/2011 1.00	C. Marianetti, A. Millis, M. Han. Chemical control of orbital polarization in artificially structured transition-metal oxides: La_{2}NiXO_{6} (X=B,?Al,?Ga,?In) from first principles, Physical Review B, (10 2010): 134408. doi: 10.1103/PhysRevB.82.134408
TOTAL:	**1**

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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05/16/2013 5.00 Hanghui Chen, Chris Marianetti, Andrew Millis. Engineering Correlation Effects via Artificially Designed
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Number of Manuscripts:

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Scientific Progress

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Technology Transfer

ARO 56032PH: Final Progress Report

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Jun 1st, 2014

This is the final progress report for *Electronic Structure at Oxide Interfaces*, contract number W911NF-09-1-0345 and proposal number ARO 56032PH, covering the period September 1st 2011 to Aug 31, 2013. The broad goal of the project is the identification of the factors controlling the nontrivial many-body physics in artificially nanostructured materials based on transition metal oxides, thereby enabling the design of materials with desired correlated electron properties such as ferromagnetism with a high Curie temperature, high transition temperature superconductivity and metal insulator transitions. The means of achieving this goal is the implementation and development of the hybrid methodology of density functional theory and dynamical mean-field theory (DFT+DMFT). A number of important milestones were achieved, among which are:

- a vastly improved understanding of the physics of the correlation-driven metal-insulator transition in real materials based on the identification of the d-valence N_d as a critical parameter controlling the transition, and identifying that this finding is insensitive to the choice of orbital provided it is well localized.

- the discovery of a new mechanism for correlation-driven metal-insulator transitions (the site-selective Mott transition) and the demonstration that this mechanism accounts for the main features of the previously mysterious metal-insulator phase diagram of the rare-earth nickelates.

- the ability to design new Mott insulators via heterostructuring.

- A fully charge self-consistent implementation of DFT+DMFT, which allows us to compute total energies. This major technical development allowed us to compute the pressure vs. rare earth phase diagram in the nickelates.

1   Overview

This grant funded one postdoctoral researcher. The broad goal of the research was to understand the degree to which many-body physics could be manipulated by materials design, in particular by growth of materials in appropriately chosen atomic-thickness heterostructure configurations. Our work was based on combining the most advanced many-body techniques available to treat strongly correlated electron systems with an unprecedented level of physical and chemical of realism. The initial focus was to demonstrate a theoretical basis for control of one fundamental correlated electron property, the orbital polarization (relative occupancy of different transition metal d orbitals). In the course of the investigation we uncovered fundamental difficulties with the conventionally accepted theory of the correlation-driven metal-insulator transition, which we investigated. We also uncovered a new kind of correlation-driven metal-insulator transition and showed that our mechanism accounts for the previously mysterious properties of the rare earth nickelates. Additionally, we demonstrated the ability to design new Mott insulators via heterostructured double perovskites. Finally, we succeeded in implementing a successful fully charge self-consistent implementation of DFT+DMFT which allows for total energy calculations. Our work has led to three papers fully supported by the grant [1, 2, 3] and three partially supported[4, 22, 23]. Below we review the major findings.

2   Accomplishments in previous funding period

2.1   Orbital Polarization: the case of Nickelate heterostructures

This work[1, 2] had a general and a specific motivation. The general motivation is to establish the body of theoretical results needed for the broad program of controlling many body physics by heterostructuring. To begin work on this large-scale project we selected for study a basic property (the orbital polarization or differential occupancy of transition metal d-orbitals) which is fundamental to many-body physics. The specific motivation was a proposal, put forth by Chaloupka et al[5] and supported by calculations of Hansmann et al[6], that with appropriate heterostructuring one could control the orbital polarization to the extent of giving a nickelate material (two-sheeted Fermi surface) a cuprate-like electronic structure, thereby producing a new class of high temperature superconductors. Our results revised the conventional picture in two important ways. First, we showed via density functional calculations [1] the incorrectness of the standard belief that the only important effect of heterostructuring was geometric confinement. In fact, the chemical composition of the supposed electrically inert counterlayers had a non-trivial effect, via shifts of the ligand energy levels. Second we showed via DFT+DMFT calculations [2] that for 'late' transition metal oxides such as the lanthanum nickelates the previously accepted theoretical analysis was irrelevant because it neglected the physically crucial consequences of charge transfer between transition metal (here, Ni) and ligand (here, O) ions. Taking charge transfer and Hunds coupling physics correctly into account reveals that the orbital polarization predicted by Chaloupka and studied (in a model which did not include the ligands) by Hansmann et al simply does not occur in the lanthanum nickelate materials; indeed when the correct

physics is incorporated into the calculation one finds that correlation effects act to decrease the magnitude of the orbital polarization (see figure 1). Very recent resonant scattering experiments appear to confirm our predictions [7].
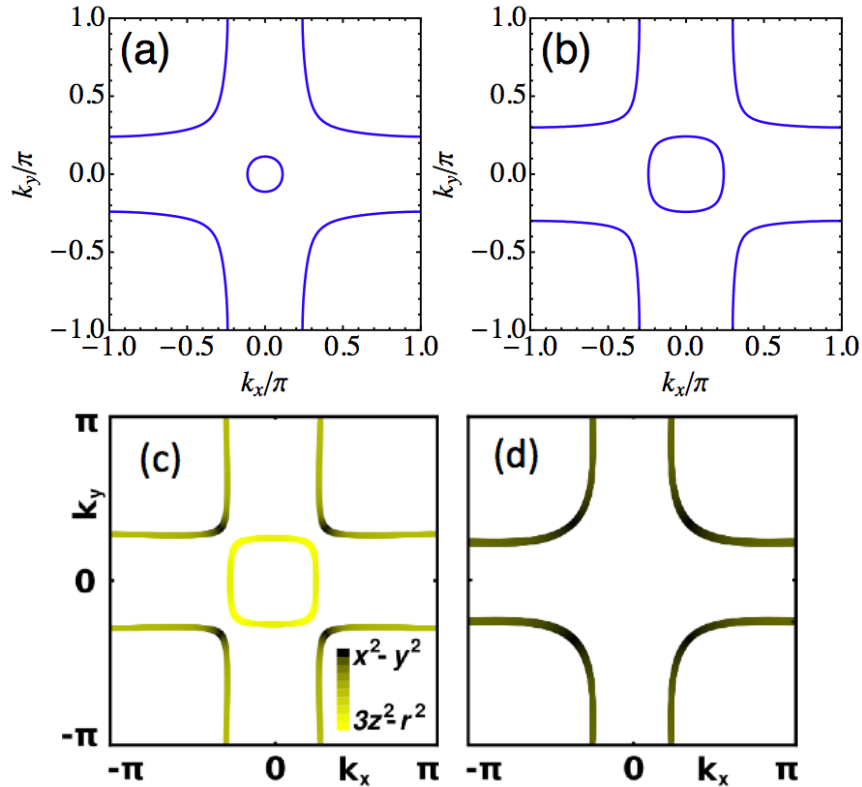

Figure 1: The Fermi surface of nickelate heterostructures (layers of LaNiO$_3$ alternating with highly insulating counterlayers along the perovskite (111) direction using DFT and DFT+DMFT. Panels **(a,b)** our results [2] including covalency effects; comparison of panels (a) (DFT) and (b) (DFT+DMFT) shows an interaction-driven decrease in orbital polarization, visible here as an increase in the size of the central Fermi surface. Panels **(c,d)**: analogous calculations[6] but with many-body physics modelled via a Hubbard Hamiltonian which does not include covalency effects. Tendency (in this approximation) of interactions to increase orbital polarization shown by correlation-driven disappearance of central pocket.

Our work was pivotal both in clarifying what can be achieved in this important and widely studied system and more broadly in revealing importance of covalency physics previously neglected in many studies of transition metal oxides.

2.2 Covalency and the metal-insulator phase diagram in transition metal oxides

The work described in the previous section highlighted the importance of covalency effects in nickelates and raised the broader question of the role of covalency effects across the full

family of transition metal oxides. The large and growing field of oxide electronics has used the Hubbard model (which neglects covalency effects) as a paradigm for strong correlation physics, and it is important to know how covalency effects change the picture. We resolved these issues[4], and we describe the main points below.

The fundamental parameter controlling covalency is the energy of the correlated (e.g. transition metal d) states relative to the other electronic states (for example the oxygen p). Theoretical analysis raises a deep question in materials theory. Methodologies for treating electronic correlations beyond density functional theory require the identification of a set of orbitals whose correlations are to be treated more accurately (e.g. the d-like orbitals centered on the transition metal sites of transition metal oxides or the f-like states centered on the actinides in heavy Fermion systems) *and* a prescription for embedding these correlated orbitals in the full electronic structure. A crucial issue in the embedding prescription is the 'double counting correction' which removes the correlation contributions from the single-particle energies obtained in density functional theory and thus adjusts the energy of the correlated orbitals relative to other electronic states. While different prescriptions have been proposed [8, 9, 10], there is no broadly agreed upon and theoretically justified expression for the double counting correction, and yet because it controls covalency it plays a crucial role in beyond DFT electronic structure methods. Lack of theoretical control over this issue is a fundamental limitation of modern theories of correlated electrons in solids.
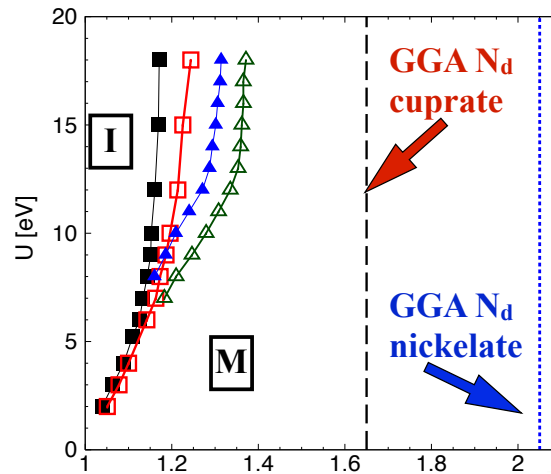

Figure 2: Metal-insulator phase diagram from Ref. [4] indicating limit of stability of metallic phase $N_{d,c2}$ (solid symbols), limit of stability of insulating phase $N_{d,c1}$ (open symbols) along with vertical lines indicating band theory estimates of N_d for model of high T_c cuprates (black and red squares, and black dashed line) and nickelates (blue and green triangles, and blue dotted line). Note that in single-site dynamical mean field theory the metal insulator transition is first order and is characterized by two spinodal lines: $U_{c1}(N_{c1})$ where the insulating phase loses stability and a slightly different value $U_{c2}(N_{c2})$ at which the metallic phase loses stability [11]. We present both lines here, but remark that the U_{c2} lines have a strong temperature dependence and are difficult to compute accurately.

As a first step towards an improved understanding of this issue we have investigated [4]

different ways of parameterizing covalency (and therefore the double counting correction) and of comparing the results to experiment. We based our investigations on underlying electronic structures obtained from density functional band theory, with the relevant correlated and ligand orbitals defined by a maximally localized Wannier function construction, and used single-site dynamical mean field theory (which instantiates the canonically accepted physics of the Mott metal-insulator transition) to treat the correlation effects. We focussed on the high-T_c cuprates (an electronically two dimensional system with one relevant correlated orbital) and the rare earth nickelates (electronically three dimensional, with two relevant correlated orbitals). We found that the double counting and covalency effects are most usefully parameterized in terms of the occupancy N_d of the transition metal d-orbital. Different theoretical models (involving different strengths of the beyond density functional theory interactions and different double counting corrections) which yield the same N_d yield essentially the same physics, and in particular the metal-insulator phase diagram takes the nearly universal form shown in the right-hand panel of Fig. 2. (Note that while the precise value of N_d of course depends on the precise definition of orbitals, all definitions based on well localized orbitals give very similar results). A particularly striking finding common to both systems is that within the single-site DMFT approximation, insulating behavior is found only for a very narrow range of d-occupancy, corresponding to weak covalency effects, irrespective of the Coulomb repulsion. Further, while as remarked above the double counting (and hence the true magnitude of covalency effects) is not known, the values required to make the theoretical models insulating are so far from the band theory values or literature estimates from various experiments that it is highly unlikely that within the single site DMFT approximation and therefore the canonical Mott picture is unable to account for the insulating behavior of these materials. We resolve this apparent paradox in the next section where we describe the site-selective Mott transition.

2.3   Metal insulator transition in rare earth nickelates.

In this work, we resolved the nature of the insulating state in the rare-earth nickelates[3]. The rare earth nickelates have emerged as one of the key paradigm systems for oxide electronics [12, 13, 14] and crucial goal of current research is to understand the metal insulator transitions which occur as a function of chemical composition, film thickness and imposed strain. A necessary first step is a theory for the metal-insulator transition occurring in the bulk compounds. The investigations outlined above show that this transition is unlikely to be due to conventional Mott physics. Experimental work [15] has showed that the transition is associated with a structural change in which Ni-O octahedra become inequivalent, with one having a decreased and the other an increased mean Ni-O bond length. These results have been interpreted as evidence for a crucial role of charge ordering [16, 15, 17, 18, 19] but charge ordering in the naive sense of a change in the Ni valence between the two sublattices is inconsistent with the large repulsive d-d interaction U expected on the Ni site and appears to be ruled out by very recent soft X-ray resonant diffraction data [20]. Our calculations also reveal negligible charge ordering. Antiferromagnetic order can drive an insulating state and induce a disproportionation as a second-order effect[21]; while this mechanism may be relevant to NdNiO$_3$ it fails to account for the paramagnetic insulating state observed in Sm,

Eu, Y, and Lu compounds. The cause of the transition has been mysterious but, we believe, our new results solve the problem.
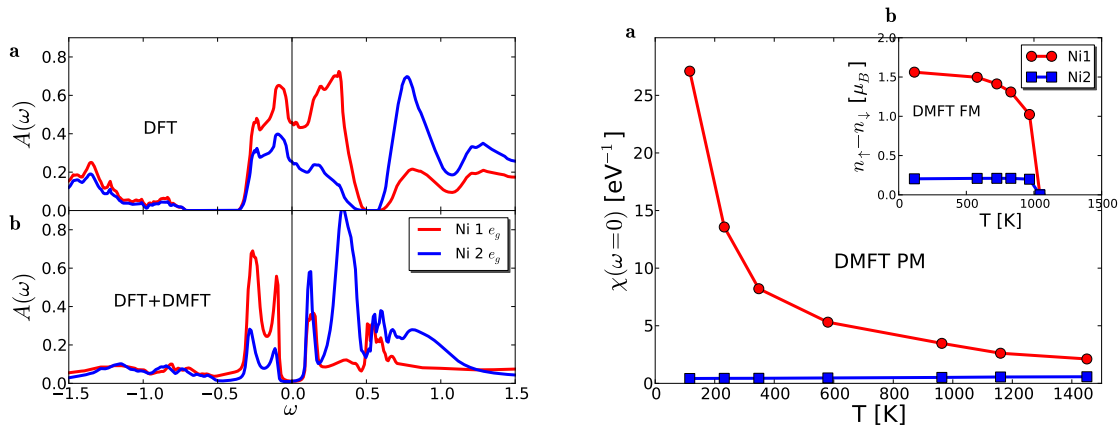

Figure 3: **Left Panel** The spectral function is projected onto the Wannier basis corresponding to the Ni e_g states on Ni_1 (dashed, red on-line) and Ni_2 (solid, blue on-line) and displayed in the near Fermi-surface frequency regime. (a) DFT spectral function. (b) DFT+DMFT spectral function obtained at U=5eV, J=1eV, Nd=8.0, and T=116K. **Right Panel:** The local magnetic susceptibility $\chi(\omega = 0)$ in a paramagnetic state as a function of temperature is obtained using the DFT+DMFT calculation. Both the Ni_1 (large Ni-O bond length, red circle) and the Ni_2 (small bond length, blue square) are compared. In the inset, the static magnetic moments $n_\uparrow - n_\downarrow$ as a function of temperature in Ni_1(red circle) and Ni_2(blue square) are computed within DFT+DMFT in a ferromagnetic state.

We studied the end member of the rare-earth nickelate series, $LuNiO_3$, using state of the art density functional theory plus dynamical mean field theory (DFT+DMFT) methods to investigate the interplay between correlation physics and structural distortions. Our calculations used the real crystal structure, including the two sublattice difference in $Ni - O$ octahedral size. We explored various values of the double counting correction but found that the key results do not depend on the double counting correction in any significant way. Our main results are shown in Fig. 3. The left panel compares the d-electron spectral function for $LuNiO_3$ obtained from a density functional calculation (Fig. 3a) to that obtained from our DFT+DMFT calculation (Fig. 3b). We see that while density functional theory predicts that the system is metallic (no gap at the chemical potential) despite the bond length disproportionation, the correlation effects captured by DMFT drive the system into an insulating state with a gap of $\sim 200meV$ (the precise gap value depends on the double counting prescription). Further, although as many workers have noted the disproportionation implies a difference in charge between the two Ni sites, we find that the total d occupancy N_d is 8.22 ± 0.08 for the DFT spectra and 8.0 ± 0.06 for the DFT+DMFT spectra shown in Fig. 3; our GGA+U calculations (not shown) give an even smaller difference between the two Ni sites. We therefore conclude that the charge order, while of course nonvanishing by symmetry, is not physically important and in particular is not the cause of the insulating behavior, which is instead due to a novel kind of insulating state which we have uncovered.

To demonstrate the new features of the insulating state found in our DFT+DMFT calculations we show in Fig. 3 the temperature dependence of the local magnetic susceptibility. A dramatic difference is visible between the two sites. The local susceptibility of the Ni_1 (long bond) site has a well defined $1/T$ behavior indicating well defined and long-lived but thermally fluctuating magnetic moments, as expected in a paramagnetic Mott insulator (in the single-site DMFT approximation). By contrast, the local susceptibility of the Ni_2 (short bond) site has a negligible temperature dependence, indicating a lack of a local moment on this site. For this reason, we identify the origin of the insulating state as a *site-selective Mott transition.* The Ni-O covalency plays a crucial role in this insulating state. The Ni valence is near d^8 (spin 1 on each Ni), and there is correspondingly one hole per every three oxygen. The Ni_1 site displays the physics of a S=1 Mott insulator, whereas the two holes on the octahedron surrounding the Ni_2 site bind with the $S = 1$ on the Ni_2 to form a singlet; this binding energy gives the excitation gap of the insulating state.

3   Progress during final year

Here we summarize the results that were obtained in the final year of funding. A total of two publications were produced during this time period[22, 23].

3.1   Designing a $S = 1$ Mott insulator via heterostructuring

The results of this section were published in Physical Review Letters[22]. In this work, the goal was to design a new Mott insulator via heterostructuring. We took two base materials, $LaNiO_3$ and $LaTiO_3$, and combined them in a heterostructure. In the bulk, $LaNiO_3$ is a metal and $LaTiO_3$ is a Mott insulator. This is somewhat easy to anticipate given that Ti is in a nominal d^1 configuration and Ni is in a nominal d^7 configuration. Due to the different relative energies of the valence states in these materials, charge will nominally flow when they are intertwined in a heterostructure. As one might expect, the Ti d states will be higher than the Ni d states, and this is illustrated schematically in figure 4 (left panel). Therefore, it is expected that charge may flow from Ti to Ni, converting $LaTiO_3$ to a band insulator and driving Ni to a 2+ state. Ni^{2+} may be expected to be a Mott insulator, as is NiO. These simple ideas can be tested in actual calculations (see figure 4 right panel). As expected, lining up the upper edge of the oxygen valence band indicates that the Ti will likely donate charge. Indeed, the heterostructure does end up being a $S = 1$ Mott insulator. The similarity to NiO can clearly be seen in the density of states.

This work demonstrates that simple intuitive reasoning combined with complex calculations can straightforwardly be used to design novel Mott insulators. More generally, this system can be viewed as a double perovskite, which refers to the fact that we have two transition metals. We believe that increasing the complexity of heterostructures by moving to double perovskites will open up many new opportunities.
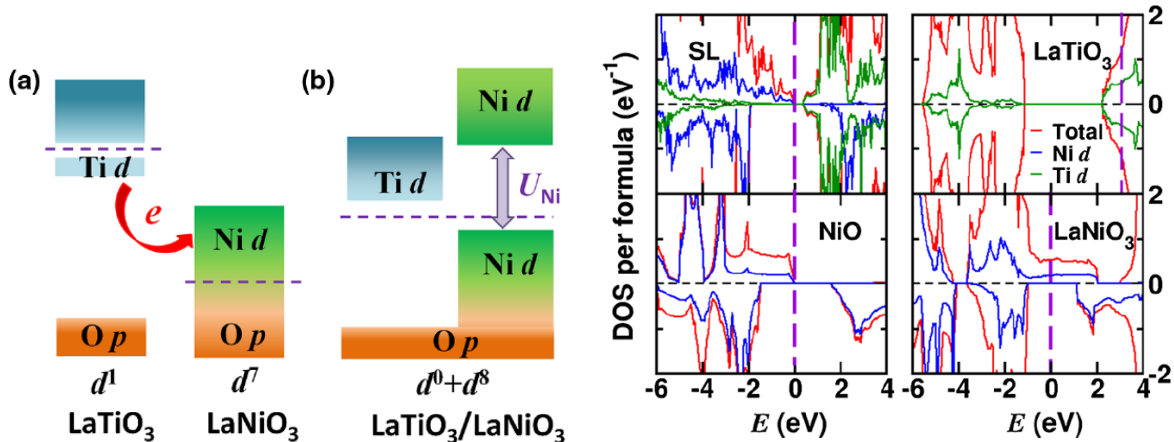
Figure 4: (**Left Panel a**) Schematic band structures of com- ponent materials $LaTiO_3$ and $LaNiO_3$. The dashed purple lines are the Fermi levels for the two materials. $LaTiO_3$ shows insulating behavior with a small excitation gap set by Ti d-d transitions and a wide energy separation between Ti d states and O p states. LaNiO3 exhibits metallic behavior with strong mixing between Ni d states and O p states. The red arrow highlights the direction of charge transfer in the superlattice. (Left panel b) Schematic band structure of the $(LaTiO_3)_1/(LaNiO_3)_1$ superlattice. Ti d states are above the Fermi level (dashed purple line). Correlation effects split Ni d states into lower and upper Hubbard bands, separated by U_{Ni} . (**Right Panel**) Densities of states for majority (above axis) and minority (below axis) spins of super- lattice (upper left) and reference materials NiO (lower left), $LaTiO_3$ (upper right; zero of energy is shifted so that oxygen bands align with those of $LaNiO_3$) and $LaNiO_3$ (lower right). The densities of states are obtained using DFT+U calculations with $U_{Ni} = 6eV$ and $U_{Ti} = 4eV$.

3.2   Computing the Pressure vs. Rare-Earth Phase digram in the Nickelates

The results of this section were submitted to Physical Review Letters[23]. We have im- plement a fully charge-self-consistent density functional theory plus dynamical mean field theory (DFT+DMFT) methodology which enables relatively efficient calculation of the total energy of realistic correlated electron systems. The DFT portion of the calculation uses a plane wave basis set within the project augmented wave method; enabling study of systems with large unit cells. The DMFT part uses maximally localized Wannier function (MLWF) methods to define the correlated orbitals, enabling a computationally efficient interface with the DFT calculation. The sensitivity of the results to the choice of double counting cor- rection is demonstrated and a physically reasonable construction is motivated and verified by comparison to experiment. The formalism is validated by application to the rare-earth nickelate family of materials. The metal-insulator and structural phase boundaries are de- termined as a function of applied pressure and choice of A-site ion and are found to be consistent with experiment. The DFT+U method is implemented within the same basis set and is shown to grossly overestimates the tendency to bond-disproportionation.

Our total energy calculation on $LuNiO_3$ is illustrated in the left panel of Figure 5. First, we recall that DFT completely fails to to predict the distortion $LuNiO_3$. Alternatively, DFT+U does predict a transition $LuNiO_3$, though it overpredicts, while it also erroneously predicts a transition in $LaNiO_3$. Our DFT+DMFT calculations are shown to successfully predict the distortion in $LuNiO_3$, though the magnitude is slightly underpredicted. Also shown in this plot is the effect of including full charge self-consistency. Somewhat unexpectedly, the effect is not terribly significant. This is encouraging in the sense that it suggests that non-charge-self-consistent calculations could be viable for total energies.

We computed the pressure phase diagram for the entire rare-earth nickelate series, and this is shown in the right panel of Figure 5. The black line corresponds to experimental measurements. The dotted lines correspond to standard DFT+U calculations, which are clearly in poor agreement with experiment. The solid lines are the result of DFT+DMFT calculations, and they are in excellent agreement with experiment. This powerful result demonstrates that DFT+DMFT is a robust method for computing total energies in strongly correlated electron systems.
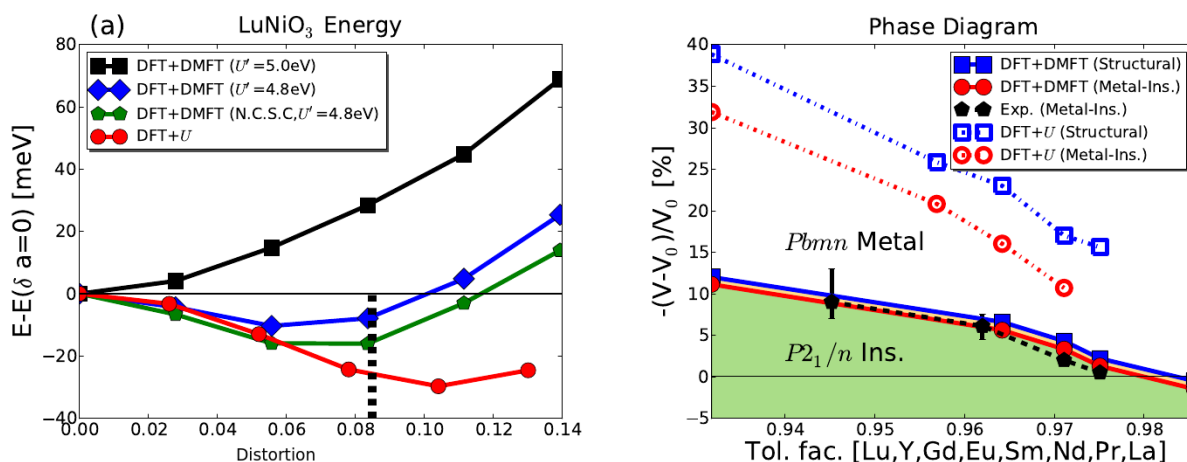

Figure 5: (**Left Panel**) Total energy as a function of bond-length difference δa for $LuNiO_3$ calculated using fully charge self consistent DFT+DMFT with original (squares, black) and modified (diamonds, blue) double counting correction and compared to DFT+DMFT energies computed using the DFT charge density (N.C.S.C, pentagons, green) and to energies obtained from the DFT+U method (circles, red). The experimentally determined values ($\delta a = 0.085 \mathring{A}$ ($LuNiO_3$) and $\delta a = 0$ ($LaNiO_3$)) are indicated by vertical dashed lines. The parameters are U=5.0eV, J=1.0eV, and T=116K. (**Right Panel**) Metal-insulator and structural phase diagram computed using DFT+DMFT (solid symbols and solid lines) as a function of unit cell volume for the series of rare earth ions and compared to results of DFT+U calculations (open symbols, dashed lines) and to experimental data (pentagons and dashed lines) obtained for $(Y,Eu,Nd,Pr)NiO_3$. V_0 is determined as the calculated ambient pressure equilibrium volume for each material while the tolerance factor is determined from the distances d_{R-O} and d_{Ni-O} as $d_{R-O}/d_{Ni-O}\sqrt{2}$. The parameters for the DMFT calculations are T=116K, U=5eV, U'=4.8eV and J=1eV.

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