Competing Electronic and Structural Effects In The Metal-Insulator Transition of Bulk and Layer-Confinned RNiO$_3$

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Fig. 1. Theoretically obtained structures for undisproportionated bulk NdNiO$_3$ (left panel), bilayer (center panel) and monolayer (right panel) NdNiO$_3$/NdAlO$_3$ (NNO/NAO) heterostructures. Ni is shown in two shades of blue corresponding to the checkerboard pattern associated with the low-symmetry structure, Al is purple, O in red and Nd in yellow.

Significance Statement

Correlated electron materials show a wide array of physical phenomena of interest for both technological applications and basic science, dictated by an interplay of electronic interactions and lattice distortions. One such property is the metal insulator transition (MIT) in which a material that at high temperatures is metallic goes through a simultaneous electronic and structural transition to a low-temperature insulating phase. In this paper we use a combination of many-body theory and electronic structure methods to show how the electronic and lattice degrees of freedom are coupled at the transition. An important new feature of our analysis is a comparison of the bulk, electronically three dimensional materials, to heterostructures in which the electrons are dimensionally confined.

The rare earth nickelates have chemical formula RNiO$_3$ (R is a rare earth metal of the lanthanide rare earth series) and, in bulk, at high T are metallic and form ortorhombic Pbnm structure (except for R=La for which the structure is trigonal) that is a slightly distorted ABO$_3$ perovskite. In the high T structure the Ni ions are equivalent up to a rotation and translation. For all R except for La, the bulk materials undergo a metal to insulator transition (MIT) as T is decreased. The transition is first order and the low T phase has a P$2_1/n$ structure with two fundamentally inequivalent Ni sites. The inequivalence is characterized by a charge disproportionation $\Delta N$ and a lattice distortion $Q$, both defined more precisely below. Recent experimental work(9) shows that in NdNiO$_3$/NdAlO$_3$ (NAO) superlattices in which one or two monolayers of NNO are separated by many layers of the wide-gap insulator NAO, the MIT occurs at a much higher temperature than in the bulk, but the X-ray signatures of the lattice distortion are somewhat less pronounced.

To obtain theoretical insight into the differences between bulk and superlattice materials, we use a general theoretical approach based on previous work as applied to bulk nickelates (5, 8, 27, 29, 31–33, 36–38) and similar to related work on ruthenates (3). We write the energy difference $\Delta E$ between the insulating and metallic phase:

$$\Delta E(Q, \Delta N) = \frac{kQ^2}{2} - \frac{1}{2} gQ\Delta N + E_{id}(\Delta N)$$  \hspace{1cm} [1]$$

The first term is the elastic energy due to structural symme-

Metal insulator transitions (MIT) in condensed matter physics typically involve changes in both the electronic and atomic structure of the materials. While the consensus is that the lattice and electronic degrees of freedom are coupled, their relative importance to the transition has not been easy to disentangle. Theoretical effort has typically focused on one or another specific system(1–8). In this paper we show that the comparison of metal-insulator transitions in bulk and heterostructured versions of the same material provides considerable insight into the relative roles of the lattice and electronic variables, because these are affected by heterostructuring in different ways. Motivated by recent experimental results (9–25) and theory (8, 13, 26–35), we focus on the rare earth nickelate family of materials. The concepts, formalism and findings are applicable to wide classes of materials.
try breaking, the middle term is the leading symmetry allowed coupling between the structural and electronic order parameters, and the final term is the energy associated with the electronic transition. $E_{el}$ is formally defined via a Legendre transform of the electronic energy computed in the undistorted structure but with an electronic symmetry-breaking field $\Delta s$.

Stationarity of $\Delta E$ with respect to variations in $\Delta N$ and $Q$ implies:

$$0 = kQ - \frac{1}{2} g \Delta N$$

and:

$$0 = -\frac{1}{2} g Q + \frac{\partial E_{el}(\Delta N)}{\partial \Delta N}$$

Equation 2 gives $Q$ as a function $\Delta N$ and requires knowledge of $k$ and $g$ which we obtain from density functional theory (DFT) calculations as described below. Equation 3 gives $\Delta N$ as a function of $Q$. We obtain $\Delta N(Q)$ via the density functional plus dynamical mean field theory (DFT+DMFT) method. For our calculations, we use structures obtained from fully relaxed DFT+U calculations and impose 0% strain relative to the theoretical bulk NNO lattice constant on the heterostructures. We use Quantum Espresso, ultrasoft pseudopotentials, either from the GBRV or generated using the Vanderbilt ultrasoft pseudopotential generator as described in previous work (39–43) and benchmark our results against experimental bulk structures. The disproportionated structures have two inequivalent Ni sites, one with relatively long Ni-O bonds ('LB') and one with relatively short Ni-O bonds ('SB'). We define the structural order $Q$ as:

$$Q = \sqrt{\frac{\sum_i (I_{i,B} - I_{i,SB})^2}{6}}$$

where $I_{i}^{(i)}$ are the lengths of the Ni-O bonds.

For each structure we then perform a self consistent DFT calculation and fit the bands arising from the frontier $e_g$ orbitals using maximally localized Wannier functions as implemented in Wannier90 (44, 45). Representative structures, bands near the Fermi surface and Wannier fits are shown in Figure 3. We define $\Delta N$ as the difference in occupancy between the Wannier orbitals on the two inequivalent Ni atoms:

$$\Delta N = N_{HF} - N_{LF}$$

with HF = Higher Filling and LF = Lower Filling. When there is structural disproportionation, HF corresponds to LB and LF corresponds to SB.

The Wannier fits define a low energy tight binding model to which we add standard Slater-Kanamori interactions and solve using dynamical mean field theory (single-shot, using the trigs library (46), ct-hyb solver (47) and dfttools (48) interface) to which we add standard Slater-Kanamori interactions and solve using dynamical mean field theory (DFT+DMFT) method.

The parameter $k$ is the stiffness to lattice distortions at fixed $\Delta N$. We argue, following (3, 8) that since the stiffness comes from the full electronic structure at fixed $\Delta N$, the frontier orbitals play a relatively minor role and for this purpose may be treated at the DFT level. We therefore obtain $k$ from the dependence of the DFT energy on $Q$ $\frac{\partial E_{DFT}}{\partial Q} = cQ$. However in the DFT calculations $\Delta N$ is relaxed at each $Q$. Referring to equation 2 we have on the DFT level (and noting the stationarity with respect to $\Delta N$):

$$cQ = \frac{\partial E_{DFT}}{\partial Q} = kQ - \frac{1}{2} g_{DFT} \Delta N(Q)$$

The parameter $g_{DFT}$ is defined in terms of the average on site energy $\Delta E_{DFT}^0$ obtained from our Wannier fits to DFT band structures as $g_{DFT} = \frac{\Delta E_{DFT}^0}{Q}$ and $\Delta N(Q)$ is obtained from the occupancy difference of the Wannier orbitals and is found to be linear in $Q$, $\Delta N = \chi_0 g_{DFT} Q$. This relation defines the on-site susceptibility $\chi_0$. $g_{DFT}$ can be read off from the on-site energy difference and is nearly identical for all three materials, namely 2.89$eV$/Å for bulk and 2.972$eV$/Å for the bilayer and 2.962$eV$/Å for the monolayer. This means that a similar movement of the ions leads to a similar change of electrostatic potential, which is something we would expect as the local environment is similar. The static electronic response however is different, with $\chi_0 = 1.16/eV$ for bulk, $\chi_0 = 1.25/eV$ for bilayer and $\chi_0 = 1.39/eV$ for the monolayer, with a larger response for the materials with lower bandwidth.

The constant stiffness $k$ extracted as in equation 6 is $k = 15.86$ $eV$/Å$^2$ for bulk, 17.1$eV$/Å$^2$ for bilayer, 20.18$eV$/Å$^2$ for monolayer. The higher stiffness of the monolayer and bilayer arises due to the increased stiffness of the Ni-O bonds along the z direction towards the NAO, while the stiffness of the other bonds remains relatively unaffected. From Figure 2 we see that in the layered structures the disproportionations have to propagate into the nearby NAO layers, i.e. the cost to disproportionate an octahedra in the monolayer is equal to the cost of disproportionating the NNO plus the cost of disproportionating the nearby NAO octahedra.

The parameter $g$ in equation 2 is defined in terms of the on-site energy difference $\Delta E = gQ$ entering our DMFT calculations. In our one-shot DMFT, $g$ is corrected from the DFT value by a double counting term (8, 32), so $g = g_{DFT}(1 + (U - \frac{3}{2}J)\chi_0)$.

We now turn to a comparison of superlattice and bulk physics. We begin with the bands and density of states shown in Figure 3. Layer confinement due to the insulating NAO material leads to a significant narrowing of the $3z^2-r^2$ orbital.
band, as well as an exaggeration of the dip in the density of states in the $x^2-y^2$ orbital in both materials and in the $3z^2-r^2$ in the bilayer. For the bulk NNO, the bandwidth of both orbitals from our calculations is 2.6eV. The monolayer’s $x^2-y^2$ orbital has a bandwidth of 2.72eV, slightly larger than bulk while the $3z^2-r^2$ has a bandwidth of 2.15eV. The bilayer is similar with a bandwidth of 2.68eV for the $x^2-y^2$ orbital and 2.21eV for the $3z^2-r^2$. The narrower bands imply the heterostructures have a stronger electronic tendency to disproportionate. The slightly higher in-plane bandwidths are caused by the straighter in-plane Ni-O-Ni bond angles in the xy plane in the heterostructures than for bulk NNO imposed by the nearby NAO octahedra. Similar to previous work (49–51), we note that this effect can be tuned by changing the insulating material to modify the relative bond angles. Within the $e_g$ Wannier picture, the monolayer also shows a crystal field splitting of $\bar{\epsilon}_{x^2-y^2} - \bar{\epsilon}_{3z^2-r^2} = 0.06eV$. The crystal field splitting has negligible effect on the phase diagram: we’ve performed calculations for the monolayer with the crystal-field splitting set by hand to 0 for U=2.1eV and found that the critical J for the MIT transition line is the same as with the crystal-field splitting set to the DFT relaxed value, within an accuracy of J=0.01eV.

To first focus on the electronic part of the disproportionation, we computed the Q=0 phase diagram shown in figure 4. We find that spontaneous disproportionation ($\Delta N \neq 0$) is achieved for a slightly smaller critical J for a given U in the monolayer and the bilayer than in the bulk. The magnitude is small (less than 10% in J) consistent with an average bandwidth change of 8% for the bilayer and 13% for the monolayer. Despite minor differences in bandwidth, the phase diagrams for the monolayer and bilayer are nearly identical, likely explained by differences in the shape of the projected density of states; within the insulating phase however the bilayer has $\Delta N$ of about the average between that of bulk and monolayer, as expected from the bandwidth analysis. The transitions are strongly first order. We also plot a dashed line corresponding to the MIT transition for the experimental bulk low temperature, insulating structure, calculated as in Ref. (33), to show the effect of the lattice distortion.

![Fig. 3. Projected density of states of low-energy $e_g$ Wannier bands for GGA-relaxed structures for bulk (top), bilayer (middle) and monolayer (bottom) structures. Dotted horizontal lines show approximate cutoff for determining bandwidths mentioned in main text.](image)

![Fig. 4. Spontaneous electronic disproportionation transition lines in the (U,J) plane for the bulk, monolayer and bilayer NNO in the absence of structural disproportionation, insulating phase always to the right of the line. The dotted line to the left shows the Metal-Insulator transition line for the bulk experimental Low T disproportionated structure calculated as in Ref (33). The solid lines show the MIT transition lines induced by spontaneous electronic disproportionation for the undisproportionated relaxed bulk, bilayer and monolayer structures. The stars correspond to the points at which the constructions in Fig. 5 are plotted.](image)

We now turn in Figure 5 to the $\Delta N(Q)$ relation. The large symbols connected by lines show the $\Delta N$ versus Q obtained from our DFT+DMFT calculations for three (U,J) points, each corresponding to one specific part of the phase diagram: when all materials require a Q to become insulating, when only the bulk does, and when neither does. As previously discussed (8), there are two regimes for the $\Delta N(Q)$ curves: a small Q regime in which $\Delta N$ is linear in Q, followed by a sudden transition to an insulating phase with higher $\Delta N$. Once in this regime, $\Delta N$ quickly becomes nearly independent of Q. For a certain range of U,J parameters, the linear response regime disappears altogether and is replaced by a...
spontaneously insulating solution at $Q=0$. A Landau theory of this transition is described in Ref (8).

![Image](image_url)

**Fig. 5.** $\Delta N$ versus bond disproportionation $Q$ within DFT+DMFT for bulk and monolayer structures as well as from the total energy model calculation in different areas of the phase space. The stars marked with A,B,C correspond to the points marked with stars in the phase diagram in Fig. 4

For all three panels, once all three materials are in the insulating range, the monolayer has a larger disproportionation than the bulk, with the bilayer in between. For A, both the bulk and the heterostructures require a particular value of Q to become insulating, with similar critical values of Q for the heterostructures and a slightly higher value for the bulk. In panel B, the two heterostructures are spontaneously disproportionated even at $Q=0$, while the bulk is not. In this range of parameters, even a large increase in stiffness would still allow for an insulating solution for the heterostructures, albeit at a very small Q, while the bulk would become metallic. Point C illustrates the part of the phase diagram in which the bulk and heterostructures are spontaneously disproportionated and are insulating regardless of K.

Also shown in Figure 5 are straight lines corresponding to the $Q(\Delta N)$ relation from equation 2. The intersection of these lines with the DMFT $\Delta N(Q)$ curves defines the actual values of $\Delta N$ and Q. We see from the relative positions of the intersections that $Q_{\text{monolayer}} < Q_{\text{bilayer}} < Q_{\text{bulk}}$ and $\Delta N_{\text{monolayer}} > \Delta N_{\text{bilayer}} > \Delta N_{\text{bulk}}$. From an electronic point of view the monolayer and bilayer are more disproportionated (\(\Delta N\) is larger) as $\Delta N$ does not depend strongly on Q, however the higher stiffness of the heterostructures leads to a lower Q. Further, as shown in the middle figure in 2, there is a range of U,J for which the heterostructures will stay insulating even at a very small Q while the bulk becomes metallic.

One of the signatures associated with the bond disproportionated phase of the RNO nickelates is an increased peak-prepeak splitting of the XAS Ni L$_3$ edge, which in the monolayer and bilayer were found to be in between the values of the bulk disproportionated and undisproportionated structures throughout the insulating temperature range scanned. Consistent with this result, we find that the predicted value of the structural disproportionation of the monolayer is lower than the bulk, with the bilayer in between the two. Further, XAS integration of the monolayer in-plane and out-of-plane Ni L$_3$ edge has found an orbital polarization of 8% favoring the $3z^2-r^2$ orbital. Within our insulating solutions we find that orbital polarization is strongly suppressed (<2%) however we consistently find that the long bond site has an orbital polarization of 5-8% in a direction consistent with experiment, while the LB site is orbitally polarized of about the same magnitude but in the opposite direction. This suggests that the XAS spectra may sample primarily the LB, however further theoretical and experimental work is needed.

**Conclusion and Outlook.** Using a combination of DFT+DMFT and many-body theory we have elucidated the relative importance of lattice and electronic effects in heterostructured materials. We have found that the higher lattice energy cost in the heterostructured materials is likely to decrease the structural signatures of the symmetry-broken phase within the correlated material going through an MIT but that the distortion associated with it can propagate into the epitaxial layer. Temperature-dependent structural modes propagating across the interface are identified as an important issue in a criteria in designing new artificial materials. We have found that, as the effect of interactions is increased in a layer-confined structure, electronic disproportionation can be higher despite lower structural distortions in a heterostructure. Finally, and in agreement with recent work, we found that the relative octahedral angles of the heterostructured materials can further play a role in controlling the effect of the interaction. These general results can be used both to understand other similar heterostructures (for example LaNiO$_3$/LaAlO$_3$) as well as to design new materials.

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Appendix A - Technical Details. We use the Quantum Espresso (40) software package for our DFT calculations, Wannier90(44) to generate the extended Wannier $e_g$ orbitals, and the TRIQS software package(46) for the DMFT calculations with its various applications: DFTTools (48) for the interface with Wannier90 and the
CT-HYB DMFT solver (47) to solve the DMFT equations using the Hybridization expansion impurity solver (52). We use ultra-soft pseudopotentials (41) and the PBE (53) version of the GGA exchange-correlation functional formalism. To simulate the bulk material, we used a 20 atom $c(2x2)x2$ unit cell, relaxed starting from the experimental structure; for the $m=1$ superlattice we used 1 layer of NNO and 3 layers of NAO, while for $m=2$ we used 2 layers of each material, making sure that the total number of layers is even in order to allow the octahedra to relax. For the bulk undisproportionated calculation, we find that our high-temperature relaxed structure within GGA has a bandwidth that is only slightly smaller than the experimental high temperature structure. In the phase diagram in figure 2, this leads to a small shift to the left in the critical J for a given U of at most 0.05eV. Of the available functionals we have tried however (LDA, PBE and PBEsol), we find that relaxations using GGA in the PBE formalism provide a bandwidth that is very close to the one using the experimental high temperature structure as well as a phase diagram that is closer to the one obtained by using said structure. We also find that the phase diagram difference between the undisproportionated structures is robust with respect to changing the functional used in order to obtain the relaxed structures. For the initial DFT relaxations without structural disproportionation, we found a k-point mesh of 5x5x4 for the 20 atom bulk unit cell or 5x5x4 for the heterostructures (equivalent to 7x7x8 and 7x7x12) per formula unit are sufficient to generate quality structures. For consistency with the DFT+U results, we also performed higher k-point calculations but found they do not affect results. For the various DFT+U relaxations involving structural disproportionation, we impose ferromagnetic order. The k-point mesh has to be higher to differentiate between the various possible local minima. Thus, for the 20 atom bulk is 7x7x3 and the 40 atom heterostructures it is 7x7x4 (roughly equivalent to a 10x10x10 k-mesh per formula unit) in order to have a 1meV accuracy in the total energies of the relaxed structures, however we have found that structures obtained using 5x5x2 and 7x7x3 k-point grids give nearly identical structural results. For all calculations, the wavefunction energy cutoff is 35 Ry, and the density cutoff is 280 Ry. A Mazziotti-Vanderbilt smearing of 0.2eV is used for the electron occupation function for all calculations. The energy convergence threshold for relaxations is $10^{-9}$eV and the force convergence threshold is $10^{-4}$a.u., the electronic energy convergence threshold within the electronic self-consistency loop is $10^{-12}$eV.

To extract the tight-binding parameters for DMFT calculations, we obtain the antibonding $e_g$ orbitals as a postprocessing step using Wannier90 within the Maximally Localized Wannier Function framework.

For the DFT+U calculations, we performed calculations in the ferromagnetic phase, as our unit cells are not large enough to reproduce the full experimentally determined magnetic structure in the bulk (with vector q=(1/4,1/4,1/4)) or bilayer (q=(1/4,1/4,0)) while the magnetic structure in the monolayer is not known but with ferromagnetism and a q=(1/4,1/4,0) vector excluded. We use the FM state as a way to break symmetry leading to bond disproportionation and an alternating S=1, S=0 state, as more important in the physics of the final structure than the exact magnetic order. A Hund J is included implicitly within spin-polarized DFT, however within the version of Quantum Espresso used for these calculations, only the effective Dudaere $U_{eff} = (U-2J)$ scheme is available, not allowing us to control U, J separately. For the two inequivalent Ni sites, as a proxy for charge disproportionation, we use the difference in local magnetic moment. We find that the total magnetization for the supercell is always equal to one Bohr magneton times the number of Nickel sites, as we would expect. However, the projected magnetic moment on the Lôwdin orbitals does not add up to this total magnetization, as the Lôwdin orbitals are not sufficient to describe the $e_g$ valence states. However, making the assumption that the Lôwdin magnetic moment is directly proportional to the magnetic moment per site, we can then write $n_{Ni} \approx n_{Lôwdin-total} \times 2pB/m_{total}$ where $n_{Lôwdin-total}$ is the total magnetization per pair of Ni sites: this is the $\Delta M$ plotted in Appendix C.

The Slater-Kanamori Hamiltonian solved by DMFT using the tight binding model extracted from the Wannier functions has the form on each lattice site:

$$\hat{H}_U = U \sum_m n_{m^\uparrow} n_{m^\downarrow} + (U - 2J) \sum_{m \neq m'} n_{m^\uparrow} n_{m'^\downarrow} + \sum_{m < m', \sigma} n_{m^\sigma} n_{m'^\sigma} + J \sum_{m \neq m'} \sum_{\sigma = \uparrow, \downarrow} c_{m \sigma}^\dagger c_{m'^\sigma}^\dagger c_{m'^\sigma} c_{m \sigma}^\dagger$$

In the DFTTools interface between DFT and DMFT we use a k-mesh of 14x14x14 for the bulk material, and a k-mesh of 12x12x6 for the heterostructure to obtain quality local density of states. Most of our DFT calculations in this paper, unless mentioned otherwise, are done at an inverse temperature $\beta = 40$eV, equivalent to a temperature of 290K. Most DMFT calculations are run for 15 steps using $10^5$ QMC cycles. Calculations that require higher precision are ran for 35 steps, the first 30 using around $10^7$ QMC cycles, and the final 5 using $3 \times 10^8$ cycles. To compare with previous literature, we’ve also performed density-density only calculations to benchmark our calculations. We find that using the Slater-Kanamori Hamiltonian shifts the metal-insulator phase boundary to slightly higher values of J given a particular U ($\approx 0.2eV$).

**Appendix B - Model Parameter Extraction.** In order to extract the relevant parameters we need, we use the structures generated within DFT+U. We need to extract the following: $g^{DFT} = \frac{\partial \Delta N}{\partial \Delta Q}$, $\chi_0 = \frac{\partial \Delta N}{\partial \Delta J}$, $\lambda = g^{DFT} \chi_0$ and finally the stiffness k, which can then be extracted by doing DFT calculations on said structures. For the $g^{DFT}(Q) = \frac{\partial E^{DFT}}{\partial Q}$, $\chi_0 = \frac{\partial E^{DFT}}{\partial \delta \chi_0}$, $\lambda = g^{DFT} \chi_0$ and $\partial E^{DFT}/\partial \Delta Q$ with $\kappa$, $\chi_0$ constants we extract from the structures we generated as a function of Q.

![Fig. 6. Plot of energy per 2 formula units of NNO for the different structures for different Q, using structures obtained from DFT+U calculations. The energy and Q^2 are plotted relative to the energy of the smallest Q that are included in the plot.](image)

In order to benchmark this method as compared to explicitly imposing a Q, we compared our results on the bulk material with previous work (8) in which multiple structures were generated by modulating the bond disproportionation Q alone, and find that our results are consistent. We also note that while using bulk structures obtained through GGA relaxation does lead to slightly lower bandwidths than those obtained using the experimental structure, this only affects the results by shifting all the phase diagrams to lower J for a given U by about 0.1eV compared to the experimental structure. As the stiffness k and the static response functions $g^{DFT} = \frac{\partial \Delta N^{DFT}}{\partial \Delta Q}$ and $\chi_0 = \frac{\partial \Delta N^{DFT}}{\partial \Delta J}$ do not depend on the bandwidth by more than a fraction of a percent within our calculations, and the bond angles of the disproportionated structures remains the same up to within $< 1$ degree within our relaxed
spin-polarized calculations, we can simulate a large number of disproportionated structures with varying Q and assuming that the DFT Hamiltonian would look like the one corresponding to the undisproportionated, nonmagnetic structure plus an on-site energy difference $\Delta_{DFT} = g_{DFT}^Q$. The spin-polarized relaxed structures have bond angles that are slightly more bent than those in the non-magnetic calculations, however as was shown in (8), neither $k$ nor $g$ depend on the bandwidth; we do expect a slightly larger $\chi_0$ in the structures obtained using spin-polarized DFT+U by about 3-5% due to the slightly reduced bandwidth.

**Appendix C - DFT+U Bulk and Heterostructure Results.** Further supporting the picture of stronger electronic disproportionation in the heterostructures as a driving mechanism, we present results for the bulk, bilayer and monolayer structures as obtained by DFT+U using spin-polarized calculations in the FM state and full relaxations in Figure 9, with further details at the end of Appendix C. We find that, for small U, the heterostructures have a critical U under which the lattice stiffness is too strong to allow disproportionation. As expected, the critical U at which the monolayer disproportionates is higher than for the bilayer. Consistent with the DFT+DMFT results, however, once electronic disproportionation is allowed the monolayer is more electronically disproportionated than the bulk, with a similar result for the bilayer with the exception of U=1eV. Q are very similar for all three structures, with the exception of large U for which both the bulk and bilayer structural disproportionation stop increasing, while the monolayer disproportionation increases past that of both.

**Appendix D - Experimental Hole Determination.** Experimental values of the Ni eg hole ratio were extracted from x-ray linear dichroism (XLD) measurements on NNO/NAO superlattices, which can be directly compared to theory. The sample growth and measurement procedures are described in Ref. (9). To extract r experimentally, the XLD sum rule (54) is applied for the Ni L edge, $r = \frac{3}{4}I_{3z^2-r^2} - \frac{1}{4}I_{x^2-y^2}$, where $I_p$ corresponds to the integrated absorption measured with the polarization parallel to p. Figure 1 shows the absorption for in-plane and out-of-plane polarizations as well as the difference spectrum of the monolayer NNO/NAO superlattice. The values of $r$ for the monolayer NNO/NAO superlattice, bilayer NNO/NAO superlattice, and bulk NNO samples are 0.91 ± 0.03, 1.00 ± 0.02, and 1.02 ± 0.02, respectively.

**Fig. 7.** Fit to obtain the static electronic response for the three materials, $\chi_{0}$.

**Fig. 8.** Fit to obtain the linear coupling coefficient within DFT, $g^DFT$.

**Fig. 9.** Electronic and structural disproportionation within DFT+U for the ground state relaxed structures for the bulk, monolayer, and bilayer.

**Fig. 10.** (top) X-ray absorption spectra and (bottom) x-ray linear dichroism of monolayer NNO/NAO superlattice. Blue and pink curves in top panel correspond to absorption with polarization in-plane and out-of-plane, respectively.
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