A Comparative Many-Body Study of Pr$_4$Ni$_3$O$_8$ and NdNiO$_2$

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We study the many-body electronic structure of the stoichiometric and electron-doped trilayer nickelate Pr$_4$Ni$_3$O$_8$ in comparison to that of the stoichiometric and hole-doped infinite layer nickelate NdNiO$_2$ within the framework of density functional plus dynamical mean field theory, noting that Pr$_4$Ni$_3$O$_8$ has the same nominal carrier concentration as NdNiO$_2$ doped to a level of 1/3 holes/Ni. We find that the correlated Ni-3d shells of both of these low valence nickelates have similar many-body configurations with correlations dominated by the $d_{x^2-y^2}$ orbital. Additionally, when compared at the same nominal carrier concentration, the materials exhibit similar many-body electronic structures, self energies, and correlation strengths. Compared to cuprates, these materials are closer to the Mott-Hubbard regime due to their larger charge transfer energies. Moreover, doping involves the charge reservoir provided by the rare earth 5d electrons, as opposed to cuprates where it is realized via the oxygen 2p electrons.

I. INTRODUCTION

Understanding the physics and chemistry underlying the extraordinary properties of the layered copper-oxide materials has been a challenge to researchers over the more than thirty years since the discovery of superconductivity in La$_2$−$x$Ba$_x$CuO$_4$ [1] and the basic questions of mechanism for superconductivity are not yet settled. One approach to this question is to identify “cuprate analog” materials that have similar physical and nominal electronic structure but differ in local chemistry. A key feature of the cuprates is a square planar coordinated transition metal with a nominal $d^9$ valence. In this context, Anisimov et al. suggested that square planar $d^9$ nickel materials such as the “infinite layer” RNiO$_2$ with $R =$ La, Pr, Nd, or other rare earth elements would provide an important comparison [2], and these and related materials were studied theoretically within various density functional (DFT and DFT+U) approximations [2–10]. Synthesis of stoichiometric LaNiO$_2$ was reported already in 1983 [11], followed by improvements in synthesis [12] and then high quality thin films [13, 14]. This went hand in hand with experimental studies of multilayer reduced Ruddlesden-Popper variants [4, 15–20]. The reduced trilayer Ruddlesden-Popper materials were found to exhibit long-ranged (La$_4$Ni$_3$O$_8$, [17–19, 21]) or short-ranged (Pr$_4$Ni$_3$O$_8$, [20, 21]) density wave order.

Things took a dramatic turn in 2019 when superconductivity was found upon hole doping the infinite layer material NdNiO$_2$ [22] and subsequently PrNiO$_2$ [23]. Further investigation of the phase diagram of NdNiO$_2$ has shown that it becomes superconducting on modest (13.5-22.5%) Sr doping [24, 25]. However, superconductivity has not yet been observed in the reduced Ruddlesden-Popper nickelates, nor has density wave order been found in the infinite layer materials, although in the cuprate family trilayer materials exhibit superconductivity with among the highest reported transition temperatures. Moreover, the transport properties of 30% hole doped NdNiO$_2$ [24] and undoped Pr$_4$Ni$_3$O$_8$ [18] differ in that the former exhibits a weak localization upturn at low temperatures, whereas the latter has a more metallic behavior of the resistivity in temperature, similar to that of overdoped cuprates.

Several recent theoretical studies of the infinite layer materials have highlighted the possible importance of the high-spin $d^8$ configuration [26–32]. Significant participation of $d^8$ in the infinite layer material has been suggested based on recent resonant x-ray studies [33, 34], while related experimental studies of the trilayer material [18, 21] have found no evidence for high-spin $d^8$. The latter studies also argued that the trilayer material is intermediate in correlation strength between the infinite layer material and the cuprates.

Motivated by these differences, in this paper, we present a comparative density functional plus dynamical mean field theory (DFT+DMFT) [35–38] study of the trilayer nickelate Pr$_4$Ni$_3$O$_8$ and infinite layer nickelate NdNiO$_2$. The Pr variant of the trilayer material was chosen because it exhibits metallic resistivity similar to that of overdoped cuprates [18]. The two materials exhibit some differences in three dimensional arrangement, leading to different $c$-axis dispersion and different electron count in the stoichiometric compounds. We use the

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thoughts in Section V. We offer some concluding
strategies, spectral functions, orbital occupations, and multi-
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further introduces the two materials and also the
magnetic phase diagrams [9].

doping. When compared at the same doping, we find that
both have similar electronic structures, self energies, and
mass enhancements, but there are significant differences
in their Fermi surfaces that can be traced to their differ-
ing c-axis dispersions. The latter will be discussed below
and is related to DFT+U findings of differences in their
magnetic phase diagrams [9].

The rest of this paper is organized as follows. Section II further introduces the two materials and also the
formalism used here. Section III presents the results
obtained from density functional theory calculations,
with Section IV presenting the DFT+DMFT self ener-
gies, spectral functions, orbital occupations, and multi-
plet occurrence probabilities. We offer some concluding
thoughts in Section V.

II. BACKGROUND AND FORMALISM

The NdNiO$_2$ crystal structure, shown in Fig. 1, is com-
posed of NiO$_2$ planes separated by layers of Nd. The
structure of Pr$_4$Ni$_3$O$_8$, also shown in Fig. 1, is composed
of blocks of three NiO$_2$ layers. The three NiO$_2$ layers
in one group of three layers are separated by Pr ions,
alogous to the structure of the infinite layer material,
but each group of three NiO$_2$ layers is separated from
the neighboring three-layer groups by a fluorite-structure
Pr$_2$O$_2$ block. Each successive group is also displaced by
one half of a lattice constant in the x and y directions so
that it sits above the centers of the Ni plaquettes in the
neighboring groups. This, along with the Pr$_2$O$_2$ block,
means that the inter-trilayer coupling is weak enough
that each three-layer group is effectively independent so
that the net c-axis dispersion is much weaker than in the
infinite layer material. Another effect of the Pr$_2$O$_2$ block
is that it absorbs one electron from the NiO$_2$ trilayer,
nominally taking 1/3 of an electron from each Ni atom,
so Pr$_4$Ni$_3$O$_8$ has a formal valence of $d^{8.67}$ while NdNiO$_2$
has a formal valence of $d^9$.

While there are three Ni atoms per formula unit, the
two Ni atoms on the outer layers are equivalent by sym-
metry, so we refer to the two types as “inner” and
“outer”. There are also two types of Pr atoms, one which
we call Pr1 in between individual NiO$_2$ layers but within
the trilayer group, and one which we call Pr2 in between
groups of three layers (i.e., in the Pr$_2$O$_2$ block).

In this paper, we perform fully charge self consistent
DFT+DMFT [35-38] calculations using Wien2k [40] and
TRIQS [41-43]. The 4f-states of the rare earths are
treated as core electrons. We use the virtual crystal ap-
proximation at the DFT level (implemented via a frac-
tional atomic charge on the rare earth sites) to per-
form the calculations for both materials at dopings corre-
spanding to nominal Ni d-valences of $d^{8.67}$ and $d^9$. That
is, we hole dope NdNiO$_2$ by 0.33 to compare it to un-
doped Pr$_4$Ni$_3$O$_8$, and electron dope Pr$_4$Ni$_3$O$_8$ by 1 (1/3
per Ni atom) to compare it to undoped NdNiO$_2$

We use projectors in a wide energy window of $-10$ eV
to 10 eV to capture all of the relevant Ni-d, O-p, and
Pr1/Nd-d states. We use a five Ni-d orbital impurity
model with a rotationally invariant Slater Hamiltonian
with $U = 7$ eV and $J = 0.7$ eV, representative of nicke-
lates [44], at a temperature $T = 290$ K. We approximate
the double counting correction using the fully localized
limit (FLL) formula [45, 46] (a brief discussion of alter-
native double counting schemes is presented in the Ap-
pendix A). We use the single site DMFT approximation
for each Ni atom and solve the impurity problem using
CTHYB [42]. In the case of Pr$_4$Ni$_3$O$_8$, we have to solve
two impurity problems, one for the Ni atom of the inner
layer and one for the equivalent Ni atoms of the outer
layers. We use the maximum entropy method to analyti-
cally continue the self energies to the real frequency axis.
Further details of the calculations can be found in the
Appendix A.

III. DFT RESULTS

Fig. 2 shows the DFT band structures along high sym-
metry directions for both materials at the two nominal
fillings in the non-magnetic state. Using the Prima pack-
age [47], we show the Ni-d, O-p and Nd/Pr1-d character
of the bands. In the Appendix B, we show the specific
orbital character of the near Fermi energy bands. First,
we point out that the overall band structures are very similar when compared at the same doping level. For both materials, the main active bands crossing the Fermi level are of Ni-$d_{x^2-y^2}$ character with some admixture of O-$p$ (see also Fig. 3). The other Ni-$d$-derived bands are lower in energy, and the O-$p$-derived bands even lower, implying a relatively large charge-transfer energy and, as discussed in previous work [3, 28, 48–51], placing the materials closer to the Mott-Hubbard than to the charge transfer regime.

The Nd/Pr-$d$-derived bands are mostly above the Fermi energy and weakly hybridized with the Ni-$d$ bands, specifically $d_{z^2}$ near $\Gamma$ and $d_{x^2-y^2}$ near $A$ (and $M$ in the case of the trilayer compound), as extensively discussed in previous works [3, 33, 48–50, 52–64]. Depending on the doping, these states can give rise to small Fermi surface sheets centered at $\Gamma$ and $A(M)$. In the case of Pr$_4$Ni$_3$O$_8$, the near Fermi energy contributions to the electronic structure come from Pr1 and not Pr2. An overall difference between the two materials is that the Pr$_4$Ni$_3$O$_8$ bands do not have much $k_z$ dispersion because of the fluorite blocks and body centered tetragonal shift mentioned above.

Comparison of the left and right columns of Fig. 2 shows that as the nominal Ni valence is reduced from $d^9$ to $d^{8.67}$, the charge transfer energy is reduced: the O-$p$-derived bands move closer to and entangle more with the Ni-$d$-derived bands. We quantify the charge transfer energies by projecting the DFT bands onto maximally localized Wannier functions [65, 66] using Wannier90 [67, 68]. We then take the charge transfer energy as the difference between the on-site energy for the Ni-$d_{x^2-y^2}$ and the O-$p_\sigma$ orbital within the same NiO$_2$ plane. The resulting charge transfer energies are shown in Table
and vary by less than 5% between the two materials at the same doping, and by less than 10% over the doping range considered. Comparison to previous DFT calculations [69] indicates that the absolute values of the charge transfer energies are somewhat dependent (∼0.2 eV) on rare earth ion, with larger Z ions having a larger charge transfer energy.

Looking now in more detail at the Nd/Pr1-derived bands, we see that these bands are weakly hybridized with the Ni-d bands, the Nd/Pr1-d_{3z^2−r^2} mainly with Ni-d_{3z^2−r^2} and the Nd/Pr1-d_{xy} mainly with Ni-d_{xz/yz}. In both our DFT and DFT+DMFT calculations, both bands cross the Fermi energy in the d^9 case, but as carriers are removed the bands empty out. For d^{8.67}, the Γ centered band is above the Fermi energy in both materials; for the d^{8.67} infinite layer material, a small A centered pocket remains, but in the trilayer material the A/M-centered pocket disappears. The difference arises from the difference in c-axis dispersions, and as discussed below may be relevant to the low energy physics (i.e., charge/spin order).

### IV. DMFT RESULTS

#### A. Self energies and mass enhancements

Fig. 4 shows the real part of the analytically continued self energies of the correlated Ni-d orbitals for undoped NdNiO2 (top left), 1/3 hole doped NdNiO2 (top right), 1 electron doped Pr_{4}Ni_{3}O_{8} (middle and bottom left), and undoped Pr_{4}Ni_{3}O_{8} (middle and bottom right). The double counting and chemical potential are subtracted from the self energies.

![Fig. 3. Near Fermi energy DFT density of states per Ni atom resolved into Ni-d and Nd/Pr1-d orbitals.](image)

### TABLE I. Charge transfer energies obtained from Wannier fits to the DFT band structure. The Ni-d, O-p, and Nd/Pr1-d_{z^2} and d_{xy} orbitals are included in the fit. The charge transfer energy is defined as the difference between the onsite energies of the Ni-d_{z^2−r^2} and O-p_{x} Wannier functions.

| Material            | d^9  |
|---------------------|------|
| NdNiO2              | 4.35 |
| Pr_{4}Ni_{3}O_{8} inner | 4.32 |
| Pr_{4}Ni_{3}O_{8} outer | 4.32 |
| Pr_{4}Ni_{3}O_{8} outer | 4.01 |
| Pr_{4}Ni_{3}O_{8} outer | 3.89 |

![Fig. 4. Real part of the analytically continued self energies of the correlated Ni-d orbitals for undoped NdNiO2 (top left), 1/3 hole doped NdNiO2 (top right), 1 electron doped Pr_{4}Ni_{3}O_{8} (middle and bottom left), and undoped Pr_{4}Ni_{3}O_{8} (middle and bottom right). The double counting and chemical potential are subtracted from the self energies.](image)
TABLE II. Mass Enhancements for Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8} and NdNiO\textsubscript{2} at studied doping levels, resolved by orbital character. The values are extracted Matsubara self energy, as described in the Appendix A.

| Material     | d\textsubscript{x\textsuperscript{2}−y\textsuperscript{2}} | d\textsubscript{xy} | d\textsubscript{x\textsuperscript{2}/y\textsuperscript{2}} |
|--------------|---------------------|---------------------|---------------------|
| NdNiO\textsubscript{2} | 1.4 | 1.4 | 3.7 |
| NdNiO\textsubscript{2} | 1.4 | 1.4 | 3.7 |
| Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8} inner | 1.5 | 1.4 | 3.0 |
| Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8} outer | 1.4 | 1.4 | 3.0 |
| Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8} inner | 1.4 | 1.4 | 3.9 |
| Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8} outer | 1.4 | 1.4 | 4.0 |

\( m^*/m = Z^{-1}\). Results are shown in Table II; they confirm further that the correlations are dominated by the \(d_{x^2−y^2}\) orbitals. We also see that the two materials have very similar \(d_{x^2−y^2}\) mass enhancements at the same doping and that the effective correlation strength is somewhat greater at \(d^9\) filling.

The \(d_{x^2−y^2}\) self energy has pronounced structures at \(\sim \pm 0.5\) eV; these structures are a consequence of Mott-Hubbard/charge transfer correlations, and at the Mott transition would coalesce near \(\omega = 0\). The structures are much more pronounced at \(d^9\), indicating the weakening of correlations upon hole doping expected of Mott-Hubbard/charge transfer materials. We also note the presence of a small structure at about \(\omega = 0.2\) eV visible especially in the \(d^9\) case; this might be a signature of Hund’s physics because a low frequency structure observed on only one side of the Fermi energy is characteristic of known Hund’s metal materials [70]. Indeed, some authors label NdNiO\textsubscript{2} as a Hund’s metal [26, 29, 71]. The peak we find, along with the \(d\)-level density matrix discussed below, may be an indication that Hund’s metal physics plays at least some role; however, the small amplitude of the feature and its presence only in the \(d_{x^2−y^2}\) self energy and not in the self energy of other orbitals, and visible only at \(d^9\), suggests that the Hund’s correlations, while present, are less important than the Mott-Hubbard correlations revealed by the large amplitude features in the self energy. The relative strength of Hund’s versus Mott-Hubbard physics depends on the ratio of \(U\) to \(J\), and comparing to results presented in Ref. [72], especially the value of \(Z\), our results are more on the Mott-Hubbard side of the \(U\)-\(T\) phase diagram.

### B. Spectral Functions

Fig. 5 shows the orbitally resolved DFT+DMFT spectral function \(A(\omega) = i [G(\omega) - G(\omega)^\dagger]/2\pi\) (\(A\) and \(G\) are matrices in orbital space). The spectral functions for the two materials are similar when compared at the same nominal carrier concentration. One difference discussed below between the two material families is that in the \(d^8\) case for Pr\textsubscript{4}Ni\textsubscript{13}O\textsubscript{8}, there is a weak shoulder in the \(O\)-\(p\) spectral function at \(\sim -2\) eV that is not present for \(d^9\) NdNiO\textsubscript{2}. This is due to the oxygen atoms in the flu-
ishes and is replaced by an A-centered pocket, while the Fermi surface of the Ni-\(d_{x^2-y^2}\)-derived band passes through a van Hove singularity, changing its topology from hole-like (\(M\)-centered) to electron-like (\(\Gamma\)-centered). The \(\text{Pr}_4\text{Ni}_3\text{O}_8\) Fermi surface has negligible \(k_z\) dispersion, but as shown in panel (d) at nominal \(d^5\) carrier concentration consists of three Ni-\(d_{x^2-y^2}\)-derived pockets: the bonding, non-bonding, and antibonding superpositions of the three layers, which all have the same hole-like topology. Pr-derived pockets at \(\Gamma\) and \(A/M\) are also evident.

For \(\text{NdNiO}_2\) at nominal \(d^8.67\) doping, we see from panels (c-g) that the van Hove singularity in the Ni-derived bands occurs at a smaller \(k_2\) and near \(k_z = \pi\) the Fermi surface becomes a small \(\Gamma\)-centered circle. The \(\Gamma\)-centered Nd-derived pocket is absent and the A-centered Nd-derived pocket is much smaller. Turning now to the trilayer material (panel h), we see that at nominal \(d^8.67\) filling both Pr-derived bands are above the Fermi energy, while the \(d_{x^2-y^2}\) antibonding Fermi around \(\Gamma\) surface becomes nearly square-like with a nesting vector similar (but not equal) to the observed density wave ordering vector [17]. DFT studies have indeed revealed that the free energy is lowered if a density wave occurs with \(q = (2\pi/3, 2\pi/3)\) is considered [8, 18].

### C. Orbital Occupancies and Occurrence Probabilities

Table III shows the fillings of the correlated orbitals, obtained from the impurity Green’s function \(G(i\omega_n)\), for both materials at both dopings. Remarkably, for both materials, within the context of our 5 orbital model, removing 1/3 of an electron/Ni leaves the total occupancy of the Ni-\(d\)-states roughly invariant. The \(d_{x^2-y^2}\) occupation decreases as expected, but this is mostly compensated by an increase in the occupation of the other orbitals. In this context, it should be remembered that there is some admixture of O-\(p\) and Pr/Nd-\(d\) in our effective orbital basis used in DMFT [29].

Table IV shows the occurrence probabilities of different \(d\) configurations of the Ni-\(d\) states obtained from the impurity density matrices determined from the CTHYB solver. We find similar results for both materials, and these results are only weakly dependent on doping. We find that the materials have \(\approx 50\% d^3\), and the rest is mostly \(\approx 40\% d^4\) with \(\approx 6\% d^7\) and \(\approx 4\% d^6\). Approximately 70\% of the \(d^8\) weight is high spin for the nominal \(d^8\) filling calculations, decreasing to \(\approx 60\%\) for nominal \(d^8.67\) filling. In all cases, the contribution to high spin \(d^8\) is mainly from one electron in \(d_{x^2-y^2}\) and the other in \(d_z\). If only the \(d_{x^2-y^2}\) orbital were relevant, as in traditional one band Mott-Hubbard systems, we would expect equal amounts of \(d^{10}\) and \(d^8\) for the nominal \(d^8\) materials. If there were more \(d^{10}\) than \(d^8\), then like cuprates [52, 73] there would be charge transfer from the oxygen orbitals. In this case, in stark contrast to cuprates, we find much more \(d^8\) than \(d^{10}\), indicating a reverse charge transfer from Ni to Nd/Pr. We should also remark that the stripe state seen for the La variant of the trilayer material is consistent with non-magnetic domain walls, implying they are occupied by low-spin \(d^8\) [18, 19, 21] as supported by DFT studies [8, 18].

Interestingly, even though the total Ni-\(d\) occupancy is essentially independent of doping and the \(d_{x^2-y^2}\) occupancy gets closer to half filling as electrons are removed, the \(d_{x^2-y^2}\) self energy evolves with doping roughly as expected in a doped Mott-Hubbard material.

| TABLE III. Ni-\(d\) orbital occupancies obtained from the impurity \(G(i\omega_n)\). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(\text{NdNiO}_2\) \(d^8\) | \(d^7\) | \(d^6\) | \(d^5\) | \(d^4\) |
| \(\text{NdNiO}_2\) \(d^8.67\) | 0.05 | 0.13 | 0.29 | 0.49 | 0.04 |
| \(\text{Pr}_4\text{Ni}_3\text{O}_8\) \(d^8.67\) inner | 0.05 | 0.17 | 0.25 | 0.48 | 0.04 |
| \(\text{Pr}_4\text{Ni}_3\text{O}_8\) \(d^8.67\) outer | 0.05 | 0.17 | 0.26 | 0.48 | 0.04 |
| \(\text{Pr}_4\text{Ni}_3\text{O}_8\) \(d^8\) inner | 0.05 | 0.12 | 0.29 | 0.49 | 0.04 |
| \(\text{Pr}_4\text{Ni}_3\text{O}_8\) \(d^8\) outer | 0.05 | 0.12 | 0.28 | 0.51 | 0.05 |

| FIG. 6. DFT+DMFT momentum-resolved spectral functions \(A(k, \omega)\) per Ni atom for undoped \(\text{NdNiO}_2\) (top left), 1/3 hole doped \(\text{NdNiO}_2\) (top right), 1 electron doped \(\text{Pr}_4\text{Ni}_3\text{O}_8\) (bottom left), and undoped \(\text{Pr}_4\text{Ni}_3\text{O}_8\) (bottom right). |
FIG. 7. DFT+DMFT momentum-resolved spectral functions $A(k_x, y, k_z, \omega = 0)$ for $d^9$ (top row) and $d^{8.67}$ (bottom row). Three left panels: NdNiO$_2$ at different $k_z$ values indicated; right panel: Pr$_4$Ni$_3$O$_8$. $k$ is given in $2\pi/a$ and $2\pi/c$ units.

being largest at nominal $d^9$ and decreasing as carriers are removed. This finding is consistent with other 5 orbital DFT+DMFT studies [29] and suggests that the effective low energy Mott-Hubbard physics arises in an interesting way from charge transfer physics. In contrast to the cuprates, where the ligand (oxygen) states both provide bandwidth for the $d$ orbitals and act as a charge reservoir, absorbing most of the doping, in the nickelate materials the charge reservoir is provided by the Nd/Pr 5$d$ states but these orbitals do not provide the $d$ bandwidths. Instead, the bandwidth is mainly due to hybridization with O-$p$ as in cuprates, which is supported by resonant x-ray inelastic (RIXS) studies showing a strong fluorescence line due to $d$-$p$ mixing [33].

The occurrence probabilities are different from those obtained in our previous work on NdNiO$_2$ [52], where we found 0.05 probability of $d^8$ and 0.26 probability of $d^{10}$. The first source of difference comes from the differently constructed low energy subspaces: by considering 5 rather than 2 $d$-orbitals we provide more possibilities for $d^8$ configurations. The second difference is methodological, and points to an interesting issue in the DFT+DMFT formalism. In this work we use a projector formalism, while in the previous work we used the selectively localized variant of the maximally localized Wannier function method. The bands obtained from the selectively localized Wannier procedure reproduce the DFT bands perfectly. However, the physical content of the orbital basis in which the correlated problem is solved differs between methods. The oxygen and Pr/Nd Wannier functions defined in the selectively localized procedure overlap in space with the Ni-$d$ orbitals; some of this “ligand” amplitude appears as Ni amplitude in the projector methodology. This difference in how the methods disentangle the Ni, Nd, and O contributions leads to the differences in $d$ occupancy; it is important to note that the differences are larger for the $d$ occupancies than for other quantities: the two methods give very similar mass enhancements and lifetimes for the near Fermi energy Ni-$d_{z^2-r^2}$-derived bands. The choice of correlated orbitals is a fundamental ambiguity in the DFT+DMFT methodology that requires further investigation [74].

V. DISCUSSION

In this paper, we presented DFT+DMFT studies of NdNiO$_2$ and Pr$_4$Ni$_3$O$_8$, representative of two families of cuprate-analog materials involving square planar coordinated near $d^9$ valence Ni ions but with other structural differences that lead to different Fermiology. In terms of formal valence, Pr$_4$Ni$_3$O$_8$ corresponds to 1/3 hole doped NdNiO$_2$. The Pr$_4$Ni$_3$O$_8$ family of materials has not previously been studied with DFT+DMFT.

Our study employed the DFT+DMFT method, with full charge self-consistency to properly account for the charge transfer between the Ni and the Nd/Pr ions; this is believed to correctly incorporate the physics of the long-ranged Coulomb interaction in moderating density inhomogeneities in solids [75, 76].

Our study was based on treating correlation effects in
a wide energy window; instabilities arising from very low energy physics is beyond the scope of our study.

In our study, we found that the materials have very similar electronic properties on the broader energy scales when compared at the same doping level: from the point of view of basic strong correlation many-body physics, the two compounds may be studied interchangeably. Our calculations indicate that differences of physics should be attributed to low energy physics arising from differences in Fermiology.

On the level of broad-band electronic structure we found, in agreement with previous work [26–29, 33], that the ground state electronic configuration has a significant admixture of $d^8$ and a relatively small admixture of $d^{10}$, unlike the cuprates where the ground state electronic configuration is an almost equal admixture of $d^9$ and $d^{10}$ with very little $d^8$. The appearance of $d^8$ without $d^{10}$ is a consequence of charge transfer from the Ni to the Nd/Pr orbitals, as which other authors have noted function as a charge reservoir. However, we found that the self energy and the spectral function displayed the characteristic forms expected in a Mott-Hubbard/charge density wave instability in hole doped NdNiO$_3$ and a density wave instability in hole doped NdNiO$_8$ and a density wave instability in hole doped NdNiO$_8$ should provide further insight on the interplay of Fermiology and local correlation physics.

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Appendix A: DFT+DMFT Calculations

We perform DFT calculations using WIEN2k [40] with the standard PBE version of the GGA functional [78]. For both materials we use the experimentally determined crystal structure. For NdNiO$_3$ this is the P4/mmm space group with $a = b = 3.92\,\text{Å}$ and $c = 3.31\,\text{Å}$ [22]. For Pr$_2$Ni$_3$O$_8$ this is the I4/mmm space group with $a = b = 3.9347\,\text{Å}$ and $c = 25.485\,\text{Å}$ [18]. The DFT calculations were converged with a $RK_{\text{max}} = 7$ and with a k-point grid of $40 \times 40 \times 40$ for NdNiO$_2$ and $20 \times 20 \times 20$ for Pr$_2$Ni$_3$O$_8$. We put the Nd/Pr-4f bands in the core. We dope the materials using the virtual crystal approximation, where we adjust the atomic numbers of the Nd/Pr ions to fractional values and correspondingly change the number of electrons. For the DMFT calculations we construct projective Wannier functions for the Ni-d shells in an energy window of $-10\,\text{eV}$ to $10\,\text{eV}$ around the Fermi energy.

We perform the DMFT calculations using the TRIQS software library [41–43]. We treat the 5 Ni-d orbitals as correlated. We use a rotationally invariant Slater Hamiltonian with $U = F^0 = 7\,\text{eV}$ and $J = (F^2 + F^4)/14 = 0.7\,\text{eV}$. We perform the calculations at a temperature of $T = 290\,\text{K}$. We solve the impurity problem using the
FIG. 8. Imaginary part of the Matsubara self energies.

CTHYB solver [42, 79]. We use a double counting correction of the FLL form [45], which we update at each iteration as the DFT density changes. We analytically continue the self energies using the maximum entropy method [80].

1. Matsubara Self Energy and Mass Enhancement

Fig. 8 shows the imaginary part of the Matsubara self energies for both materials at their nominal fillings. The Matsubara self energies clearly show that correlations are stronger for the $d_{x^2-y^2}$ orbital and similar in strength for the other orbitals.

We obtain the quasiparticle mass enhancement directly from the Matsubara self energy to avoid error in the analytic continuation. The mass enhancement is given by:

$$Z^{-1} = \left( 1 - \frac{\partial \text{Im} \Sigma(i\omega_n)}{\partial \omega_n} \bigg|_{\omega_n \to 0} \right). \quad (A1)$$

We determine $Z$ by fitting a polynomial of fourth order to the lowest six points of the Matsubara self-energies and extrapolate $\text{Im} \Sigma(i\omega_n \to 0)$, a procedure also used in previous work [81, 82].

2. Comparison to Cuprate

|        | $d^6$ | LS $d^8$ | HS $d^6$ | $d^7$ | $d^{10}$ |
|--------|-------|----------|----------|-------|----------|
| NdNiO$_2$ | 0.05  | 0.12     | 0.28     | 0.50  | 0.04     |
| CaCuO$_2$ | 0.00  | 0.03     | 0.04     | 0.54  | 0.38     |

TABLE V. Multiplet occurrence probabilities for the NdNiO$_2$ and CaCuO$_2$ Ni/Cu-$d$ shells obtained from one-shot DFT+DMFT calculations.

To investigate the effect of using projectors on CaCuO$_2$, we ran one-shot DFT+DMFT calculations on NdNiO$_2$ and CaCuO$_2$ using a wide energy window of $-10\text{eV}$ to $10\text{eV}$ and used a $5d$ orbital impurity model. We ran both calculations on the stoichiometric (nominal $d^9$) materials.
Table V shows the resulting multiplet occurrence probabilities. Similar to the Wannier function case [52], the cuprate has a high percentage of $d^{10}$ and a relatively small amount of $d^8$.

### 3. Double Counting

We examined the effect of changing the double counting correction by running a one-shot DFT+DMFT calculation on stoichiometric NdNiO$_2$ using the around mean field (AMF) double counting scheme and compare the results to those of the one-shot FLL scheme.

|        | $d^z$ | $d_{x^2-y^2}$ | $d_{xy}$ | $d_{xz/yz}$ | total |
|--------|-------|---------------|----------|-------------|-------|
| FLL    | 1.61  | 1.12          | 1.96     | 1.92        | 8.52  |
| AMF    | 1.46  | 1.05          | 1.96     | 1.90        | 8.27  |
| DFT    | 1.58  | 1.19          | 1.95     | 1.89        | 8.50  |

**TABLE VI.** Comparison of multiplet occurrence probabilities for the NdNiO$_2$ Ni-$d$ shell using FLL and AMF double counting schemes.

Table VI shows the resulting multiplet occurrence probabilities and Table VII shows the orbital occupancies. The AMF double counting scheme empties out the $e_g$ orbitals, particularly the $d_{z^2}$ orbital, more than the FLL scheme. Consequently, the AMF results in significantly more high spin $d^8$ than FLL.

**Appendix B: Fat band analysis**

Figs. 9 and 10 show the orbital character of the near Fermi energy region for stoichiometric NdNiO$_2$ and Pr$_4$Ni$_3$O$_8$, respectively. The plots show that the main bands crossing the Fermi energy are of Ni-$d_{x^2-y^2}$ character with some O-$p$ admixture. For NdNiO$_2$, Fig. 9 shows that the Γ pocket is a mixture of Ni-$d_{z^2}$ and Nd-$d_{z^2}$, and the A pocket is a mixture of Ni-$d_{xz/yz}$ and Nd-$d_{xy}$. For the case of stoichiometric Pr$_4$Ni$_3$O$_8$, Fig. 10 shows that the band which goes down to $\sim 0.8$ eV at the Γ point, and goes below the Fermi energy upon electron doping, is a mixture of Ni-$d_{z^2}$ and Pr$_1$-$d_{z^2}$, but does not contain significant amounts of Pr$_2$. Likewise, the band which goes down to $\sim 0.2$ eV at the M point and goes below the Fermi level upon doping is of Ni-$d_{xz/yz}$ and Pr$_1$-$d_{xy}$ character, but not any significant Pr$_2$ character.
FIG. 9. Orbital character of energy bands for undoped (nominal $d^9$) NdNiO$_2$. 
FIG. 10. Orbital character of energy bands for undoped (nominal $d^{8.67}$) Pr$_4$Ni$_3$O$_8$
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