Low Valence Nickelates: Launching the Nickel Age of Superconductivity

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The discovery of superconductivity in thin films (~10 nm) of infinite-layer hole-doped NdNiO2 has invigorated the field of high temperature superconductivity research, reviving the debate over contrasting views that nickelates are isostructural with cuprates are either 1) sisters of the high temperature superconductors, or 2) that differences between nickel and copper at equal band filling should be the focus of attention. Each viewpoint has its merits, and each has its limitations, suggesting that such a simple picture must be superseded by a more holistic comparison of the two classes. Several recent studies have begun this generalization, raising a number of questions without suggesting any consensus. In this paper, we organize the findings of the electronic structures of n-layered NiO2 materials (n = 1 to ∞) to outline (ir) regularities and to make comparisons with cuprates, with the hope that important directions of future research will emerge.

Keywords: superconductivity, electronic structure ab-initio calculations, nickelates, magnetism, cuprates, electronic structure

1 BACKGROUND

After much synthesis and characterization of low-valence layered nickelates over three decades [1–7], superconductivity was finally observed [8] in hole-doped $\text{RNiO}_2$ (initially for rare earth $R = \text{Nd}$, later for $R = \text{La}$ [9, 10] and Pr [11]) with $T_c$, exhibiting a dome-like dependence [12, 13] being maximal (10–15 K) near 20% doping. This series of discoveries in $\text{RNiO}_2$ materials marked the beginning of a new, nickel age of superconductivity [14, 15] launching a plethora of experimental [16–22] and theoretical [23–43] work.

$\text{RNiO}_2$ materials are the $n = \infty$ member of a larger series of layered nickelates with chemical formula $(\text{RO})_x [\text{R} (\text{NiO}_2)_y]^+$ ($R = \text{La, Pr, and Nd}$; $n = 2, 3, \ldots, \infty$) that possess n cuprate-like NiO2 planes in a square-planar coordination. Except for the $n = \infty$ case, groups of $n$-NiO2 layers are separated by $\text{R}_2\text{O}_3$ blocking layers that severely limit coupling between adjacent units (see Figure 1). These layered square-planar compounds are obtained via oxygen deintercalation from the corresponding parent perovskite $\text{RNiO}_3$ ($n = \infty$) [2] and Ruddlesden-Popper $R_{m+1}\text{Ni}_n\text{O}_{3m+1}$ ($n \neq \infty$) phases [1]. As shown in Figure 1, the $(\text{RO})_{x-1} (\text{RNiO}_2)_x$* series can be mapped onto the cuprate phase diagram in terms of the nickel 3$d$-electron count, with nominal fillings running from $d^9$ ($n = \infty$) to $d^5$ (for $n = 1$). That superconductivity arises in this series suggests that a new family of superconductors has been uncovered, currently with two members, $n = \infty$ and $n = 5$ [44], the only ones (so far) where an optimal Ni valence near $d^{8.8}$ has been attained.

Some overviews on experimental and theoretical findings in this family of materials have been recently published [45–48]. In this paper, we focus on the electronic structure of layered nickelates,
doping, with $T_c$ exhibiting a dome-like dependence \[12, 13, 49\] akin to cuprates, as shown in Figure 1. However, in parent infinite-layer nickelates the resistivity shows a metallic $T$-dependence (but with a low temperature upturn) \[7, 8\] and there is no signature of long-range magnetic order, even though the presence of strong antiferromagnetic (AFM) correlations has recently been reported via resonant inelastic x-ray scattering (RIXS) experiments \[50\]. This is in contrast to cuprates, where the parent phase is an AFM charge-transfer insulator.

Noteworthy differences from cuprates were already reflected in early electronic structure calculations as well \[51, 52\]. For the parent material $R$NiO$_2$, non-magnetic density functional theory (DFT) calculations show that besides the Ni-$d_{x^2-y^2}$ band, additional bands of $R$-5$d$ character cross the Fermi level. The electronic structure of $R$NiO$_2$ is three-dimensional-like, with a large $c$-axis dispersion of both (occupied) Ni and (nearly empty) $R$-5$d$ bands (see Figure 2) due to the close spacing of successive NiO$_2$ planes along the $c$-axis. The $R$-5$d_{x^2}$ dispersion leads to the appearance of electron pockets at the $\Gamma$ and $A$ points of the Brillouin zone which display mainly $R$-5$d_y$ and $R$-5$d_{xy}$ character, respectively, that self-dope the large hole-like Ni-$d_{x^2-y^2}$ Fermi surface. This self-doping effect (absent in the cuprates) introduces a substantial difference between nominal and actual filling of the Ni-$d$ bands, accounting for conduction and possibly also disrupting AFM order. The presence of the 5$d$ electrons is consistent with experimental data, which reveal not only metallic behavior but also evidence for negative charge carriers as reflected in the negative Hall coefficient \[8, 12, and 13\]. However, as the material becomes doped with Sr, the $R$-5$d$ pockets become depopulated, the Hall coefficient changes sign \[8\], and the electronic structure becomes more single-band, cuprate-like \[39, 53\].

Besides the presence of $R$-5$d$ electrons, infinite-layer nickelates have some other relevant differences from the cuprates, particularly their much larger charge-transfer energy between the metal 3$d$, and oxygen 2$p$ states. In cuprates, the charge-transfer energy $\varepsilon_{3d-2p}$ is as small as 1–2 eV \[54\], indicative of a large $p$-$d$ hybridization, and enabling Zhang-Rice singlet formation. In NdNiO$_2$, the charge-transfer energy is much larger, ~4.4 eV, as obtained from the on-site energies derived from a Wannier analysis \[39\]. The lack of a pre-peak in x-ray absorption (XAS) data at the oxygen K-edge \[18\] in NdNiO$_2$ has indeed been associated to the presence of a large charge-transfer energy. Because of this increase in charge transfer energy, the nickelate is more Mott-like, whereas the cuprate is more charge-transfer-like, in the scheme of Zaanen, Sawatzky, and Allen \[35, 38\]. In addition, theoretical investigations of $R$NiO$_2$ find decreasing oxygen content as one traverses from La to Lu \[55\].

The doped holes tend to be on the Ni sites, as opposed to cuprates where they tend to reside on the oxygen sites. Recent DFT + DMFT Ni 2$p_{3/2}$ core-level XPS, XAS, and RIXS calculations (consistent with available core-level spectroscopies) indeed confirm that the Ni-O hybridization does not play an important role in connection with doping, implying that the physics of NdNiO$_2$ is well described by a single-band Hubbard model \[56\]. This in turn brings up the issue of the nature of the doped holes on the Ni sites. That is, do

2 FROM $\infty$ TO ONE

2.1 “Infinite-Layer” $n = \infty$ Nickelate: $R$NiO$_2$

In parent $R$NiO$_2$ materials, Ni has the same formal 3$d^9$ electronic configuration as in cuprates. As mentioned above, superconductivity in $R$NiO$_2$ materials emerges via hole confining ourselves to materials with the basic infinite-layer structure: $n$ square planar NiO$_2$ layers each separated by an $R^{3+}$ ion without the apical oxygen ion(s) that are common in most cuprates and nickelates.
they behave as effective $d^8$ dopants, and if so, is $d^9$ high-spin ($S = 1$) or low-spin ($S = 0$)? If the former, then these materials would fall in the category of Hund’s metals, and thus would deviate substantially from cuprates. DMFT calculations are consistent with this picture as they systematically favor high-spin $d^9$ ($S = 1$) states \[40, 57\]. DFT calculations point instead towards a cuprate-like low-spin ($S = 0$) picture due to the large crystal-field splitting of the $e_g$ states in a square planar environment \[53\]. Along these lines, impurity calculations show that in the NiO$_2$ layers a Zhang-Rice singlet (like in CuO$_2$) is indeed favored upon hole-doping \[35\]. Further, cluster calculations find that hole doping distributes over the entire cluster, in contrast to local $S = 1$ states \[61\].

Because of their lower degree of $p-\text{d}$ hybridization, the superexchange in $\text{RNiO}_2$, as determined by resonant inelastic x-ray scattering experiments \[50\], is about half that of the cuprates. Still, its value ($J = 64$ meV) confirms the existence of significant AFM correlations \[30, 50\]. Long-range AFM order has however not been reported, with NMR data suggesting the ground state is paramagnetic \[62\], and susceptibility data interpreted as spin-glass behavior \[63\]. Neél type order is consistently obtained in DFT studies \[24, 27, 29, 51\], as in $d^9$ insulating cuprates. The predicted AFM ground state in DFT + $U$ calculations \[64\] is characterized by the involvement of both $d_{x^2-y^2}$ and $d_{z^2}$ Ni bands \[65\]. This state is peculiar in that it displays a flat-band one-dimensional-like van Hove singularity of $d_{z^2}$ character pinned at the Fermi level. These flat-band instabilities should inhibit but not eliminate incipient AFM tendencies \[65\].

Discussing the origin of superconductivity in $\text{RNiO}_2$, as in the cuprates, is a controversial topic. But certainly the reduced $T_c$ of the nickelate compared to the cuprates is consistent with the reduced value of the superexchange, and the larger charge-transfer energy. $t$-$J$ model and RPA calculations building from tight-binding parameters derived from DFT calculations show that the dominant pairing instability is in the $d_{x^2-y^2}$ channel, as in cuprates \[66\]. Indeed, single-particle tunneling measurements on the superconducting infinite-layer nickelate have revealed a V-shape feature indicative of a $d$-wave gap \[67\]. On a broader level, several theoretical papers have speculated that the superconductivity is instead an interfacial effect of the infinite-layer film with the SrTiO$_3$ substrate \[68-71\], though recently superconductivity has been observed when other substrates are used \[72\]. In this context, it should be noted that superconductivity has not been observed in bulk samples yet; since the precursor is cubic, there is no set orientation for the $c$-axis, meaning the bulk is far less ordered than the film \[20, 21\].

### 2.2 The Superconducting $n = 5$ Material

Recently, a second superconducting member has been found in the $\text{RO}_2^-$ ($\text{RNiO}_2$)$_2^+$ family: the $n = 5$ layered nickelate Nd$_6\text{Ni}_5\text{O}_{12}$, also synthesized in thin-film form \[44\]. As schematically shown in Figure 1, this material has a nominal valence near that of the optimally-doped infinite-layer material (that is, Ni$^{2+}$: $d^{8.8}$ nominal filling) and so, in contrast to its infinite-layer counterpart, it is superconducting without the need for chemical doping. While $\text{RNiO}_2$ displays NiO$_2$ layers separated by $\text{R}$ ions, this quintuple-layer material (with five NiO$_2$ layers per formula unit) has an additional fluorite $R_2$O$_2$ slab separating successive five-layer units. Further, each successive five-layer group is displaced by half a lattice constant along the $a$ and $b$ directions (i.e., the body centered translation of the $I4/mmm$ space group). These additional structural features effectively decouple the five-layer blocks, so the $c$-axis dispersion of this material is much weaker than its infinite-layer counterpart. Despite these significant structural
differences, $T_c$ is similar to that of the doped infinite-layer materials (with the onset of the superconducting transition taking place at $\sim 15$ K), reducing the chances that yet to be synthesized low valence nickelates will have substantially higher transition temperatures.

In terms of its electronic structure [73], the $n = 5$ material is intermediate between cuprate-like and $n = \infty$-like behavior. From DFT calculations, the charge-transfer energy of Nd$_3$Ni$_5$O$_{12}$ is $\sim 4.0$ eV. This reduced energy compared to the undoped infinite-layer material means that the Ni-$3d$ states are not as close in energy to the Nd-$5d$ states, consistent with the presence of a pre-peak in the oxygen K-edge (similar to what happens with Sr-doped NdNiO$_2$ [53]). As a consequence, the electron pockets arising from the Nd-$5d$ states are significantly smaller than those in the infinite-layer material (see Figure 2). This reduced pocket size along with the large hole-like contribution from the Ni-$3d$ states is consistent with experiment in that the Hall coefficient remains positive at all temperatures, with a semiconductor-like temperature dependence reminiscent of under- and optimally-doped layered cuprates. Aside from the appearance of these small Nd-derived pockets at the zone corners, the Fermi surface of Nd$_3$Ni$_5$O$_{12}$ is analogous to that of multilayer cuprates with one electron-like and four hole-like $d_{x^2-y^2}$ Fermi surface sheets. Importantly, the Fermi surface of the quintuple-layer nickelate is much more two-dimensional-like compared to the infinite-layer nickelate material, as the presence of the fluorite blocking slab reduces the $c$-axis dispersion, as mentioned above.

### 2.3 The $n = 3$ Material, the Next Superconducting Member of the Series?

The materials discussed above can be put into the context of earlier studies of bulk reduced RP phases with $n = 2, 3$ NiO$_2$ layers [5, 74–76], separated by fluorite $\text{R}_2\text{O}_3$ blocking slabs that enforce quasi-2D electronic and magnetic behavior.

The $n = 3$ member of the series, $\text{R}_2\text{Ni}_3\text{O}_8$ (with Ni$^{4+}$: $d^{6.67}$ filling), has been studied extensively over the past decade (both single crystal and polycrystalline samples) [74]. Since the charge-transfer energy decreases with decreasing $n$ [73], the $n = 3$ class is more cuprate-like than its $n = \infty$ and $n = 5$ counterparts. Both La and Pr materials are rather similar regarding their high-energy physics, with a large orbital polarization of the Ni-$e_g$ states, so that the $d^8$ admixture is low spin [75, 77] (but see Ref. [78]). The primary difference is that La$_4$Ni$_3$O$_8$ exhibits long-range stripe order [76, 79] (similar to that seen in 1/3 hole-doped La$_3$NiO$_4$, consisting of diagonal rows of Ni$^{4+}$ (S = 1/2) and Ni$^{2+}$ (S = 0) in a two to one ratio [80]. In contrast, the Pr counterpart appears to have short-range order instead [81]. This results in the La material being insulating [82] in its low-temperature charge-ordered phase [80], whereas Pr$_4$Ni$_3$O$_8$ remains metallic at all temperatures [75], with an intriguing linear $T$ behavior in its resistivity for intermediate temperatures (similar to that of cuprates at a comparable hole doping). Nd samples have also been studied [83], but the degree of insulating/metallic behavior seems to be sample dependent.

### 2.4 The $n = 2$ Material

The $n = 2$ member of the series, La$_3$Ni$_2$O$_6$, has been synthesized and studied as well [5, 88]. In terms of filling, it lies further away from optimal $d$-filling, being nominally Ni$^{5+}$: $d^5$. Experimentally, it is a semiconducting with no trace of a transition occurring at any temperature, although NMR data suggest that the AFM correlations are similar to those of the $n = 3$ material. Electronic structure studies [80] have predicted its ground state to have a charge-ordered pattern with Ni$^{2+}$ cations in a low-spin state and the Ni$^{3+}$: $d^5$ cations forming a S = 1/2 checkerboard pattern. This charge-ordering between S = 1/2 Ni$^{4+}$: $d^9$ and non-magnetic Ni$^{2+}$: $d^5$ cations is similar to the situation in the $n = 3$ material [80]. Calculations suggest that it is quite general in these layered nickelates that the Ni$^{2+}$ cations in this square-planar environment are non-magnetic. This has been shown by $ab$ initio calculations to be the case also with the Ni$^{2+}$ dopants in the $\text{R}$NiO$_2$ materials [53].
2.5 The \( n = 1 \) Case

The long-known \( \mathcal{R}_2 \text{NiO}_4 \) materials, with the \( n = 1 \) formula as above, contain Ni ions with octahedral coordination. We instead consider \( \text{Ba}_2 \text{NiO}_2(\text{AgSe})_2 \) (BNOAS) [89], as it represents the extreme opposite of the \( n = \infty \) member, not only in regards to its \( d^\text{n} \) valence, but also because its square planar coordination with long Ni-O bond is thought to promote “high-spin” (magnetic) behavior, that is, one hole in \( d_{z^2} \) and one hole in \( d_{x^2-y^2} \). Unlike the other \( n \) cases, the charge balanced formula is \( \text{(BaAg}_2\text{Se}_2)^3(\text{BaNiO}_2)^8 \); both blocking and active layers are formally neutral. BNOAS is insulating, distinguished by a magnetic susceptibility that is constant, thus non-magnetic, above and below a peak at \( T^* \approx 130 \text{ K} \). This increase from and subsequent decrease to its high-T value reflects some kind of magnetic reconstruction at \( T^* \) that was initially discussed in terms of canting of high-spin moments. That interpretation does not account for the constant susceptibility above and below the peak.

Valence counting indicates Ni \( ^{2+} : d^8 \), so a half-filled \( e_g \) manifold. Conventional expectations are either 1) both 3d holes are in the \( d_{z^2} \) orbital—a magnetically dead singlet that cannot account for the behavior around \( T^* \), or 2) a Hund’s rule \( S = 1 \) triplet, which would show a Curie-Weiss susceptibility above the ordering temperature, but that is not seen in experiment. Correlated DFT calculations [90] predict an unusual Ni \( d^8 \) singlet: a singly occupied \( d_{z^2} \) orbital anti-aligned with a \( d_{x^2-y^2} \) spin. This “off-diagonal singlet” consists of two fully spin-polarized 3d orbitals singlet-coupled, giving rise to a “non-magnetic” ion, however one having an internal orbital texture. Such tendencies were earlier noted [51] in \( \text{LaNiO}_2 \), and related Ni spin states were observed to be sensitive to modest pressure in the \( n = 2 \) and \( n = 3 \) classes [77]. Attempts are underway [91, 92] to understand this “magnetic transition in a non-magnetic insulator”.

3 OUTLOOK

While this new nickelate family seems to be emerging as its own class of superconductors, its connections to cuprates (crystal and electronic structures, formal \( d \) count in the superconducting region, and AFM correlations) retain a focus on similarities between the two classes. Apart from the obvious structural analogy, the cuprate-motivated prediction of optimal \( d^8\text{ filling has been realized in two nickelate materials, one achieved through chemical doping, and the other by layering dimensional. In this context, the (so far) little studied } n = 6 \) and \( n = 4 \) members of the series [73] may provide some prospect for superconductivity. Oxygen-reduced samples of these materials are so far lacking (though the \( n = 4 \) member of the RP series has been epitaxially grown [93]), and even if they are synthesized, they might require additional chemical tuning to achieve superconductivity. They share a similar electronic structure to the \( n = 5 \) material, but with slightly different nominal filling of the 3d bands [73]. Calculations show that as \( n \) decreases from \( n = \infty \) to \( n = 3 \), the cuprate-like character increases, with the charge-transfer energy decreasing along with the self-doping effect from the rare earth 5d states. In contrast, the particular \( n = 1 \) member discussed above seems distinct from other nickelates, and provides a different set of questions in the context of quantum materials [91, 92].

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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