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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 $NdNiO_2$ has invigorated the field of high temperature superconductivity research, reviving the debate over contrasting views that nickelates that 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 Each viewpoint has its merits, and each has its limitations, suggesting that such a simple picture must be superseded by a more holistic comparison of the two classes.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 NiO_2 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

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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 $\mathcal{R}NiO_2$ (initially for rare earth $\mathcal{R}$ = Nd, later for $\mathcal{R}$ = 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 $\mathcal{R}NiO_2$ 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.

$\mathcal{R}NiO_2$ materials are the $n = \infty$ member of a larger series of layered nickelates with chemical formula $(\mathcal{R}O_2)^-[\mathcal{R}(NiO_2)_n]^+$ ($\mathcal{R}$ = La, Pr, and Nd; $n = 2, 3, \ldots, \infty$) that possess n cuprate-like NiO_2 planes in a square-planar coordination. Except for the $n = \infty$ case, groups of n-NiO_2 layers are separated by $\mathcal{R}_2O_2$ 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 $\mathcal{R}NiO_3$ ($n = \infty$) [2] and Ruddlesden-Popper $\mathcal{R}_{n+1}Ni_nO_{3n+1}$ ($n \neq \infty$) phases [1]. As shown in **Figure 1**, the $(\mathcal{R}O_2)^-[(\mathcal{R}NiO_2)_n]^+$ series can be mapped onto the cuprate phase diagram in terms of the nickel 3d-electron count, with nominal fillings running from d^9 ($n = \infty$) to d^8 (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,

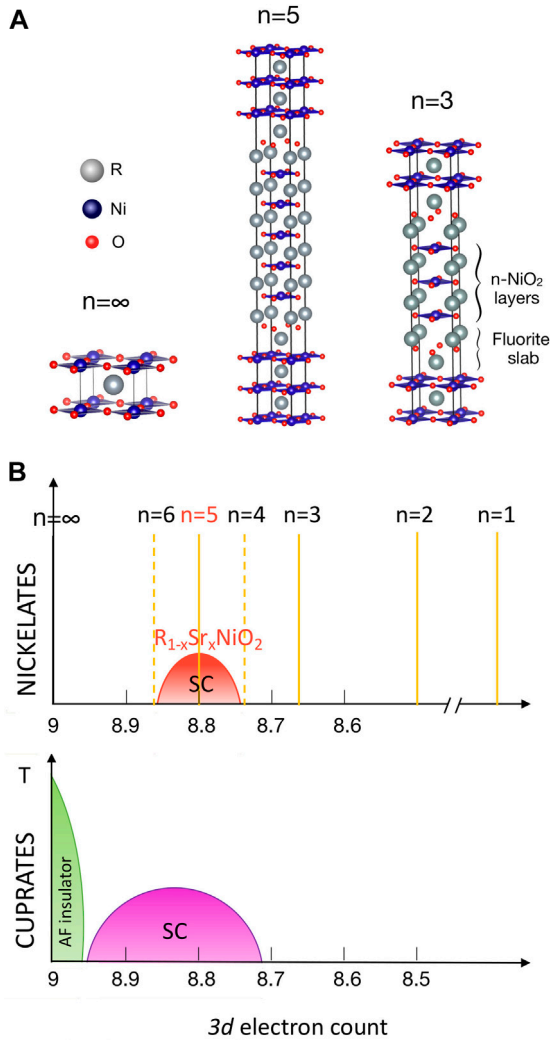

FIGURE 1 | (A) Crystal structures of the $n = \infty$, $n = 5$, and $n = 3$ layered nickelates highlighting the presence of the n-NiO_2 layers and the fluorite blocking slabs present in the $n \neq \infty$ materials. $\mathcal{R}$, Ni and O atoms are shown in gray, blue, and red, respectively. **(B)** Schematic phase diagram as a function of nominal d filling for layered nickelates (top) and cuprates (bottom), highlighting the regions where superconducting domes have been experimentally reported. The members of the $\mathcal{R}_{n+1}Ni_nO_{2n+2}$ series are marked with lines (dashed lines correspond to materials that have not been synthesized yet). The $n = 5$ member falls close to the optimal doping value for both cuprates and the infinite-layer nickelate.

confining ourselves to materials with the basic infinite-layer structure: n square planar NiO_2 layers each separated by an $\mathcal{R}^{3+}$ ion without the apical oxygen ion(s) that are common in most cuprates and nickelates.

2 FROM ∞ TO ONE

2.1 "Infinite-Layer" $n = \infty$ Nickelate: $\mathcal{R}NiO_2$

In parent $\mathcal{R}NiO_2$ materials, Ni has the same formal $3d^9$ electronic configuration as in cuprates. As mentioned above, superconductivity in $\mathcal{R}NiO_2$ materials emerges via hole 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 $\mathcal{R}NiO_2$, non-magnetic density functional theory (DFT) calculations show that besides the Ni-$d_{x^2-y^2}$ band, additional bands of $\mathcal{R}$-5d character cross the Fermi level. The electronic structure of $\mathcal{R}NiO_2$ is three-dimensional-like, with a large c-axis dispersion of both (occupied) Ni and (nearly empty) $\mathcal{R}$-5d_{z^2} bands (see **Figure 2**) due to the close spacing of successive NiO_2 planes along the c-axis. The $\mathcal{R}$-5d_{z^2} dispersion leads to the appearance of electron pockets at the Γ and A points of the Brillouin zone which display mainly $\mathcal{R}$-5d_{z^2} and $\mathcal{R}$-5d_{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 5d 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 $\mathcal{R}$-5d 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 $\mathcal{R}$-5d electrons, infinite-layer nickelates have some other relevant differences from the cuprates, particularly their much larger charge-transfer energy between the metal 3d, and oxygen 2p states. In cuprates, the charge-transfer energy ε_{3d}-ε_{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 $\mathcal{R}NiO_2$ 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 $2p_{3/2}$ 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

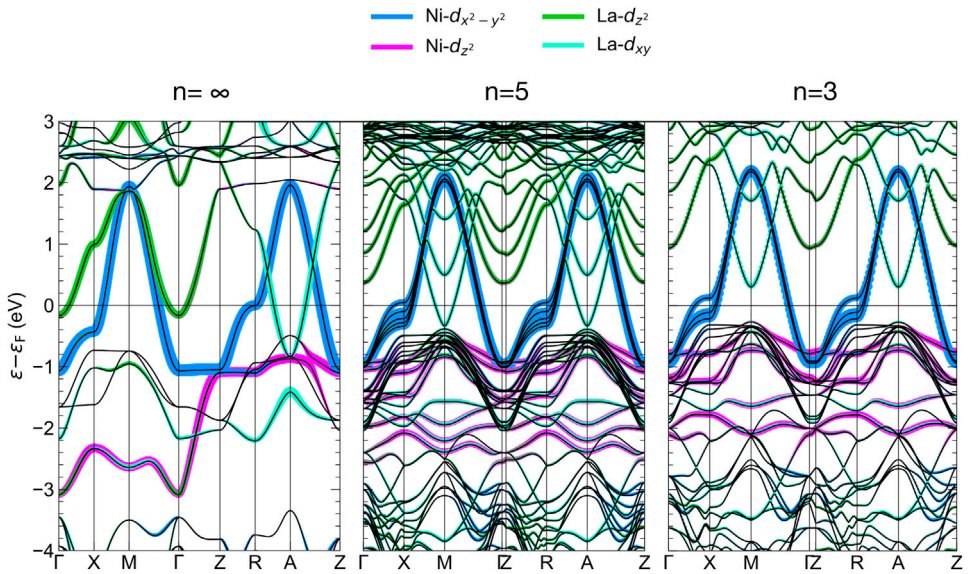

FIGURE 2 | DFT band structures in the paramagnetic state for the $n = \infty$, $n = 5$, and $n = 3$ layered nickelates. The two types of Ni e_g bands are highlighted, as well as the two relevant $\mathcal{R}$-5*d* bands (La is used as an example). It can be observed how the involvement of $\mathcal{R}$-d bands around the Fermi level is reduced with decreasing *n*.

they behave as effective d^8 dopants, and if so, is d^8 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^8 (S = 1) states [40, 57–60]. 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 $p - d$ hybridization, the superexchange in $\mathcal{R}NiO_2$, 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, and 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 $\mathcal{R}NiO_2$, 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 $(\mathcal{R}O_2)^-[(\mathcal{R}NiO_2)_n]^+$ family: the $n = 5$ layered nickelate $Nd_6Ni_5O_{12}$, 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, $Ni^{1.2+}$: $d^{8.8}$ nominal filling) and so, in contrast to its infinite-layer counterpart, it is superconducting without the need for chemical doping. While $\mathcal{R}NiO_2$ displays NiO_2 layers separated by $\mathcal{R}$ ions, this quintuple-layer material (with five NiO_2 layers per formula unit) has an additional fluorite $\mathcal{R}_2O_2$ 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 *I*4/*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 ~ 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 $Nd_6Ni_5O_{12}$ is ~ 4.0 eV. This reduced energy compared to the undoped infinite-layer material means that the Ni-3*d* states are not as close in energy to the Nd-5*d* 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-5*d* 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-3*d* 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 $Nd_6Ni_5O_{12}$ 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 $\mathcal{R}_2O_2$ blocking slabs that enforce quasi-2D electronic and magnetic behavior.

The $n = 3$ member of the series, $\mathcal{R}_4Ni_3O_8$ (with $Ni^{1.33+}$: $d^{8.67}$ filling), has been studied extensively over the past decade (both single crystal and polycrystralline 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 $La_4Ni_3O_8$ exhibits long-range stripe order [76, 79] (similar to that seen in 1/3 hole-doped La_2NiO_4), consisting of diagonal rows of Ni^{1+} (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 $Pr_4Ni_3O_8$ 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.

The difference between La and Pr trilayer materials could be due to the reduced volume associated with Pr (one of the motivations for the authors of Ref. [8] to study Sr-doped $NdNiO_2$ rather than Sr-doped $LaNiO_2$). The Ni spin state and metal versus insulator character have indeed been calculated to be sensitive to modest pressure [77]. Another factor is possible mixed valency of Pr as observed in cuprates (though Pr-M edge data on $Pr_4Ni_3O_8$ did not indicate mixed valent behavior [75]). Because of its decreased charge-transfer energy relative to $n = 5$, the rare-earth derived pockets no longer occur [84] (see **Figure 2**). This lack of $\mathcal{R}$-5*d* involvement is confirmed by the Hall coefficient that stays positive at all temperatures [44], (it remains to be understood why the thermopower in the case of $La_4Ni_3O_8$ is always negative [82], also seen in the metallic phase). In addition, these trilayer nickelates show a reduced charge-transfer energy (~ 3.5 eV as obtained from a Wannier analysis [73]) that, along with the larger effective doping level, is consistent with the strong oxygen K edge pre-peak seen in x-ray absorption data [75]. Oxygen K edge RIXS data indicate a significant contribution of oxygen 2*p* states to the doped holes [85]. As the effective hole doping level is 1/3, these materials are outside the range where superconductivity would be expected (see **Figure 1**). Reaching the desired doping range for superconductivity might be possible via electron doping. This could be achieved by replacing the rare earth with a 4 + ion (such as Ce,Th, or Zr) [86], intercalating with lithium, or gating the material with an ionic liquid.

If superconductivity were to occur, one might hope for a higher T_c as has indeed been predicted via $t - J$ model calculations [87]. Recent RIXS measurements [81], though, and find a superexchange value for $n = 3$ nearly the same as that reported for the infinite-layer material. This suggests the possibility that T_c in the whole nickelate family may be confined to relatively low temperatures compared to the cuprates. The similar value of the superexchange for $n = \infty$ and $n = 3$ is somewhat of a puzzle. Though their t_{pd} hoppings are very similar, the difference in the charge-transfer energy should have resulted in a larger superexchange for $n = 3$. The fact that it is not larger is one of the intriguing questions to be resolved in these low valence layered nickelates.

2.4 The $n = 2$ Material

The $n = 2$ member of the series, $La_3Ni_2O_6$, has been synthesized and studied as well [5, 88]. In terms of filling, it lies further away from optimal *d*-filling, being nominally $Ni^{1.5+}$: $d^{8.5}$. Experimentally, it is a semiconductor 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^{1+}: d^9 cations forming a S = 1/2 checkerboard pattern. This charge-ordering between S = 1/2 Ni^{1+}: d^9 and non-magnetic Ni^{2+}: d^8 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 $\mathcal{R}NiO_2$ materials [53].

2.5 The $n = 1$ Case

The long-known $\mathcal{R}_2NiO_4$ materials, with the $n = 1$ formula as above, contain Ni ions with octahedral coordination. We instead consider $Ba_2NiO_2(AgSe)_2$ (BNOAS) [89], as it represents the extreme opposite of the $n = \infty$ member, not only in regards to its d^8 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 $d_{x^2-y^2}$, and one hole in d_{z^2}. Unlike the other n cases, the charge balanced formula is $(BaAg_2Se_2)^0(BaNiO_2)^0$; both blocking and active layers are formally neutral. BNOAS is insulating, distinguished by a magnetic susceptibiliy that is constant, thus non-magnetic, above and below a peak at T* ~130 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 $d_{x^2-y^2}$ 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 $LaNiO_2$, 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 $d^{8.8}$ filling has been realized in two nickelate materials, one achieved through chemical doping, and the other by layering dimensionality. 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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