Is there a proximate antiferromagnetic insulating phase in infinite-layer nickelates?

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We provide a set of computational experiments based on ab initio calculations to elucidate whether a cuprate-like antiferromagnetic insulating state can be present in the phase diagram of the infinite-layer nickelate family (RNiO$_2$, R=rare-earth). We show that metallicity in the parent phase is produced by an R-d band that requires hybridization with the Ni-d bands to become largely dispersive. If this off-plane R-Ni coupling is suppressed, the system is an antiferromagnetic insulator since that largely dispersive band is no longer able to cross the Fermi level. As such, the reduction of the strong out-of-plane Ni-d hopping leads to an electronic structure closer to the nominal Ni-d$^9$ occupation as the self-doping effect -understood as charge transfer from the Ni-d to the R-d orbitals- disappears. This can be achieved if a structural element that suppresses the c-axis dispersion is introduced (i.e. vacuum in a monolayer of NdNiO$_2$, or a blocking layer in multilayers formed by (NdNiO$_2$)$_n$/(NdNaO$_2$)$_1$). We also show how the reduced Ruddlesden-Popper counterparts (R$_4$Ni$_3$O$_8$) are able to produce the same effect due to the presence of fluorite RO$_2$ blocking slabs.

BACKGROUND

Superconductivity in cuprate-like systems has been long sought for [1]. Among different approaches, targeting nickelates has been an obvious strategy as nickel and copper are next to each other in the periodic table [2]. After a 30 year search, Li and coworkers reported superconductivity in Sr-doped infinite-layer nickelate NdNiO$_2$ last year [3], and more recently in PrNiO$_2$ [4]. These infinite-layer nickelates are formed by NiO$_2$ planes shown in Fig. 1 (like the CuO$_2$ planes of cuprates), with Ni adopting the unusual Ni$^{1+}$ valence, with 9 d-electrons, (analogous to Cu$^{2+}$) [5,6]. Importantly, RNiO$_2$ (R=rare-earth) materials belong to a larger series represented by R$_n$+1Ni$_n$O$_{2n+2}$ ($n = 2, 3, \ldots, \infty$) in which each member contains n-NiO$_2$ layers [7] opening up the door to a whole family of nickelate superconductors.

In spite of the similarities described above, while parent cuprates are antiferromagnetic (AF) insulators [5], parent infinite-layer nickelates are metallic and there is no signature of long-range magnetic order in LaNiO$_2$ [8,9] or NdNiO$_2$ [10]. Based on these findings, magnetism has been at first ruled out as being a key ingredient for superconductivity in RNiO$_2$-based (R=rare-earth) systems, even though many theories of superconductivity in cuprates rely on the existence of strong AF correlations [12]. A recent NMR study has in fact found the presence of AF fluctuations and quasi-static AF order below 40 K in Sr-doped NdNiO$_2$ [11]. Along these lines, first principles calculations do predict that the main correlations in RNiO$_2$ are indeed AF, but less strong than in the cuprates [3], and embedded in a metallic environment. While magnetism in these infinite-layer nickelates is still under intense study [13,16], it is then important to understand: i) Why parent infinite-layer nickelates are metallic and do not show any signature of long-range magnetic order (their cuprate analog CaCuO$_2$ is AF and insulating [17]). ii) Whether the phase diagram of these newly discovered superconducting nickelates [18,20] can host a magnetic (and/or insulating) phase by modifying parameters such as, e.g. dimensionality. iii) If other members of the layered nickelate family are more similar to cuprates at d$^9$ filling in terms of their electronic structure [21].

In this paper, using first-principles calculations, we argue that the metallic non-cuprate-like behavior of parent infinite layer nickelates can be attributed to the strong Ni-R-Ni off-plane hopping. This gives rise to extremely dispersive R-d bands, strongly hybridized with the Ni-d occupied bands. These R-d bands cross the Fermi level leading to a deviation from half-filling in the Ni-d$_{xz-y^2}$ band via a self-doping mechanism. We show that if structural modifications are used in layered nickelates to provide a means to suppress the Ni-Ni off-plane hopping, an AF insulating state can be naturally obtained. As such, we reveal that in the purely two-dimensional limit, RNiO$_2$ materials are indeed AF insulators. Likewise, the n=3 members of the layered nickelate family (with a fluorite blocking slab between NiO$_2$ planes) can be AF insulators at d$^9$ filling without any structural changes.
COMPUTATIONAL METHODS

Our electronic structure calculations were performed within density functional theory [22] using the all-electron, full potential code Wien2k [23] based on the augmented plane wave plus local orbital (APW+lo) basis set [24]. The generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) scheme [25] was used as the exchange-correlation functional. To deal with possible strong correlation effects we apply the LDA+U scheme [26] including an on-site repulsion U and Hund’s coupling J (J = 0.7 eV was used) for the Ni 3d states. When thin films are discussed, a sufficient vacuum of 20 Å was introduced, enough to guarantee the lack of interaction between two planes (periodic boundary conditions are utilized along the three spatial directions). In multilayers, atomic positions were fully relaxed within GGA-PBE using the in-plane lattice parameter of RNiO$_2$. The muffin-tin radii used were: 2.50 a.u. for Nd and La, 1.93 a.u. for Ni and 1.73 a.u. for O. \( R_{K_{\text{max}}} = 7.0 \) was used.

TURNING INFINITE LAYER NICKELATES INTO ANTIFERROMAGNETIC INSULATORS.

Figure 1 shows the GGA band structure and density of states (DOS) of bulk NdNiO$_2$ in its AF C-type (in-plane AF checkerboard) ground state. All Nd moments are considered parallel, and the figure shows only the minority spin channel for clarity, since in that situation the Nd-f bands are unoccupied, located 2-3 eV above the Fermi level. The metallic character can be seen to be brought about, as it has been analyzed in the past [14, 16], by the presence of strongly dispersive bands (in particular along the Γ-Z direction) of mixed R-d and Ni-d$^z$ character. In the non-magnetic state, R-d bands also cross the Fermi level, as pointed out before [27, 29]. Introducing a large U, either in the R-d or the Ni-d bands, does not lead to a band splitting that would open up a gap in this system [13]. As such, the R-d bands lead to a so-called self-doping effect, i.e. the depletion in occupation of the Ni-d$_{x^2-y^2}$ band, away from the nominal half-filling that would correspond to a Ni$^{1+}$ cation.

Is there a way one can get an insulating AF phase from here? To answer this question, we start by taking the system towards the purely two-dimensional limit. We have constructed an RNiO$_2$ (R=La, Nd) monolayer from the constituting NiO$_2$ planes, with the standard square planar environment for the Ni cations (see Fig. 2). The additional rare-earth cations are placed alternatively on top and below the NiO$_2$ planes to ensure the stoichiometry and provide the highest possible symmetry. If all these rare-earth cations are all placed on a single plane above or below the NiO$_2$ plane, the resulting total energy is much higher.

Figure 2 shows the band structure of this single-layer NdNiO$_2$ system at the GGA level (without introducing correlations via the LDA+U method) in an AF checkerboard state. As above, the Nd moments are considered all parallel and the figure shows only the minority spin channel for clarity. A small gap opens up at the Fermi level already within GGA. The R-d bands do not cross the Fermi level and the only Ni-d band that remains unoccupied is a single minority-spin d$_{x^2-y^2}$ band per Ni. The Nd-d bands cannot hybridize strongly with the Ni-d ones (once the periodicity along c is lost) and as a conse-
FIG. 2: Top panel. Structure of an RNiO$_2$ monolayer of the type used for the calculations discussed in the text. Bottom left panel. Band structure of the NdNiO$_2$ monolayer with AF ordering of the Ni atoms, showing only the minority spin channel (Nd moments are parallel). The Ni-d$_{z^2}$ states are highlighted for both Ni atoms (a Hund splitting can again be observed between them). The flat Nd-f bands (unoccupied) appear 2-3 eV above the Fermi level. The O-p bands (not shown) start to appear below -3 eV. A gap opening together with the antiferromagnetic ordering occurs when the off-plane coupling is suppressed. This is visible even at the U= 0 limit (bands shown), similar to the situation in bulk CaCuO$_2$, and unlike the self-doped metallic phase appearing in bulk NdNiO$_2$. Bottom right panel. Corresponding Nd, O and Ni atom-resolved density of states (both Ni atoms have opposite spins).

In order to illustrate the lack of Nd-d - Ni-d hybridization in this case, we have highlighted in the bandstructure of Fig. 2 the Ni-d$_{z^2}$ character for both Ni atoms in the structure. These bands become completely occupied and very flat (in contrast to the bulk plot of Fig. 1) and no Ni-d$_{z^2}$ character can be seen in the unoccupied part of the spectrum. The DOS plot helps locate the different characters of the bands shown. R-d bands start appearing above 1 eV (the minority spin channel is analyzed only for clarity). The O-p bands start to emerge below -3 eV in this case, further away from the Fermi level than in the cuprates.

In order to study the band(s) that bring about metallicity in the bulk in more detail, we have constructed a hypothetical system, like the one shown in Fig. 3. This is a multilayer that alternates one NdNiO$_2$ and one NdNaO$_2$ unit cell stacked along the (001) direction. This system provides continuity along the z-axis for the rare-earth Nd-d - Nd-d direct hopping. However, in this structure the hopping paths for the transition metal Ni-d bands are largely confined into the xy plane. Their off-plane hopping is largely blocked by the NdNaO$_2$ layer, since the Na atoms do not provide continuity for a direct off-plane Ni-d$_{z^2}$ hopping. Also, note that the Nd-d - Ni-d hybridization is also largely hampered by the NaO$_2$ blocking layer. NdNaO$_2$ exists but it is not isostructural to NdNiO$_2$. In this work, for the purpose of comparison, we assume the same crystal structures. We have used the in-plane lattice parameter of NdNiO$_2$ as a basis, and then all the internal atomic positions and the off-plane lattice parameter have been relaxed. It is not relevant for our discussion whether this system is experimentally achievable or not, it just provides another way of suppressing the c-axis dispersion to confirm the reasoning exposed above.

The band structure of the multilayer is shown in Fig. 3. As in the two previous calculations, we have set up all Nd moments parallel and we present here the minority spin channel only (also for the accompanying DOS plot). As above, the Nd-f bands are fully unoccupied in this spin channel and high in energy (the very flat bands located 2 eV above the Fermi level in Fig. 3). Similar to the NdNiO$_2$ monolayer, the system is an AF insulator. The only subtle
FIG. 3: Top panel. Supercell constructed alternating one layer of NdNiO$_2$ and one layer of NdNaO$_2$ using the NdNiO$_2$ structure with a square planar NiO$_4$ environment as a basis. The Ni-Ni direct off-plane hopping is blocked structurally by a single layer of NdNaO$_2$. However, the Nd-d off-plane hopping is not blocked. Na atoms in yellow, R atoms in green, O atoms in red, Ni atoms in gray. Bottom left panel. Band structure of a multilayer (NdNaO$_2$)$_1$/(NdNiO$_2$)$_1$ obtained with a very small $U$= 0.7 eV. A gap opening together with antiferromagnetic ordering occurs when the off-plane coupling is geometrically suppressed, even when the Nd-d - Nd-d off-plane hopping is permitted. Only the minority spin is shown so that the Nd-f states are unoccupied and away from the Fermi level. The Ni-d$^z_2$ bands are highlighted for both Ni atoms antiferromagnetically coupled (a Hund splitting can be noticed between them as before). Bottom right panel. Corresponding Nd, O (only the O atoms in the NiO$_2$ plane are shown), and Ni atom-resolved density of states.

CAN OTHER LOW-VALENCE LAYERED NICKELATES BE AF INSULATORS AT HALF FILLING?

Given that the necessary ingredient to be able to obtain an AF insulating ground state in layered nickelates at $d^9$ filling is a structural barrier to suppress the Ni-d$_{z^2}$ - R-d off-plane hopping, a natural choice is to turn to other members of the series [32–35], as they all contain a fluorite blocking slab (see Fig. 4). The only known members as of now are the n=2 and n=3 materials with an average Ni d-filling of $d^{8.5}$ [30, 37] and $d^{8.67}$ [38, 41], respectively. As the n=2 material is farther from $d^9$, we will focus here on the n=3 nickelate (R$_4$Ni$_3$O$_8$). In the paramagnetic state, R$_4$Ni$_3$O$_8$ at $d^9$ filling (achieved using the virtual crystal approximation (VCA)) has been shown to have a similar electronic structure to that of RNiO$_2$ [42]. However, its AF ground state (with checkerboard AF moments in-plane, ferromagnetically coupled out-of-plane, and more stable than a nonmagnetic one by 0.2 eV/Ni) is remarkably different from that of RNiO$_2$. Figure 4 shows the electronic structure in this AF state for R$_4$Ni$_3$O$_8$ (in this case, R=La) at $d^9$ filling using VCA. When an AF order is imposed at $d^9$ filling a gap opens up naturally at very small $U$ (U=2.5 eV is shown), in contrast to bulk NdNiO$_2$ or LaNiO$_2$, where this is not possible. This is due to the same mechanism difference is that a very small $U$= 0.7 eV was needed in this case to open up a gap. This gapped AF solution occurs even though there is a continuity of the rare-earth sublattice along the off-plane direction. This confirms that the key factor in order to open up a gap is for the geometry to provide a way to suppress the R-Ni off-plane hopping that leads to hybrid bands with a large dispersion, crossing the Fermi level. When the Ni-d$_{z^2}$ bands (highlighted in the band structure shown) have no mechanism to hybridize along the z-direction, these bands remain very flat and fully occupied. Then, the Nd-d bands do not disperse below the Fermi level and the system is an analog of parent cuprates at $d^9$ filling: an AF insulator, with no self-doping. As such, at the electronic structure level, this computational experiment of a multilayered system works similar to the single-layer NdNiO$_2$. We show that reducing dimensionality is a way to reach a parent phase that is AF and insulating in parent RNiO$_2$ like that in cuprates.

It is important to explain this result in detail. If one looks at the band character of the band crossing the Fermi level in bulk LaNiO$_2$ [31] or NdNiO$_2$ [23], it is mostly Nd-d in character. If this were the whole story, in this multilayered system, such a band would have room for still being largely dispersive. What our calculations show is that its large dispersion requires a strong hybridization with the Ni-d$_{z^2}$ band. When this hybridization is cut by, e.g. introducing NaO$_2$ planes in the structure, then this band is no longer living close to the Fermi level and the electronic structure becomes cuprate-like, AF correlations become stronger (larger moments closer to the nominal ionic S=1/2 value), and the ground state becomes AF and insulating even at the GGA level (with a very small U in the case of the multilayer).
FIG. 4: Top panel. Structure of R$_4$Ni$_3$O$_8$. Along the z axis, the NiO$_2$ tri-layers are separated from each other by fluorite RO$_2$ blocking slabs. These RO$_2$ layers block the c-axis dispersion of the hybrid R-d - Ni orbitals. Bottom panels. (Left) Antiferromagnetic band structure of La$_4$Ni$_3$O$_8$ at d$^9$ filling (see text for the details of the calculation, based on the virtual crystal approximation). Such filling, together with the blocking of the out-of-plane coupling caused by the fluorite slab, leads to an AF insulating phase also in this system. (Right) Corresponding density of states plot for the same energy interval, highlighting the atom-resolved contributions of La, Ni and O separately.

described above. In this case, it is the fluorite slab that allows to cut off the c-axis dispersion. As such, the n=3 member of this nickelate family helps understanding how an AF insulating phase can be a part of the phase diagram of layered nickelates, as it is for superconducting cuprates. We note that an AF insulating ground state at d$^9$ filling had already been obtained in Pt$_4$Ni$_3$O$_8$ via electron doping using a 4+ ion like Ce as a dopant [43].

This situation (a highly dispersive band crossing the Fermi level) does not occur in the parent cuprates. There are various reasons for this. In the isostructural cuprate (CaCuO$_2$) the Ca-d bands are very far above the Fermi level to be able to produce any effects in the electronic structure. In other cuprates containing atoms with available unoccupied d bands such as La in La$_2$CuO$_4$ or Y in the YBCO family, there are important structural differences. The case of La$_2$CuO$_4$ allows for a direct comparison with the layered nickelate family. Such a structure [47] consists of CuO$_2$ planes but separated by a spacing La$_2$O$_2$ blocking layer, which provides a barrier for the off-plane hoppings, in a similar fashion to the NdNaO$_2$ layer in the hypothetical multilayered system described above. The same can be said about YBCO [48]. It is this kind of structural spacing (that strongly suppresses the c-axis hopping) that occurs also in other members of the layered nickelate family (such as La$_4$Ni$_3$O$_8$) allowing for an AF insulating phase to appear naturally when they are doped towards the Ni$^{1+}$:d$^9$ limit.

Our work shows that a parent insulating AF phase can take place in the phase diagram of the superconducting RNiO$_2$ nickelates. The calculations presented here in various material platforms show how the mechanism that leads to a metallic solution operates. All this physics is hidden in the electronic structure of RNiO$_2$, where the largely dispersive R-d band that crosses the Fermi level leads to a self-doping effect, changing the Ni-d electron count, producing metallicity and screening the underlying AF correlations, which are still visible in the DFT calculations. Our work shows yet another piece of evidence of the similarities between layered nickelates and cuprates, which were not apparent at first but can be elucidated digging deeper into the properties of these new nickel-oxide materials.

**DISCUSSION**

Our computational experiments show that the origin of the self-doping effect in RNiO$_2$ is not simply in the rare-earth d bands – the existence of the electron pockets with R-d parentage requires a strong hybridization with the Ni-d$_{z^2}$ bands. This hybridization leads to the formation of wide bands that arise due to the large hopping taking place along the c-axis. This provides further evidence of the active role of the Ni-d$_{z^2}$ orbitals in the electronic structure of infinite-layer nickelates [14, 44–46].

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