Doped holes in NdNiO$_2$ and high-$T_c$ cuprates show little similarity

Mi Jiang,$^{1, 2}$ Mona Berciu,$^{1, 2}$ and George A. Sawatzky$^{1, 2}$

$^1$Department of Physics and Astronomy, University of British Columbia, Vancouver B.C. V6T 1Z1, Canada
$^2$Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver B.C. V6T 1Z4, Canada

Superconductivity was recently demonstrated in thin films of hole-doped NdNiO$_2$, with a rather high $T_c \approx 15K$ [1]. At first sight this seems reasonable, given its similar lattice structure with that of LaCuO$_4$, with Ni$^{1+}$ replacing Cu$^{2+}$. We argue that NdNiO$_2$ is on the Mott insulator and not the charge transfer side of the (ZSA) [2] classification scheme, with a superexchange energy at least an order of magnitude smaller than in cuprates. Hole-doping should therefore produce Ni$^{2+}$ with spin $S = 1$, as in common Ni$^{2+}$ oxides. This is not compatible with robust superconductivity.

We show that in fact, NdNiO$_2$ falls inside a “critical” region of the ZSA scheme, where for large $pd$ hybridization the lowest energy hole-doped state can be $^1A_1$ as in the cuprates. However, small changes in the parameters resulting from changes in lattice parameters through chemical composition could also stabilize the more common $^3B_1$ lowest energy hole state.

**Introduction:** The discovery by Bednorz and Mueller, in 1986, that the oxide La$_{2-x}$Sr$_x$CuO$_4$ becomes superconducting (SC) with critical temperatures $T_c$ of up to 35K [3], initiated one of the most intense research efforts in condensed matter physics and chemistry. After extensive investigations, SC persisting up to 133.5 K [4] has now been reported in cuprates. However, after more than 35 years, there is no consensus regarding its mechanism.

Superconductivity occurs in a metal if the Coulomb repulsion between electrons is over screened by the response of the surrounding material. The resulting effective attraction can bind electrons into pairs with bosonic character. According to the Bardeen-Cooper-Schrieffer (BCS) theory [5], at low enough temperatures these pairs condense into a superfluid with zero electrical resistance.

The question, then, is what is the nature of the “pairing glue” [6]. The conventional BCS mechanism arises from electron-phonon coupling, but theoretical estimates based on band structure approaches to electron-phonon coupling, as used in conventional superconductors, indicate that this cannot facilitate such a high transition temperature [7]. (For completeness, we note that a different view is espoused in Refs. [8], [9], [10]).

Many other scenarios have been proposed, the current leading “glue” candidate being the magnetic excitations associated with the spin-$\frac{1}{2}$ of the Cu$^{2+}$ ions and the strong superexchange coupling them. The parent compounds are insulators because the strong on-site $U_{dd}$ repulsion between electrons in the Cu 3d orbitals freezes their charge fluctuations. The resulting magnetic moments are locked into long-range antiferromagnetic (AFM) order by a strong super-exchange $J_{dd}$, and spin fluctuations occur at energies of up to 300meV. Additional doped holes enter the O2$p$ bands [11], and their spin couples to adjacent Cu spins through an even larger AFM exchange and a spin-swapping process [12]. Both of these allow holes to emit and absorb magnetic excitations of the Cu background. An exchange of such excitations could therefore mediate the effective attraction between holes, necessary for pairing. The resulting $T_c$ would be determined by the magnon energy scale and by the strength of the hole-spin coupling, both of which are large in the cuprates. A major success of this magnetic mechanism was the theoretical prediction of unconventional superconductivity with d-wave symmetry [13], subsequently confirmed experimentally [14–16]. Nevertheless, a comprehensive understanding of cuprate phenomenology is still eluding us.

This impasse motivated the search for similar but non-Cu based SC, which might help solve the mystery. One of the routes being pursued is to replace Cu$^{2+}$ with Ni$^{1+}$ in compounds such as LaNiO$_2$ and NdNiO$_2$, which crystallize in a similar structure, with infinite NiO$_2$ planes as the counterparts of the CuO$_2$ planes. After several failed attempts [17–19], SC with $T_c$ of up to 15K was recently found in doped Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ single crystal thin films [1]. This is a very exciting development, suggesting the existence of a Ni-based family of high-$T_c$ SC that may be more like the cuprates than the Fe-based ones [20].

![FIG. 1: (color online) Sketch of a Mott insulator (top) vs. a charge transfer insulator (bottom). The narrow (blue) bands are the Hubbard 3d bands while the broader (red) band is the O2p band before the pd hybridization has been switched on. The sketch assumes a similar $U$ but a significantly larger $\Delta$, like for NdNiO$_2$ as compared to LaCuO$_4$. Below (above) the chemical potential $\mu$ are the electron removal (addition) states, if the starting state is Ni/Cu d$^8$ and a full O 2p band.](image-url)
We assume that, like in cuprates: (i) only the O 2p and Ni 3d states determine the low-energy physics, and (ii) the stoichiometric NdNiO$_2$ is a large gap insulator. (Note that the parent compound studied in Ref. 1 is metallic, perhaps due to small differences in stoichiometry). Even so, a major difference is that according to the Zaanen-Sawatzky-Allen (ZSA) scheme 2, NdNiO$_2$ is a Mott insulator while the cuprate parent compounds are charge-transfer insulators, see sketch in Fig. 1. This is due to a charge transfer energy $\Delta \approx 9$ eV in NdNiO$_2$ vs. $\Delta \approx 3$ eV in cuprates, because the smaller nuclear charge of Ni causes a 5-6eV upward shift of the $d^{10}$ state in NdNiO$_2$. The other energy scales $U_{dd}, U_{pp}, t_{pd}$, are very similar to those of cuprates.

One consequence is that the superexchange $^{21}$:

$$J_{dd} = \frac{4t_{pd}^4}{\Delta^2 U_{dd}} + \frac{8t_{pd}^4}{\Delta^2 (U_{pp} + 2\Delta)}$$

is around ten times smaller in NdNiO$_2$, explaining the lack of AFM order $^{13,19}$.

The bigger consequence is what happens upon doping. Holes doped in a Mott insulator should reside on the Ni, not in the O 2p band like in cuprates. But Ni$^{2+}$ ($3d^{8}$) has $S = 1$ in other Ni$^{2+}$ oxides, suggesting not only very different physics from the cuprates, but also making the appearance of rather high-$T_c$ SC extremely puzzling.

In this Letter, we argue that NdNiO$_2$ lies in the critical crossover region of the ZSA diagram $^{2}$, where the lowest eigenstates with $S = 0$ and $S = 1$ cross. Thus, it is possible that holes doped in NdNiO$_2$ still have a strong O 2p component with the same $^1A_1$ symmetry like the Zhang-Rice singlet in cuprates $^{22}$. In other words, the new SC could indeed be similar to cuprates SC from this point of view, although many other questions remain open.

Model: We study a hole doped into a system consisting of a Ni$^{1+}$ ($3d^{9}$) impurity properly embedded in an infinite square lattice of O2p ions. The Hamiltonian is:

$$\mathcal{H} = \hat{U}_{dd} + \hat{T}_{pd} + \hat{T}_{pp} + \hat{\Delta} + \hat{U}_{pp},$$

(1)

Here, $\hat{U}_{dd}$ includes all Coulomb and exchange integrals of the $3d^9$ multiplet, which determine the spin and symmetry of the lowest-energy hole addition state. Matrix elements between the 3d orbitals $b_1(d_{x^2-y^2}), b_2(d_{xy}), c_2(d_{xz})$, and $c_3(d_{yz})$ are in terms of the Racah parameters $A, B, C$. The 3d orbitals are assumed to be degenerate, i.e. we omit point-charge crystal splittings. (This is a good approximation because it is the hybridization with the O orbitals, included in our model, that accounts for most of the difference between the effective on-site energies of the 3d levels). $\hat{T}_{pd}$ and $\hat{T}_{pp}$ describe hopping of holes between the Ni3d orbitals and adjacent O2p ligand orbitals, and between nearest neighbour O ligand orbitals, respectively. We note that we have checked explicitly that including the second pair of in-plane, $\pi$-type O2p orbitals has essentially no effect on the results reported below. Finally, $\hat{\Delta}$ measures the difference in the on-site energies of 3d and 2p orbitals, as measured from the full O 2p band to the Ni $d^{10}$ state, while $\hat{U}_{pp}$ is an on-site Hubbard repulsion when two holes are in the same O ligand orbital.

We recently used this model to study a Cu$^{2+}$ impurity embedded in a square O lattice $^{23}$: we refer the reader there for further details on the Hamiltonian and our solution for the one-hole doped case. We choose what we believe to be reasonable values for the parameters: we estimate a magnitude $t_{pd} \approx 1.5eV$ for the hybridization between the Ni impurity and neighbor O, about the same as in cuprates. This is because of a cancellation of changes due to the larger lattice constant of the nickelates, and to the larger orbital radius of their $d$ orbital, because of the smaller nuclear charge. We keep the same values for the Racah parameters $B, C$. $U_{pp}$ plays little role for the results discussed below, so we set it to $U_{pp} = 0$ (very similar results are obtained for $U_{pp} \approx 3eV$). As already mentioned, we expect the on-site Coulomb repulsion on the Ni$^{1+}$ to be comparable to that on the Cu$^{2+}$, $A = U_{dd} \approx 6-7eV$, while the charge transfer $\Delta \approx 7-9eV$ as opposed to $\Delta \approx 3eV$ in cuprates.

It is important to note that while this work is conceptually similar to older work investigating a multi-band impurity embedded in a lattice $^{24}$, the key difference is that we keep the square-lattice structure for the O 2p band, instead of approximating it with a featureless band with a semielliptical density of states. This has significant quantitative implications, as also emphasized in Ref. $^{23}$. These turn out to be particularly important for a Ni$^{1+}$ impurity, as we discuss now.

Results: Figure 2 shows the one-hole phase diagram
a function of $A$ and $\Delta$. It consists of two regions with
ground-states of $^1A_1$ and $^3B_1$ symmetry, respectively. In
the $^3B_1$ region the doped hole primarily sits on the Ni
and locks into a triplet with the other hole, by Hund’s
exchange. More specifically (also see below), one hole oc-
cupies a wavefunction with dominant $3d_{x^2-y^2}$ character
plus a small contribution from the $x^2 - y^2$ linear com-
bination of adjacent O2p orbitals, while the second hole
occupies the $3z^2 - r^2$ counterpart. In contrast, in the
$^1A_1$ region the doped hole occupies primarily the $x^2 - y^2$
“molecular”-like O2p orbital with a small admixture of
the $3d_{x^2-y^2}$ orbital, and is locked in a singlet with the
other hole which has primarily $3d_{x^2-y^2}$ character.

The three lines show how the boundary shifts with $t_{pd}$,
and the shaded ellipse is the area we believe to be rel-
vant for NdNiO$_2$. Clearly, this compound falls in the
borderline regime where the ground-state changes its na-
ture. This is to be contrasted with what is predicted
by the older work with a featureless O band, where the
ground-state would be deeply inside the $^3B_1$ region.

To better understand what happens, and how it is pos-
sible for the doped states of a a Mott insulator to in-
stead look more like those of a charge-transfer insulator,
we plot in Fig. 3 spectral densities for the addition of
the doped hole, resolved by point symmetry. The three
panels correspond to $\Delta = 7, 8, 9\, \text{eV}$ while $t_{pd} = 1.5\, \text{eV}$
and $A = 6.0\, \text{eV}$. They show that with increasing $\Delta$, the
ground-state transitions from having $^1A_1$ symmetry to
having the $^3B_1$ symmetry expected in the large $\Delta$ limit.
The same transition from a ground state with $^1A_1$ sym-
metry to $^3B_1$ symmetry is realized by varying $t_{pd}$.

With increasing $\Delta$, we see an increasing separation be-
tween the discrete peaks showing the low-energy states
(with the doped hole bound to the impurity Ni with var-
ious symmetries; these include the ground-state, always
shifted to occur at zero energy), and the continuum be-
low, which describes excited states (with the doped hole
moving freely in the O band). The band is a sequence
of closely spaced peaks because for computational conve-
nience, we limit the size of the O lattice to be $20 \times 20$. In
the thermodynamic limit, this consequence of confinement
to a “finite-box” disappears and the continuum becomes
smooth, but its band-edges do not move).

Physically, what happens is that when the separation
between the $3d^8$ peak and the O band sketched in Fig. 1
is smaller or comparable with $t_{pd}$, their hybridization is
responsible for the appearance of these low-energy bound
states in all the channels; in particular, the one with $^1A_1$
symmetry as the ground-state. As $\Delta$ increases and the
distance between the two features becomes larger than
$t_{pd}$, the ground-state switches to the expected $^3B_1$
character for a Mott insulator.

It is interesting to analyze in more detail the nature of
the $^1A_1$ ground-state, and what happens when it switches
to $^3B_1$. In Figure 4 we show the evolution of the ground
state weights of the various components with increasing
$\Delta$, for $t_{pd} = 1.5\, \text{eV}$ and $A = 6\, \text{eV}$. These components
of the two-hole wavefunction are products of the single
particle states of various symmetries. Included in this
analysis are all the $d^8$, $d^9L$ and $d^{10}L^2$ states. The weights
of the states involving the hole continua are summed over
energy.

We see that the only $d^8$ basis states with reasonable
weights are the $a_1a_1$, $b_2b_1$, and $a_1b_1$ states. These are
also the only symmetries that are important for the $d^8L$
and $d^{10}L^2$ continuum states. We see that for $\Delta < A$, i.e.
in the charge transfer gap region, the amount of total
$d^8$ character is very small, with an increasing amount

FIG. 3: (color online) Spectral weight for addition of a doped hole, for $\Delta = 7, 8, 9\, \text{eV}$ while $t_{pd} = 1.5\, \text{eV}$ and $A = 6.0\, \text{eV}$. Spectra
are shifted such that the ground-state is located at zero energy. With increasing $\Delta$, its character changes from $^1A_1$ to $^3B_1$. 

FIG. 4: (color online) Evolution of ground state weights as $\Delta$ increases. The graph shows the weights of the various components with increasing $\Delta$, for $t_{pd} = 1.5\, \text{eV}$ and $A = 6\, \text{eV}$. The components of the two-hole wavefunction are products of the single particle states of various symmetries. Included in this analysis are all the $d^8$, $d^9L$ and $d^{10}L^2$ states. The weights of the states involving the hole continua are summed over energy.
FIG. 4: (color online) Variation of the ground state weights of the dominant components versus Δ, for fixed $t_{pd} = 1.5$ eV, $A = 6.0$ eV. Note that the dominant component changes dramatically as the ground state switches from $^1A_1$ to $^3B_1$. The vertical line denotes the critical value $\Delta = 8.1$ eV separating the two phases.

Two holes in $d_{x^2-y^2}(b_1)$ as we approach the transition to the $^3B_1$ ground state. Simultaneously, the amount of $d^{10}L^2$ is gradually decreasing because the separation between the $d^{10}L^2$ and the $d^9L$ continua is increasing as $\Delta$ increases. The transition occurs at $\Delta = 8.1$ eV, which is considerably higher than where the transition from the Mott to the charge transfer insulator occurs in the ZSA diagram. This is because the $L_{b_1}$ symmetry states in the O 2$p$ band are located at the top of the O band and not at its center, so their effective $\Delta$ is about 1.5 eV lower. Note the abrupt change in the weights of the $d^8$ components, especially the $a_1b_1$ component, as we enter the region where the ground-state is $^3B_1$. Here, $d^8(a_1b_1)$ is the dominant component, unlike the ZRS-like $d^9(b_1)L_{b_1}$ dominating for the $^1A_1$ symmetry.

**Summary and discussion:** To conclude, we performed an impurity calculation to argue that despite nominally being in the Mott region of the ZSA scheme, in fact NdNiO$_2$ falls inside a critical region of the parameter space where the strong pd hybridization may favor a $S = 0$ hole-doped state with $^1A_1$ symmetry, somewhat similar to the cuprates. However, the triplet $^3B_1$ state is close in energy so that small changes in the parameters resulting from changes in the lattice structure with chemical substitution or with epitaxial strain could stabilize the triplet state, making superconductivity unlikely. We also argued that these XNiO$_2$ compounds with Ni$^{3+}$-like 3$d^9$ occupation have very large charge transfer energies $\Delta$. This makes them very different from the cuprates in terms of their superexchange interaction, expected to be at least an order of magnitude smaller. This fact should severely challenge the scenario of spin fluctuations as the glue for superconductivity here, despite that being the prevalent scenario in cuprates. In addition, we note that our calculations were done with the assumption that the only electronic state of relevance for low-energy properties are the Ni 3$d$ and the O 2$p$ states. If, as pointed out recently [25], there are other bands close to the chemical potential or even crossing it, the whole scenario changes and a Kondo lattice like Hamiltonian may be a more appropriate starting point. In conclusion, in almost any reasonable scenario, the electronic structure and likely also the mechanism for superconductivity in hole-doped NdNiO$_2$ is very different from that of the cuprates.

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