Infinite Layer LaNiO$_2$: Ni$^{1+}$ is not Cu$^{2+}$

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The Ni ion in LaNiO$_2$ has the same formal ionic configuration 3$d^9$ as does Cu in isostructural CaCuO$_2$, but it is reported to be nonmagnetic and probably metallic whereas CaCuO$_2$ is a magnetic insulator. From ab initio calculations we trace its individualistic behavior to (1) reduced 3$d$–2$p$ mixing due to an increase of the separation of site energies ($\varepsilon_d$–$\varepsilon_p$) of at least 2 eV, and (2) important Ni 3$d$(3$z^2$–r$^2$) mixing with La 5$d$(3$z^2$–r$^2$) states that leads to Fermi surface pockets of La 5$d$ character that hole-dope the Ni 3$d$ band. Correlation effects do not appear to be large in LaNiO$_2$. However, ad hoc increase of the intraatomic repulsion on the Ni site (using the LDA+U method) is found to lead to a novel correlated state: (i) the transition metal d$(x^2$–$y^2$) and d$(3z^2$–r$^2$) states undergo consecutive Mott transitions, (ii) their moments are antialigned leading (ideally) to a “singlet” ion in which there are two polarized orbitals, and (iii) mixing of the upper Hubbard 3$d$(3$z^2$–r$^2$) band with the La 5$d$(xy) states leaves considerable transition metal 3$d$ character in a band pinned to the Fermi level. The magnetic configuration is more indicative of a Ni$^{2+}$ ion in this limit, although the actual charge changes little with $U$.

I. INTRODUCTION

The perovskite oxide LaNiO$_2$, purportedly an example of a correlated metallic Ni$^{3+}$ system, has been investigated over some decades by a few groups\cite{1, 2} for possible exotic behavior. The oxygen-poor lanthanum nickelate LaNiO$_2$ has also attracted attention, because of characteristic changes of its electronic and magnetic properties as the oxygens are removed. It is metallic at 2.75 < x < 3, but semiconductor for 2.50 < x < 2.65.\cite{3} For x = 2.6, it shows ferromagnetic ordering with 1.7 $\mu_B$/Ni below 230 K\cite{4} and magnetic behavior of the x = 2.7 material has been interpreted in terms of a model of ferromagnetic clusters.\cite{5} At x = 2.5, where formally the Ni is divalent, a perovskite-type compound La$_2$NiO$_5$ forms in which NiO$_6$ octahedra lie along c axis directed chains and NiO$_3$ square-planar units alternate in the a–b plane. This compound shows antiferromagnetic ordering of the NiO$_6$ units along the c axis but no magnetic ordering of the NiO$_3$ units.\cite{6}

Since LaNiO$_2$ with formally monovalent Ni ions was synthesized by Crespin et al.\cite{7, 8} it has attracted interest\cite{9, 10, 11} because it is isostructural to CaCuO$_2$\cite{12}, the parent “infinite layer” material of high T$_c$ superconductors, and like CaCuO$_2$ has a formal d$^9$ ion amongst closed ionic shells. However, it is difficult to synthesize and was not revisited experimentally until recently by Hayward et al. who produced it as the major phase by oxygen intercalation from LaNiO$_3$.\cite{13} Their materials consist of two phases, the majority being the infinite-layer (NiO$_2$–La–NiO$_2$) structure and the minority being a disordered derivative phase. Magnetization and neutron powder diffraction reveal no long-range magnetic order in their materials. Its paramagnetic susceptibility has been fit by a Curie-Weiss form in the 150 < T/K < 300 range with S = $\frac{1}{2}$ and Weiss constant $\theta$ = -257 K, but its low T behavior varies strongly from this form. More recently, this same group has produced the isostructural and isovalent nickelate NdNiO$_2$.\cite{14}

One of the most striking features of LaNiO$_2$ is that it potentially provides a structurally simple example of a monovalent open shell transition metal d$^9$ ion. Except for the divalent Cu$^{2+}$ ion, the d$^9$ configuration is practically nonexistent in ionic solids. In particular, the formal similarity of Ni$^{1+}$ and Cu$^{2+}$ suggests that Ni$^{1+}$ compounds might provide a “platform” for additional high temperature superconductors. It is these and related questions that we address here.

In this paper we present results of theoretical studies of the electronic and magnetic structures of LaNiO$_2$, and compare with the case of CaCuO$_2$ (or isovalent Ca$_{1-x}$Sr$_x$CuO$_2$) which is well characterized. A central question in transition metal oxides is the role of correlation effects, which are certainly not known a priori in LaNiO$_2$. We look at results both from the local density approximation (LDA) and its magnetic generalization, and then apply also the LDA+U correlated electron band theory that accounts in a self-consistent mean-field way for Hubbard-like intraatomic repulsion characterized by the strength U. Our results reveal very different behavior between LaNiO$_2$ and CaCuO$_2$, in spite of the structural and formal d$^9$ charge similarities. The differences can be traced to (1) the difference in 3$d$ site energy between Ni and Cu relative to that of Cu, (2) the ionic charge difference between Ca$^{2+}$ and La$^{3+}$.
and associated Madelung potential shifts, and (3) the participation of cation 5d states in LaNiO$_2$.

We also discuss briefly our discovery of anomalous behavior in the transition metal 3d ion as described by LDA+U at large U. Although well beyond the physical range of U for LaNiO$_2$, we find that LDA+U produces what might be characterized beyond the physical range of U for LaNiO$_2$. Although well beyond the physical range of U for LaNiO$_2$, we find that LDA+U produces what might be characterized by LDA+U at large U. Although well beyond the physical range of U for LaNiO$_2$, we find that LDA+U produces what might be characterized by LDA+U at large U.

already this band indicates importance of Ni 5d states range from -0.2 eV to 8 eV. Unlike in PM cuprates, rather broad due to the strong d$p$ antibonding interaction with oxygen $p_x,p_y$ states and enclosing holes centered at the M point. The other band, lying at -0.2 eV at $\Gamma$ and also having its maximum at the M=($\frac{\pi}{a}$, $\frac{\pi}{a}$, 0) point, is a mixture of La 5d($3z^2-r^2$) states and some Ni 3d($3z^2-r^2$) character. Already this band indicates importance of Ni 3d-La 5d band mixing.

Using a simple one-band tight binding model

$$\varepsilon_k = \varepsilon_0 - \sum_R t_R e^{i\k \cdot \mathbf{R}},$$

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III. RESULTS

A. LDA Results

We present first the LDA results. The paramagnetic (PM) band structure with its energy scale relative to Fermi energy $E_F$ is given in Fig. 2. A complex of La 4f bands is located at +2.5 eV with bandwidth less than 1 eV. The O 2p bands extend from about -8 eV to -3.2 eV. The Ni 3d bands are distributed from -3 eV to 2 eV, with the localized $t_{2g}$ complex near -1.5 eV, while the broad La 5d states range from -0.2 eV to 8 eV. Unlike in PM CaCuO$_2$, there are two bands crossing $E_F$. One is like the canonical $d(x^2-y^2)$ derived band in the cuprates, rather broad due to the strong $d\sigma$ antibonding interaction with oxygen $p_x,p_y$ states and enclosing holes centered at the M point. The other band, lying at -0.2 eV at $\Gamma$ and also having its maximum at the M=($\frac{\pi}{a}$, $\frac{\pi}{a}$, 0) point, is a mixture of La 5d($3z^2-r^2$) states and some Ni 3d($3z^2-r^2$) character. Already this band indicates importance of Ni 3d-La 5d band mixing.

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due to the different Madelung potential in the two parameters with those of CaCuO.

It should be noted that the state in mind is an on-neighboring Ni/Cu ions, i.e. an $x^2 − y^2$ symmetry Wannier orbital. In Ni, the on-site energy is 0.3 eV above what it is in CaCuO, lying above $E_F$ rather than below. This difference is partially due to the different Madelung potential in the two differently-charged compounds, but it also reflects some intrinsic hole-doping in the nickelate that leads to a lower Fermi level. The largest hopping amplitude (the conventional $t$) is 71% of its value in the cuprate, while the second ($t'$) is essentially the same. The $t(001) = t_z$ is also 70% of its value in the cuprate, while the other amplitudes are the almost unchanged.

The LDA Fermi surfaces are shown in Fig. 4. As for the cuprates, the Fermi surface is dominated by the M-centered hole barrel. In this system neighboring barrels touch at $R = (π/a, 0, π/c)$ because the saddle point at R happens to lie at $E_F$. The Fermi surfaces also include two spheres containing electrons. The sphere at $Γ$, with mixed Ni and La, $d(3z^2 − r^2)$ character of Ni and La, $d(3z^2 − r^2)$ character of Ni and La. The cylinder with radius 0.8 ($π/a$) contains Ni $d(x^2 − y^2)$ holes, whereas another sphere (a radius 0.4 ($π/a$)) at each corner contains Ni $d(zx)$ electrons.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
parameters & LaNiO$_2$ & CaCuO$_2$ & Ratio \% \\
\hline
$\varepsilon_0$ & 93 & -200 & \\
$\ v(100)$ & 381 & 534 & 71 \\
$\ v(110)$ & -81 & -84 & 96 \\
$\ v(001)$ & 58 & 83 & 70 \\
$\ v(011)$ & 0 & -2 & 0 \\
$\ v(111)$ & -14 & -19 & 74 \\
\hline
\end{tabular}
\end{table}

the Ni $3d(x^2 − y^2)$ band shown in Fig. 3 can be reproduced with a few hopping amplitudes, but requiring more than might have been anticipated. The site energy is $\varepsilon_0 = 93$ meV, slightly above the Fermi level, and the hopping integrals (in meV) are $v(100) = 381$, $v(110) = -81$, $v(001) = 58$ and $v(111) = -14$. There is no hopping along the (101) direction. As anticipated from the cuprates, the largest hopping is via $v(100)$. However, to correctly describe the $k_z$ dispersion from X-R (i.e. along $π/a, 0, k_z$) together with the lack of dispersion from $Γ - Z (0, 0, k_z)$ and also M-A ($π/a, π/a, k_z$), the third neighbor hopping terms $v(111)$ must be included.

The comparison of the single band tight binding parameters with those of CaCuO$_2$ is given in Table I. It should be noted that the state in mind is an $x^2 − y^2$ symmetry state that is orthogonal to those on neighboring Ni/Cu ions, i.e. an $x^2 − y^2$ symmetry Wannier orbital. In Ni, the on-site energy is 0.3 eV above what it is in CaCuO$_2$, lying above $E_F$ rather than below. This difference is partially due to the different Madelung potential in the two differently-charged compounds, but it also reflects some intrinsic hole-doping in the nickelate that leads to a lower Fermi level. The largest hopping amplitude (the conventional $t$) is 71% of its value in the cuprate, while the second ($t'$) is essentially the same. The $t(001) = t_z$ is also 70% of its value in the cuprate, while the other amplitudes are the almost unchanged.

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To investigate magnetic tendencies, attempts to find both ferromagnetic (FM) and antiferromagnetic (AFM) states were made. A stable $\sqrt{2} \times \sqrt{2} \times 2$ AFM state was obtained, with spin moment 0.53 $µ_B$ per Ni. This state has lower energy by 6 meV/Ni than that of PM state. Just as for the paramagnetic case, the AFM state has entangled bands of La $5d$, Ni $3d$ and O $2p$ character near the Fermi energy. In contrast to the unpolarized case (and CaCuO$_2$), with AFM order the large electron pocket has primarily

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{“Fatband” representation of Ni $3d(x^2 − y^2)$ in LDA. This band appears at first very two-dimensional, but is not because (1) the saddle point at X(0, $π/a, 0$) is not midway between the $Γ$ and M($π/a, π/a, 0$) energies, and (2) $k_z$ dispersion between the X and R(0, $π/a, π/c$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(Color online) Paramagnetic Fermi surface in the local density approximation. In the center (not visible), i.e. $Γ$, there is a sphere (a radius 0.25($π/a$)) having $d(3z^2 − r^2)$ character of Ni and La. The cylinder with radius 0.8($π/a$) contains Ni $d(x^2 − y^2)$ holes, whereas another sphere (a radius 0.4($π/a$)) at each corner contains Ni $d(zx)$ electrons.}
\end{figure}
La 5$d(xy)$ character and the slightly occupied electron pocket at $\Gamma$ has a combination of La 5$d(3z^2-r^2)$ and Ni 3$d(3z^2-r^2)$ character. Attempts to obtain a FM solution always led to a vanishing moment.

B. Consideration of Correlation with LDA+U

As noted in the introduction, no magnetic order has been observed in LaNiO$_2$, either by magnetization or by neutron scattering. Although the local density approximation often does quite well in predicting magnetic moments, for weakly or nearly magnetic systems renormalization by spin fluctuations becomes important and such effects are not included in the local density approximation. There is also the question of the strength of correlation effects due to an intra-atomic repulsion $U$ on the Ni site. Analogy to CaCuO$_2$ (same formal $d^9$ configuration, neighboring ion in the periodic table), which is a strong antiferromagnetic insulator, suggests that effects due to $U$ might have some importance. Here we apply the LDA+U “correlated band theory” method to assess effects of intra-atomic repulsion and compare with observed behavior. In the following subsection we compare and contrast with CaCuO$_2$.

Upon increasing $U$ from zero in the antiferromagnetically ordered phase, the spin magnetic moment of Ni increases from the LDA value of 0.53 $\mu_B$ to a maximum of 0.8 $\mu_B$ at $U = 3$ eV. Surprisingly, for $U > 4$ eV the moment steadily decreases and by $U = 8$ eV it has dropped to 0.2 $\mu_B$/Ni, which is less than half of its LDA value. We emphasize that this behavior is unrelated to the observed behavior of LaNiO$_2$ (which may need little or no additional correlation beyond LDA). However, this unprecedented response of the transition metal ion to the imposition of a large $U$ gives new insight into a feature of the LDA+U method that has not been observed previously.

This “quenching” of the local moment with increasing $U$ results from behavior of Ni 3$d(3z^2-r^2)$ states that is analogous to those of the 3$d(x^2-y^2)$, but with the direction of spin inverted (then with additional complications). As usual for a $d^9$ ion in this environment, the majority 3$d(x^2-y^2)$ state of Ni is fully occupied even at $U = 2$ eV, while the minority state is completely unoccupied at $U = 3$ eV, where the moment is maximum and the system is essentially Ni$^{1+}$ $S = \frac{1}{2}$. One can characterize this situation as a Mott insulating 3$d(x^2-y^2)$ orbital, as in the undoped cuprates. At $U = 3$ eV, the density of states has a quasi one-dimensional van Hove singularity due to a flat band just below (bordering) the Fermi energy as can be seen in the 3$d$ DOS shown in Fig. 6. Upon increasing $U$ to 4 eV, rather than reinforcing the $S = \frac{1}{2}$ configuration of Ni and thereby forcing the La and O ions to cope with electron/hole doping, the Ni 3$d(3z^2-r^2)$ states begin to polarize. The charge on the Ni ion drops somewhat, moving it in the Ni$^{1+} \rightarrow$ Ni$^{2+}$ direction, with the charge going into the La 5$d$ -- O 2$p$ states. Idealizing a bit, one might characterize the movement of (unoccupied) majority character of 3$d(3z^2-r^2)$ well above $E_F$ as a Mott transition of these orbitals, which is not only distinct from that of the 3$d(x^2-y^2)$ states, but is oppositely directed, leading to an on-site “singlet” type of cancellation.

This movement of states with increasing $U$ has been emphasized in Fig. 6 for easier visualization. The resulting spin density on the transition metal ion at $U = 8$ eV is pictured in Fig. 6. There is strong polarization in all directions from the core except for the position of nodes. The polarization is strongly positive (majority) in the lobes of the 3$d(x^2-y^2)$ orbital, and just as strongly negative (minority spin) in the lobes of the 3$d(3z^2-r^2)$ orbital. The net moment is (nearly) vanishing, but this results from a singlet combination (as nearly as it can be represented within classical spin picture) of spin-half up in one orbital and spin-half down in another orbital that violates Hund’s first rule. The magnetization density is large throughout the ion, but integrates to (nearly) zero.

This behavior is however more complicated than...
a Mott splitting of occupied and unoccupied state, as can be seen from the substantial Ni 3d character that remains, even for \( U = 8 \) eV, in a band straddling \( E_F \) while the rest of the weight moves to \( \sim 4 \) eV. In both of these bands there is strong mixing with La 5d\((xy)\) states. What happens is that as the “upper Hubbard 3d\((3z^2 - r^2)\) band” rises as \( U \) is increased, it progressively mixes more strongly with the La 5d\((xy)\) states, forming a bonding band and an antibonding band. While the antibonding combination continues to move upward with increasing \( U \), the bonding combination forms a half-filled band which remains at \( E_F \).

Thus we have found that for the Ni\(^{1+}\) ion in this environment, increasing \( U \) (well beyond what is physically plausible for LaNiO\(_2\)) results in \( S = \frac{1}{2} \) Ni\(^{1+}\) being converted into a nominal Ni\(^{2+}\) ion (the actual charge changes little, however) in which the two holes are coupled into an intraatomic \( S = 0 \) singlet. This behavior involves yet a new kind of correlation between the 3d\((3z^2 - r^2)\) states and the 3d\((x^2 - y^2)\) states, but one which is due to (driven by) the local environment.

This behavior is quite different from the results for \( U = 8 \) eV reported by Anisimov, Bukhvalov and Rice\(^{10}\) using the Stuttgart TBLMTO-47 code. They obtained an AFM insulating solution analogous to that obtained for CaCuO\(_2\),\(^{12}\) with a single hole in the 3d shell occupying the 3d\((x^2 - y^2)\) orbital that antibonds with the neighboring oxygen 2p\(_o\) orbital. The reason for this different result is not known, but it is now well established that multiple solutions to the LDA+U equations often exist.\(^{23, 24}\)

\section*{IV. COMPARISON WITH CaCuO\(_2\) AND DISCUSSION}

Although Ni\(^{1+}\) is isoelectronic to Cu\(^{2+}\), both the observed and the calculated behavior of LaNiO\(_2\) are very different from CaCuO\(_2\). In contrast to CaCuO\(_2\), LaNiO\(_2\) is (apparently) metallic, with no experimental evidence of magnetic ordering for LaNiO\(_2\). The differing electronic and magnetic properties mainly arise from two factors. First, the Ca 3d bands lying in the range of 4 eV and 9 eV are very differently distributed from the broader and lower La 5d bands in the range of -0.2 eV and 8 eV. Second, in CaCuO\(_2\), O 2p states extend to Fermi level and overlap strongly with Cu 3d states, and the difference of the two centers is less than 1 eV, as can be seen in Fig.\(^5\). Thus, there is a strong 2p–3d hybridization that has been heavily discussed in high

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{(Color online) Change of the Ni 3d\((3z^2 - r^2)\) and 3d\((x^2 - y^2)\) densities of states as on-site Coulomb interaction \( U \) increases. One can easily identify a splitting \( \sim 4 \) eV. In both of these bands there is strong mixing 3d\(^{-}\) and overlap strongly with Cu 3d states, while the rest of the weight moves to \( \sim 4 \) eV.

\begin{itemize}
  \item \( U = 3 \) eV
  \item \( U = 4 \) eV
  \item \( U = 6 \) eV
  \item \( U = 8 \) eV
\end{itemize}

\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{Isocontour plot of the spin density of the “singlet” Ni ion (\( U = 8 \) eV) when there is an \((x^2 - y^2)\) with spin up and a \((3z^2 - r^2)\) hole with spin down. Dark and light surfaces denote isocontours of equal magnitude but opposite sign.}
\end{figure}
usual monovalent Ni ion. As we have found and in apparent agreement with experiment, this compound is a metal, and the "charge state" of a transition metal atom in a metal usually has much less significance than it is in an insulator. It may be because the compound is metallic that it is stable, but in this study we are not addressing energetics and stability questions.

Hayward et al. [13] had already suggested that the experimental findings could arise from reduced covalency between the Ni 3d and O 2p orbitals, and the 30% smaller value of the hopping amplitude \( t \) indeed reflects the smaller covalency, as does the increased separation between the Ni 3d and O 2p bands. It is something of an enigma that in CaCuO\(_2\) and other cuprates, LDA calculations fail to give the observed antiferromagnetic states, while in LaNiO\(_2\) LDA predicts a weak antiferromagnetic state when there is no magnetism observed. In the cuprates the cause is known and is treated in a reasonable way by application of the LDA+U method. In this nickelate, application of the LDA+U method does not seem to be warranted (although novel behavior occurs if it is used). Rather, the prediction of weak magnetism adds this compound to the small but growing number of systems (ZrZn\(_2\), [25] Sc\(_3\)In, [24] and Ni\(_3\)Ga, [22] for example) in which the tendency toward magnetism is overestimated by the local density approximation. It appears that this tendency can be corrected by accounting for magnetic fluctuations. [21, 22]

VI. ACKNOWLEDGMENT

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