Charge–spin–orbital states in the tri-layered nickelate La$_4$Ni$_3$O$_8$: an ab initio study

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**Abstract.** The electronic and magnetic structures of La$_4$Ni$_3$O$_8$, an analogue of the hole doped cuprates, are studied using the configuration state constrained local-spin-density approximation plus Hubbard $U$ calculations. It is found to be a C-type antiferromagnetic Mott insulator, in which an orbital hybridization strongly reduces an otherwise possible charge disproportionation. This state accounts for several experimental observations. The involved Ni$^{2+}$ high-spin state and its orbital configuration are found to be against a crystal-field level picture, which predicts an Ni$^{2+}$ low-spin state in the NiO$_2$ square lattice. We note, however, that La$_4$Ni$_3$O$_8$, if in the low-spin state, would be a charge-homogeneous ferromagnetic half-metal with only the up-spin $x^2–y^2$ conduction band. Therefore, low-spin nickelates may be explored for any interesting property.

Transition-metal oxides have long been of great concern for condensed matter physicists and material scientists. They are significantly important not only scientifically but also technologically. For example, the superconductivity of cuprates and colossal magnetoresistance of manganites are among their spectacular functionalities. They are mostly classified as a strongly correlated system. Electron Coulomb correlation is a key ingredient of the involved
Figure 1. (a) Body-centered tetragonal structure of the tri-layered \( \text{La}_4\text{Ni}_3\text{O}_8 \). Spin-density contour plot of the C-type AF insulating ground state (\( -0.35 \) to \( 0.35 \) \( e \text{Å}^{-3} \) in a step of \( 0.1 \) \( e \text{Å}^{-3} \)) on (b) the outer-layer NiO plane and (c) the inner-layer NiO plane. The \( x^2-y^2 \) orbital character and intra-layer AF coupling are apparent. (d) Spin-density contour plot (\( 0.05-0.35 \) \( e \text{Å}^{-3} \)) on the (110) plane containing the Ni\(_o\)–Ni\(_i\)–Ni\(_o\) tri-layer. The \( 3z^2-r^2 \) orbital character and inter-layer FM coupling are apparent.

many-body physics, and it plays a vital role in determining their abundant properties. The strong correlation effects manifest themselves very often via a fascinating interplay among the charge, spin, orbital and lattice degrees of freedom [1].

In this paper, we study the tri-layered nickelate \( \text{La}_4\text{Ni}_3\text{O}_8 \). This nickelate was synthesized very recently [2, 3], motivated by searching analogues of the superconducting cuprates [4–14]. The Ni atom can be in a formal +1, +2 or +3 valence state. As Ni\(^+\) is isoelectronic to Cu\(^{2+}\), a nickelate having a mixed Ni\(^+\)–Ni\(^{2+}\) state could have a similar electronic structure as the hole-doped superconducting cuprates. Note that unlike Ni\(^+\) (3d\(^9\), \( S = 1/2 \)), Ni\(^{2+}\) could be either in a high-spin (HS, \( S = 1 \)) state or in a low-spin (LS, \( S = 0 \)) state, and the corresponding orbital occupations are different. The tri-layered \( \text{La}_4\text{Ni}_3\text{O}_8 \) has a body-centered tetragonal structure, see figure 1. Each formula unit has one inner-layer Ni (Ni\(_i\)) and two outer-layer Ni (Ni\(_o\)), three of which are in total in the 4+ valence state. Thus, this nickelate is a Ni\(^z\)–Ni\(^{2+}\) mixed valent system and has an average valent state of 4/3. According to magnetization, resistivity and thermoelectric power measurements, \( \text{La}_4\text{Ni}_3\text{O}_8 \) is an antiferromagnetic (AF) insulator at low temperature [3, 14].

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Figure 2. (a) Configuration state of the Ni\(^+\) (\(S = 1/2\)) and the LS Ni\(^{2+}\) (\(S = 0\)), according to the crystal-field level diagram for the NiO\(_2\) square plane, see also (c) the Ni\(_i\) 3d density of states by a nonmagnetic LDA calculation (the Ni\(_o\) 3d being almost the same, not shown here). The \(x^2 - y^2\) electron hopping would give rise to a charge-homogeneous metallic state. (b) The inter-site Coulomb repulsion between the 3\(z^2 - r^2\) electrons within the tri-layer along the \(c\)-axis (see figure 1(a)) could force the Ni\(^{2+}\) ion to transit into a stable HS \(S = 1\) state. Then, a hopping of the down-spin 3\(z^2 - r^2\) electron becomes possible and thus reduces a charge disproportionation (CD).

As sketched in figure 2(a), if the Ni\(^{2+}\) ion is in the LS state according to the crystal-field level diagram for the NiO\(_2\) square plane [12], the \(x^2 - y^2\) electron would readily hop from the Ni\(^+\) ion to the Ni\(^{2+}\). This would give rise to a charge-homogeneous metallic state. This solution can be partially seen from the Ni 3d density of states calculated by local density approximation (LDA) for the nonmagnetic state (figure 2(c)), which shows the crystal-field level sequence. The crystal-field excitation energy from the antibonding 3\(z^2 - r^2\) to \(x^2 - y^2\) is 0.9 eV, and it is close to the Hund exchange of about 1 eV typically for late 3d transition metals. However, as seen in figure 2(b), the inter-site Coulomb repulsion between the 3\(z^2 - r^2\) electrons within the tri-layer along the \(c\)-axis could make the Ni\(^{2+}\) favor the HS over the LS state. That is to say, the Coulomb repulsion from the four 3\(z^2 - r^2\) electrons of two Ni\(_o\) ions would prompt an electron excitation from the Ni\(_i\) 3\(z^2 - r^2\) to \(x^2 - y^2\). Then all the Ni ions would have each a half-filled \(x^2 - y^2\) orbital. This would force La\(_i\)Ni\(_o\)O\(_8\) to be a Mott insulator with a strong intra-layer AF coupling (see figures 1(b) and (c)) as in the parent cuprate. However, a hopping of the down-spin 3\(z^2 - r^2\) electron (figure 2(b)) would gain kinetic energy and could thus stabilize an inter-layer FM coupling within the tri-layer (see figures 1(a) and (d)).

La\(_4\)Ni\(_3\)O\(_8\) is an interesting material for the above reasons, and therefore its electronic structure and magnetism are worth an investigation. Very recently, La\(_4\)Ni\(_3\)O\(_8\) was studied by electron-correlation corrected density-functional calculations [9, 12]. While Pardo and Pickett [9] suggest an HS molecular correlated insulating state, Sarkar et al [12] report on a possible bistability between LS and HS states and favors an LS metallic solution. Apparently, these two theoretical works give conflicting results and conclusions, and there exist competing possibilities. Therefore, we are motivated to check those different possibilities, to clarify the
situation and to isolate the most important factors playing a role here. As seen below, using a set of configuration-state constrained density functional calculations, we are able to find a variety of electronic states of concern and compare them directly. Then we demonstrate that the crystal-field level diagram of the LS Ni$^{2+}$ state is insufficient and La$_4$Ni$_3$O$_8$ is indeed in an HS state due to inter-site orbital interaction (see figure 2). Moreover, we provide an alternative view that the AF Mott insulator La$_4$Ni$_3$O$_8$ somewhat has a charge disproportionation (CD), which is strongly reduced by orbital hybridization.

We have carried out band structure calculations using the local-spin-density approximation plus Hubbard $U$ (LSDA + $U$) method [15]. We have studied a number of configuration states, which include the FM, A-type AF, C-type AF and G-type AF magnetic structures, the LS and HS states and different orbital multiplets. For those configuration states, our LSDA + $U$ calculations were initialized by setting the corresponding occupation-number matrix and hence orbital-polarized potential. Then those calculations were carried out self-consistently with a full electronic relaxation. (Otherwise, some states of concern cannot be achieved in LSDA + $U$ calculations.) Such configuration-state constrained calculations turn out to be quite useful for the study of the charge, spin and orbital states in correlated electron systems [16, 17]. We have used the experimental structural data [2, 3] and the full-potential augmented plane wave plus local orbital code (WIEN2k) [18]. The muffin-tin spheres were chosen to be 2.8, 2.1 and 1.5 Bohr for La, Ni and O atoms, respectively; the plane-wave cutoff of 12 Ryd for the interstitial wave functions and 400 $k$ points for integration over the Brillouin zone. The results presented below are obtained with the effective $U = 6$ eV ($U_{\text{eff}} = U - J$). Note that the results remain qualitatively unchanged when using the $U_{\text{eff}}$ values of 4 and 8 eV.

We start with the calculations for the FM state. As seen in figure 3, La$_4$Ni$_3$O$_8$ would be a half-metal in the FM state. Only the up-spin $x^2-y^2$ wide bands cross the Fermi level. Although the 3d DOSs of the Ni$_i$ and Ni$_o$ have a somewhat different shape, they have almost the same energy positions. This indicates a charge homogeneous solution with the average Ni$^{+4/3}$ charge state. The Ni$_i$–2Ni$_o$ ions are all in the LS state, and each contributes 2/3 $\mu_B$ (the 2/3 occupied up-spin $x^2-y^2$ band) to the calculated total integer spin moment of 2 $\mu_B$ fu$^{-1}$. Note, however, that this LS metallic solution disagrees with the experimental insulating behavior.

As the wide $x^2-y^2$ bands of concern have an in-plane character, an A-type AF state (intra-layer FM but inter-layer AF within the tri-layer) turns out to have a similar band structure (not shown here) as the above metallic solution. Both metallic solutions have the 2/3 filled $x^2-y^2$ bands. Such a filling might induce a charge or spin density wave and then give a low-temperature insulating behavior. However, a consequent in-plane $3 \times 3$ superstructure has not been observed [3]. As such, we could think of a CD as the origin of the AF insulating behavior. Note that a CD is most probably suppressed in the above (intra-layer) FM state, which has a largest bandwidth (a maximal electron hopping to smear out the CD). As we will see below, a CD of the formal Ni$^{2+}_i$–2Ni$^+_o$ type is indeed possible but is strongly reduced by an orbital hybridization, and it accounts for several experimental observations.

To proceed, we calculate the intra-layer AF states, which reduce the in-plane $x^2-y^2$ bandwidth significantly (see figures 3 and 4 for a comparison). Thus, a charge disproportionated Mott insulating state could be obtained. The studied C-type AF state has intra-layer AF and

Note that 4–8 eV is a reasonable range of the $U$ parameter for nickelates [3, 4, 9, 10]. For the most concerned C-AF state (see table 1), our calculations using $U = 4.7$ eV and $J = 0.7$ eV (being the same as in [9]) show that the HS$^*$ state is more stable than the LS state by 650 meV fu$^{-1}$. The corresponding values are 250 and 1020 meV fu$^{-1}$ when using $U_{\text{eff}} = 4$ and 8 eV, respectively. Therefore, the HS state is constantly more stable than the LS state.

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Figure 3. Total density of states (DOS) and orbitally resolved Ni-3d DOS for the LS FM half-metallic state of La$_4$Ni$_3$O$_8$. The red bold (blue thin) lines stand for the up (down) spin channel. The Fermi level is set at zero energy. One Ni$_i$ and two Ni$_o$ ions are in a homogeneous charge state of +4/3, and their 3d states have almost the same energy positions. Only three up-spin $x^2-y^2$ wide bands cross the Fermi level and each has an occupation number of 2/3, giving a total spin moment of $2 \mu_B f u^{-1}$.

inter-layer FM within the tri-layer, and the G-AF has both intra-layer and inter-layer AF. We performed configuration-state constrained (HS and LS states) LSDA + $U$ calculations, in order to study the relative stability of the formal Ni$_i^{2+}$ HS and LS states, and the relevant electronic/magnetic structures.

As seen in table 1, the most stable C-AF HS$^a$ state formally has one hole on the down-spin $x^2-y^2$ and $3z^2-r^2$ orbitals of the Ni$_i$ ion, respectively. Band hybridization brings about 0.18$e$ and 0.33$e$ on both orbitals, respectively. All other orbitals are fully occupied. For the two Ni$_o$ ions, the corresponding nominal occupation numbers are 0.17$e$ and 0.47$e$ (larger than the above 0.33$e$). We could tentatively assign the Ni$_i$ ion to the formal +2 valence state and Ni$_o$ to +1 (for more results and discussion see below). Then the down-spin $3z^2-r^2$ electron of the formal Ni$_i^+$ ion can hop to the formally empty down-spin $3z^2-r^2$ orbital of the Ni$_i^{2+}$ ion (see figure 2(b)). This stabilizes the inter-layer FM coupling (see figure 1(d)) and strongly reduces the amplitude of the CD. This also explains why the local spin moment of 1.25 $\mu_B$ has increased at the formal $S=1/2$ Ni$_i^+$ ion and that of 1.39 $\mu_B$ has reduced at the formal $S=1$ Ni$_i^{2+}$ ion. It is important to note that in the metal–insulator transition nickelate NdNiO$_3$, the CD is experimentally found to be about 0.4$e$ for the formal charge order 2Ni$^{3+} \rightarrow$ Ni$^{2+}$ + Ni$^{4+}$ [19, 20]. Very similarly, in
LiNiO$_2$ the CD is calculated to be 0.2–0.4\,e for the formal Ni$^{2+}$ + Ni$^{4+}$ state [21], i.e. 0.1–0.2\,e per valence difference of 1. Therefore, the small difference of the above two occupation numbers, 0.47–0.33 = 0.14\,e, is meaningful and reasonable. It stands for the formal Ni$^{1+}$/Ni$^{3+}$ CD, which is strongly reduced by orbital hybridization.

Moreover, our assignment of the formal Ni$^{1+}$/Ni$^{3+}$ CD and the above analysis are also backed by the calculated results for the HS$^{a}$ G-AF state (see table 1). Owing to the assumed inter-layer AF coupling and to the constraint of the Hund exchange, a hopping of the down-spin 3z$^2$−r$^2$ electron from the formal Ni$^{1+}$ ion to the HS Ni$^{2+}$ is suppressed. Thus, the occupation number of the down-spin Ni$^{1+}_o$ 3z$^2$−r$^2$ orbital restores to 0.78\,e, and that of the down-spin Ni$^{2+}_i$ 3z$^2$−r$^2$ orbital decreases to 0.19\,e. As a result, the CD is well manifested by the difference of the two occupation numbers, being about 0.6\,e. The corresponding spin moments, 0.82\,\mu_B at Ni$^{1+}_o$ and 1.52\,\mu_B at Ni$^{2+}_i$ both reduced from their respective formal spin $\frac{1}{2}$ and 1 by a common covalency, manifest again the CD. As the 3z$^2$−r$^2$ electron hopping is prompted in the C-AF state but not in the G-AF state, it makes the former energetically more favorable by 430 meV fu$^{-1}$.

Apparently, an NiO$_2$ square lattice strongly lowers the 3z$^2$−r$^2$ crystal-field level and gives rise to a much higher xy and the highest x$^2$−y$^2$ levels. A possible HS$^{b}$ state of the formal Ni$^{1+}$ would have one hole on the x$^2$−y$^2$ and xy orbitals, respectively. LS state with two holes on the x$^2$−y$^2$ orbital could also be possible. We therefore performed constrained LSDA + U calculations for them. As seen in table 1, the HS$^{b}$ state has an energy higher than that of the above-discussed HS$^{a}$ state by 710 meV fu$^{-1}$. This is because the 3z$^2$−r$^2$ orbitals of all the HS$^{b}$

\[\text{Figure 4. Total DOS and orbitally resolved Ni-3d DOS for the HS C-type AF insulating state of La$_4$Ni$_3$O$_8$. The red bold (blue thin) lines stand for the up (down) spin channel. The Fermi level is set at zero energy.}\]
we show its DOS results.

Figure 1. Mn-TM (2013) 023038.

Table 1. The relative total energies $\Delta E$ (meV fu$^{-1}$), spin moments $m$ ($\mu_B$) and spin-resolved orbital occupations for two HS C-type AF states, one LS C-AF and one HS G-AF state of La$_4$Ni$_3$O$_8$. HS$^a$ (HS$^b$) means that the formal Ni$^{2+}$ ion has one hole on the $x^2-y^2$ and $3z^2-r^2$ ($x^2-y^2$ and $xy$) orbitals, respectively. In the most stable C-AF (HS$^a$) state, a hopping of the down-spin $3z^2-r^2$ electron from the formal Ni$_i^+$ to Ni$_i^{2+}$ strongly reduces the CD, see also figure 2(b).

| State          | $\Delta E$ | Ni$_i$: $m$ | $x^2-y^2$ | $3z^2-r^2$ | $xy$ | $xz$, $yz$ | Ni$_o$: $m$ | $x^2-y^2$ | $3z^2-r^2$ | $xy$ | $xz$, $yz$ |
|---------------|------------|-------------|-----------|-----------|-----|------------|-------------|-----------|-----------|-----|------------|
| C-AF (HS$^a$) | 0          | 1.39        | 0.98      | 0.91      | 0.94 | 1.87       | 1.25        | 0.98      | 0.89      | 0.94 | 1.85       |
|               |            | 0.18        | 0.33      | 0.93      | 1.84 |            | 0.17        | 0.47      | 0.93      | 1.82 |            |
| C-AF (HS$^b$) | 710        | 1.28        | 0.98      | 0.88      | 0.94 | 1.85       | 0.81        | 0.85      | 0.85      | 0.93 | 1.83       |
|               |            | 0.19        | 0.83      | 0.55      | 1.82 |            | 0.16        | 0.77      | 0.93      | 1.81 |            |
| C-AF (LS)     | 690        | 0.01        | 0.40      | 0.86      | 0.94 | 1.85       | 1.00        | 0.93      | 0.86      | 0.94 | 1.84       |
|               |            | 0.40        | 0.87      | 0.94      | 1.85 |            | 0.16        | 0.68      | 0.93      | 1.81 |            |
| G-AF (HS$^a$) | 430        | 1.52        | 0.98      | 0.93      | 0.95 | 1.87       | -0.82       | 0.16      | 0.77      | 0.93 | 1.80       |
|               |            | 0.21        | 0.19      | 0.94      | 1.85 |            | 0.94        | 0.78      | 0.93      | 1.83 |            |

Ni$_i^{2+}$ and Ni$_o^+$ ions are fully occupied. Then the direct inter-site Coulomb repulsion between the $3z^2-r^2$ electrons, and the cost of the kinetic energy of the $3z^2-r^2$ electrons both make the HS$^b$ state less stable than the HS$^a$ state. Moreover, the HS$^a$ state is also more stable than the LS state by 690 meV fu$^{-1}$, see table 1. In the LS state, the Ni$_i^{2+}$ $x^2-y^2$ orbital has an occupation number of 0.4$e$ for each spin channel due to the strong $p\sigma$ covalency, but the induced local spin moment is calculated to be only 0.01 $\mu_B$. This tiny moment and the calculated spin moment of 1.0 $\mu_B$ at the Ni$_o$ ions well indicate that this less stable state has the LS ($S = 0$) Ni$_i^{2+}$ and $S = 1/2$ Ni$_o^+$. So far, we have found to be the most stable the HS$^a$ C-type AF insulating solution, which has a spin moment of 1.39 $\mu_B$ for Ni$_i$ and 1.25 $\mu_B$ for Ni$_o$. In figure 4 we show its DOS results. It has an insulating gap of 0.7 eV. (These results are close to those reported in [9].) The Ni$_i$ 3d states have lower energy positions (about 0.5 eV in terms of the center of gravity) than the Ni$_o$ 3d states. This indicates a higher (lower) charge state of the Ni$_i$ (Ni$_o$) ions, i.e. an emerging CD of the formal Ni$_i^{2+}$–2Ni$_o^+$ type. The finite-electron (hole) occupation on the Ni$_i$ (Ni$_o$) down-spin $3z^2-r^2$ orbital just below (above) the Fermi level can be traced back to an electron transfer from the formal Ni$_o^+$ ion to Ni$_i^{2+}$ after an orbital hybridization, see also figure 2(b). Such an orbital hybridization is similar to the molecular formation proposed in [9]. This stabilizes the inter-layer FM coupling within the tri-layer, see figure 1(d). For both Ni$_i$ and Ni$_o$ ions, the $x^2-y^2$ orbital is half-filled and thus gives rise to an intra-layer superexchange AF coupling, see figures 1(b) and (c).

Note that our AF Mott insulating solution agrees with the experiments [3, 14]. The Hubbard $U$ stabilizes the charge-disproportionated and orbital-polarized state and opens the Mott insulating gap. The formal HS Ni$_i^{2+}$ ion involved is found to have, respectively, one hole on the $x^2-y^2$ and $3z^2-r^2$ orbitals. The hopping of the down-spin $3z^2-r^2$ electron from the Ni$_o^+$ ions to Ni$_i^{2+}$ helps to enhance the inter-layer coupling of the tri-layer. This qualitatively accounts for the observed displacement of the two outer-layer Ni$_o^+$ ions toward the inner-layer Ni$_i^{2+}$ [2]. Our calculations during atomic relaxation show that the optimized Ni$_o$–Ni$_i$ distance is 3.13 Å after Ni$_o$ displacement. Within an error bar (a few per cent) of density functional calculations, this value agrees with the experimental one of 3.25 Å. Moreover, the ‘2/3 filling’ of the down-spin $3z^2-r^2$ orbitals in the formal 2Ni$_o^+$–Ni$_i^{2+}$ state seems relevant to the formation of the tri-layer.
structure of La$_4$Ni$_3$O$_8$. Otherwise, either the HS Ni$^{2+}$ with respectively one hole on the $x^2-y^2$ and $xy$ orbitals, or the LS Ni$^{2+}$ with two holes on $x^2-y^2$, would have the fully occupied $3z^2-r^2$ orbital, together with the Ni$^+_0$ ions. Then the inter-layer coupling would be mostly weakened and thus the tri-layer structure could be readily destabilized.

In summary, we have studied the electronic structure and magnetism of the tri-layered La$_4$Ni$_3$O$_8$ using a set of configuration-state constrained LSDA+U calculations. Our results show that the C-type AF insulating ground state somewhat has a CD of the formal 2Ni$^+$–Ni$^{2+}$ type. The formal Ni$^{2+}$ is in an HS ($S=1$) state with respectively one hole on the $x^2-y^2$ and $3z^2-r^2$ orbitals, but not in an LS ($S=0$) state with two holes on the $x^2-y^2$ orbital. Thus, the half-filled $x^2-y^2$ orbitals in both the $S=1/2$ Ni$_0^+$ and $S=1$ Ni$_i^{2+}$ ions are responsible for the intra-layer AF. The inter-layer FM coupling within the tri-layer prompts the down-spin $3z^2-r^2$ electron hopping from two Ni$_0^+$ to Ni$_i^{2+}$ to gain a kinetic energy. The amplitude of the CD is thus strongly reduced. We note that our results account for several experimental observations.

Against the crystal-field level picture which predicts the LS state of the Ni$^{2+}$ ion in a square NiO$_2$ lattice, the Ni$^{2+}$ HS state is stabilized in the multi-layered nickelates. This is due to the reduction of inter-site Coulomb repulsion between the $3z^2-r^2$ electrons and due to the kinetic energy gain. As only the LS Ni$^+–$Ni$^{2+}$ mixed-valent nickelates have a partially occupied $x^2-y^2$ band that is similar to the hole-doped cuprates, see figures 2(a) and 3, they would be worth exploring for an interesting property. Attention may therefore be focused on single-layered nickelates with the square NiO$_2$ lattice which favors the LS state, rather than on multi-layered nickelates in which the HS Ni$^{2+}$ state instead is more favorable.

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