Oxygen vacancy induced site-selective Mott transition in LaNiO$_3$

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While defects such as oxygen vacancies in correlated materials can modify their electronic properties dramatically, understanding the microscopic origin of electronic correlations in materials with defects has been elusive. Lanthanum nickelate with oxygen vacancies, LaNiO$_{3-x}$, exhibits the metal-to-insulator transition as the vacancy level $x$ increases from the stoichiometric LaNiO$_3$. In particular, LaNiO$_{2.5}$ exhibits a paramagnetic insulating phase, also stabilizing an antiferromagnetic state below $T_N \simeq 152$K. Here, we study the electronic structure and energetics of LaNiO$_{3-x}$ using first-principles. We find that LaNiO$_{2.5}$ stabilizes a vacancy-ordered structure with an insulating ground state and the nature of the insulating phase is a “site-selective” paramagnetic Mott state as obtained using density functional theory plus dynamical mean field theory (DFT+DMFT). The Ni octahedron site develops a Mott insulating state with strong correlations as the Ni $e_g$ orbital is half-filled while the Ni square-planar site with apical oxygen vacancies becomes a band insulator. Our oxygen vacancy results can not be explained by the pure change of the Ni oxidation state alone.

I. INTRODUCTION

Rare-earth nickelates $R$NiO$_3$ ($R$ is the rare-earth ion) have attracted significant research interests due to their rich electronic properties. These include the metal-insulator transition, charge order, magnetism, multiferroicity, and the site-selective Mott transition. Although the $R$ ion can be treated as electrically inert, the phase boundaries of the metal to insulator transition and the paramagnetic (PM) to anti-ferromagnetic (AFM) transition depend sensitively on the subtle structural tolerance factor controlled by the size of the $R$ ion. This close interplay between the structural, electronic, and magnetic degrees of freedom puts the rare-earth nickelate into an intriguing correlated material.

Oxygen vacancy is one of the common defects in transition metal oxides and it can play a central role in oxide electronic. It is also known that oxygen vacancies in LaNiO$_3$, one of the rare-earth nickelates, also change its electronic and magnetic properties significantly as they can modify electronic correlation effects. Although LaNiO$_3$ is the only metallic case among the known rare-earth nickelate series, Ni $d$ orbitals are still moderately correlated as indicated by experimental spectroscopic measurements. Experimental measurements on the conductivity in LaNiO$_{3-x}$ show that the increase of the vacancy level $x$ reduces the conductivity and the metal-to-insulator transition occurs as $x$ approaches to 0.5. As the oxygen vacancy level $x$ increases further, LaNiO$_{2.5}$ is found to be semiconducting or poorly conducting. The complete absence of the apical oxygens leads to the infinite-layer structure of LaNiO$_2$ and the role of electronic correlations in LaNiO$_2$ has been drawing much attention recently as similar nickelates such as NdNiO$_2$ and PrNiO$_2$ exhibit superconductivity when they are hole-doped. Although LaNiO$_2$ is metallic, resistivity increases at low temperatures hinting possibly strong correlation effects. In addition to electronic properties, oxygen vacancies also have significant effects on magnetism. While LaNiO$_3$ remains paramagnetic at all temperatures, B. Wang et al. found that LaNiO$_{2.5}$ has the AFM structure below 152K, and LaNiO$_{2.75}$ is ferromagnetic (FM) below 225K. LaNiO$_2$ does not show any clear evidence of the long-range magnetic order.

Spectroscopic measurements of LaNiO$_{3-x}$ are also widely performed using X-ray Absorption Spectroscopy (XAS) and Photo-Emission Spectroscopy (PES) to study electronic structure in experiments. Consistently with the transport measurement, spectra at the Fermi energy decreases as the vacancy level $x$ increases from LaNiO$_3$, opening a spectral gap near the level at $x = 0.5$. An interesting feature measured from XAS in LaNiO$_{3-x}$ bulk as well as the thin-layer structure is the splitting of the spectral peak above the Fermi energy, which has been attributed to the oxygen vacancy effect.

There have been some first-principles studies of oxygen vacancy effects on rare-earth nickelates. Previous density functional theory (DFT) and GW study on LaNiO$_{3-x}$ systems addressed the metal-insulator transition and resulting spectra due to the vacancy effect. A. Malashchevich et al. did a systematic study on LaNiO$_{3-x}$ with small $x$ value and found that oxygen vacancies stay around the same Ni ion and localize extra electrons created by the vacancy. The strong localization of electrons due to the oxygen vacancies in other rare-earth nickelates also has been studied using DFT+U. However, the microscopic origin of the strongly correlated insulating phase induced by oxygen vacancies and the changes of the correlated spectra in LaNiO$_{3-x}$ compared to experiments have not been systematically investigated.

In this paper, we study the strong correlation effect on the electronic structure and the energetics of
LaNiO$_{3-x}$ from first-principles as the oxygen vacancy level $x$ evolves. We adopt dynamical mean field theory (DMFT) in combination with DFT to treat strong correlations in the paramagnetic phase as well as DFT+U for the long-range magnetic state. We show that the vacancy-ordered structure becomes thermodynamically stable in LaNiO$_{2.5}$ and the metal-to-insulator transition due to the change of the vacancy level $x$ can be captured correctly in DFT+DMFT. The insulating nature of the vacancy-ordered LaNiO$_{2.5}$ structure with two nonequivalent Ni ions originates from the site-selective Mott phase due to both structural and electronic correlation effects. While bulk LaNiO$_3$ forms a rhombohedral structure with the octahedral geometry of the Ni ion surrounded by six O ions, oxygen vacancies can change both the oxidation number of the Ni ion and the local structure, which can lead to the substantial change of electronic structures in LaNiO$_{3-x}$.

Our paper is organized as follows. First, we explain the computational methods we used including DFT, DFT+U and DFT+DMFT in Sec. II and show the structural details and magnetism in Sec. III A. We also study formation energies of LaNiO$_{3-x}$ in Sec. III B. Then we display the spectral functions of LaNiO$_{3-x}$ computed using DFT+DMFT and DFT+U, and compare to experimental measurements in Sec. III C. The DMFT self-energies in LaNiO$_{3-x}$ are displayed to explain the nature of the insulating phase in Sec. III D and compare our results to the rigid band shift approximation in Sec. III E. And we conclude our discussion in Sec. IV.

II. COMPUTATIONAL METHODS

First, we performed structural relaxation calculations for LaNiO$_{3-x}$ ($x=0$, 0.25, 0.5, 0.75, and 1) systems and obtained the ground-state energies and magnetism using both DFT and DFT+U. Vienna Ab-initio Simulation Package (VASP) has been used in all DFT and DFT+U calculations adopting the Perdew-Burke-Ernzerhof for solids (PBE-sol) as the exchange and correlation energy functional. We set 0.001 eV/Å as the force convergence condition fully relaxing the cell shape, volume and internal ionic positions.

Then we calculate the correlated electronic structure using DFT+DMFT and DFT+U for LaNiO$_3$, LaNiO$_{2.5}$, and LaNiO$_2$. To study magnetism, DFT+U is adopted to relax structures imposing experimental magnetic orderings and to study the electronic structure from those relaxed structures. For a paramagnetic ground-state, we adopt DFT+DMFT using the DFT relaxed structure with the PM order. The relaxed structures obtained using DFT and DFT+U are quite similar, as will be shown in next section. We adopt the DMFTwDFT package for DFT+DMFT calculations. Wannier90 package has been adopted to obtain maximally localized Wannier functions for the construction of the DMFT correlated subspace. Nickelates show a rather strong $d-p$ hybridization due to the covalent bonding between Ni and O ions. Therefore, it is important to construct both Ni 3$d$ and O 2$p$ orbitals for the Wannier basis to treat the hybridization effect. To construct the Wannier orbitals, we take an energy window from -9 eV to 5 eV from the Fermi energy, which basically all Ni 3$d$ and O 2$p$ orbitals.

For DFT+U and DFT+DMFT, we need to define interaction parameters to treat the on-site Coulomb interaction within the $d$-orbitals of the Ni ion. A rather small value of $U$ ($\approx 2$ eV) was used in the $d$-orbital model of previous rare-earth nickelates studies, while $U=5$–7 eV was used for the wide-energy window calculation including both $d$- and $p$-orbitals to reproduce the metal-insulator and structural phase diagram and to compare with the angle resolved photoemission spectra. Similar $U$ value ($\approx 5.7$ eV) was also obtained from the constrained DFT calculation. For both DFT+DMFT and DFT+U calculations in this paper, we use the Hubbard $U=5$eV and the Hund’s coupling $J=0.8$eV which are parameterized by the Slater integrals. To account for the double-counting correction of DFT+DMFT, the modified fully-localized-limit form of the double-counting potential, which was used for the phase diagram study of rare-earth nickelates, has been used. To solve the DMFT impurity problem, we use the continuous-time quantum Monte Carlo solver with temperature $T \approx 290$K. After DFT+DMFT calculations are converged, we used the post-processing tool from the DMFTwDFT package to calculate the spectral function $A(\omega)$ for LaNiO$_{3-x}$. More details of the DMFT calculation method are shown in the Supplemental Material.

III. RESULTS

A. Structural relaxation and magnetism

Bulk LaNiO$_3$ forms a rhombohedral structure given by the $R3c$ space symmetry group. This structure has two La, two Ni, and six O ions in a unit-cell, which can be obtained by rotating the Ni-O octahedra from the cubic perovskite structure. Namely, without any defects, each Ni ion is surrounded by six O ions forming the octahedron and all Ni-O octahedra are equivalent with the same Ni-O bond lengths (see Fig. 1). The oxygen vacancy formation induces the local structural distortion due to the absence of apical oxygens, which breaks the cubic symmetry. While it is challenging to measure the crystal structure with vacancies, several experiments suggest the LaNiO$_{2.5}$ structure such that NiO$_6$ octahedra and NiO$_4$ square-planes are alternating in the $x-y$
plane as shown in Fig. 1. Previous DFT calculations\(^{23}\) also provides the insight that the apical divacancy configuration lowers the formation energy than other configurations meaning a four-coordinated Ni-O square plane is energetically favored when oxygen vacancies are introduced. In this paper, we denote Ni in the octahedral environment as Ni\(_0\) and Ni in the square-planar symmetry as Ni\(_{sp}\). We also construct LaNiO\(_{2.75}\) and LaNiO\(_{2.25}\) structures with vacancy orderings such that Ni\(_0\) and Ni\(_{sp}\) ions modulated along the \(x-y\) plane, as shown in Fig. 1c and Fig. 1d. LaNiO\(_3\) becomes a tetragonal structure of purely Ni\(_{sp}\) ions with NiO\(_4\) square-planes (see Fig. 1f).

While LaNiO\(_3\) remains a PM metallic state at all temperatures, LaNiO\(_{3-x}\) (\(x > 0\)) undergoes the magnetic transition for most cases. In Table I\(^{[1]}\) we list the experimentally observed long-range magnetic orderings of LaNiO\(_{3-x}\) including the ground state (metal or insulator) and the Neel temperature (\(T_N\)) with relevant references. Most LaNiO\(_3\) structures with O vacancies become FM except LaNiO\(_{2.5}\). Previous experimental work\(^{[20]}\) in LaNiO\(_{2.5}\) suggests that LaNiO\(_{2.5}\) is the G-type AFM and the Ni\(_0\) ions have relatively large magnetic moments, while the Ni\(_{sp}\) ions have almost no magnetic moment. All LaNiO\(_{3-x}\) structures become paramagnetic above \(T_N\).

To study the structural and magnetic properties, we fully relaxed the oxygen-vacancy ordered structures of LaNiO\(_{3-x}\) with \(x = 0, 0.25, 0.5, 0.75\) and 1 using both DFT and DFT+U. In Table II\(^{[2]}\) we provide the structure details obtained from the relaxations with magnetic structures observed in experiments for \(x=0, 0.5\) and 1. That is to say, we impose the G-type AFM order on LaNiO\(_{2.5}\) relaxations, and the PM order on LaNiO\(_2\) and LaNiO\(_3\), which are the ground state magnetic order in experiments. In LaNiO\(_3\), DFT Ni-O bond length and Ni-O-Ni bond angle are similar to experiment while DFT+U overestimate the bond angle along with the contracted bond length. LaNiO\(_{2.5}\) has two nonequivalent Ni ions and the Ni\(_{sp}\)-O bond length is much larger than the Ni\(_{sp}\)-O bond length. LaNiO\(_{2.5}\) structure relaxed with DFT shows the Ni-O bond length difference to be 0.14Å. DFT+U predicts the similar Ni-O bond difference (∼ 0.22Å) as the experimental value (∼ 0.21Å) although the absolute values of the bond lengths in DFT+U are smaller than experimental values. In LaNiO\(_2\), the Ni-Ni distance along \(z\)-axis is quite smaller than along the \(x-y\) plane due to the loss of apical oxygens and the DFT structural parameters are closer to experimental values than the DFT+U parameters.

In Table III\(^{[3]}\) we calculate the ground-state energies of LaNiO\(_{3-x}\) using DFT and DFT+U. Different magnetic orderings including PM, G-type AFM, and FM are imposed during the relaxation calculations and subtract the resulting FM energy from the G-type AFM energy for each system. In each structure, different magnetism can be obtained by converging the solutions from different initial configurations. In LaNiO\(_3\), the ground-state converges to the PM structure regardless of FM or AFM initial configurations in DFT while DFT+U predicts it to be FM. Also in LaNiO\(_2\), DFT converges to the PM con-

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**TABLE I: Experimental magnetic and transport (metal/insulator) properties of LaNiO\(_{3-x}\)**

| LaNiO\(_{3-x}\) | M/I | MAG. | \(T_N\) |
|-----------------|-----|------|--------|
| LaNiO\(_3\)     | M   | PM   | 0K     |
| LaNiO\(_2.75\)  | M   | PM   | 225K   |
| LaNiO\(_2.5\)   | N/A | FM   | N/A    |
| LaNiO\(_2\)     | I   | AFM  | 152K   |
| LaNiO\(_1\)     | M   | PM   | N/A    |

| Parameters | LaNiO\(_3\) | LaNiO\(_{2.75}\) | LaNiO\(_2\) |
|------------|-------------|----------------|-------------|
| \(d_{Ni-O}[\AA]\) | 1.90 | 1.88 | 1.88 |
| \(a_{Ni-O-Ni}[\degree]\) | 164.5 | 168.3 | 164.3 |
| \(d_{Ni-Ni}[\AA]\) | 3.83 | 3.82 | 3.83 |
| \(d_{Ni-Ni}[\AA]\) | 3.64 | 3.67 | 3.67 |
| \(d_{Ni-Ni}[\AA]\) | 1.86 | 1.83 | 1.83 |
| \(d_{Ni-Ni}[\AA]\) | 2.00 | 2.05 | 2.05 |
| \(d_{Ni-Ni}[\AA]\) | 1.86 | 1.88 | 1.88 |
| \(d_{Ni-Ni}[\AA]\) | 3.34 | 3.32 | 3.32 |
| \(d_{Ni-Ni}[\AA]\) | 1.95 | 1.92 | 1.92 |

\(^a\) Along the \(x-y\) plane.  
\(^b\) Along the \(z\) axis.

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**TABLE II: Structural information of LaNiO\(_3\), LaNiO\(_{2.5}\), and LaNiO\(_2\) obtained from DFT and DFT+U relaxation calculations.**

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**TABLE III:**

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FIG. 1: Crystal structures of (a) LaNiO\(_3\), (b) LaNiO\(_2\), (c) LaNiO\(_{2.5}\), (d) LaNiO\(_{2.25}\), and (e) LaNiO\(_{2.75}\).
configuration while AFM is more stable in DFT+U. Therefore, the experimental FM structures can be captured for LaNiO$_3$ and LaNiO$_2$ within DFT. In LaNiO$_{2.5}$, DFT+U predicts the ground-state to be AFM consistently with the experiment (see Table I) while DFT converges to the FM ground state. This implies that the correlation treated in DFT+U can be important to capture the ground-state magnetic configuration in structures with vacancies. Both DFT and DFT+U give the FM order lower energy than AFM order in LaNiO$_{2.75}$, which is also consistent with experiments.

In LaNiO$_{2.5}$, the spin-state ordering occurs as the Ni$_o$ ion in NiO$_6$ exhibits a high-spin state while the Ni$_{sp}$ ion in NiO$_4$ shows a low-spin state. This spin-state ordering induced by the oxygen vacancy ordering is also consistent with our DFT+U calculation. We find the Ni$_o$ ion shows a high-spin state with the magnetic moment of 1.62$\mu_B$, which is much larger than the low-spin moment in Ni$_{sp}$ (0.16$\mu_B$). This spin-state ordering is also accompanied by the in-plane Ni-O bonding disproportionation in which the Ni$_o$-O bond length is much larger than the Ni$_{sp}$-O bond length by $\sim$0.22Å (see Table II). LaNiO$_{2.75}$ and LaNiO$_{2.25}$ with FM order also show the similar trends of the spin-state ordering in our calculations in that the Ni$_o$ ion has a larger moment than the Ni$_{sp}$ ion, as shown in Table IV.

**TABLE III: Total energy difference per formula unit [meV] between FM and AFM in LaNiO$_{3-x}$.**

| LaNiO$_{3-x}$  | DFT       | AFM-FM  | DFT+U     | AFM-FM |
|----------------|-----------|---------|-----------|--------|
| LaNiO$_3$      | 0$^a$     | 0$^a$   | -741$^b$ | -741$^b$ |
| LaNiO$_{2.75}$ | 4$^a$     | -41$^b$ | 40        | 40     |
| LaNiO$_{2.5}$  | 10        | -41$^b$ | 68        | 68     |
| LaNiO$_{2.25}$ | 2$^a$     | 68      | 51        | 51     |
| LaNiO$_{2}$    | 2$^a$     | 51      | -51$^b$  | -51$^b$ |

$^a$ Both FM and AFM converged to zero magnetic moment.  
$^b$ FM converged to zero magnetic moment.

**TABLE IV: Magnetic moments [$\mu_B$] of LaNiO$_{3-x}$ computed using DFT+U.**

| LaNiO$_{3-x}$  | Ni$_o$  | Ni$_{sp}$ |
|----------------|---------|-----------|
| LaNiO$_{2.75}$ | 1.04/1.47/1.04 | 0.11     |
| LaNiO$_{2.5}$  | 1.62    | 0.16      |
| LaNiO$_{2.25}$ | 1.60    | 0.8/0.8/0.8 |

**B. Formation energies**

The stability of the oxygen vacancy ordered structure can be determined by the formation energy calculation. Here, we compute the vacancy formation energy per formula unit for LaNiO$_{3-x}$ structures as a function of the oxygen chemical potential related to the given oxygen pressure. The formation energy can be given by

$$E_{\text{form}} = E_{\text{LaNiO$_{3-x}$}} - E_{\text{LaNiO$_3$}} + x \cdot \frac{1}{2} E_{\text{O}_2} + x \cdot \mu_O \quad (1)$$

where $E_{\text{form}}$ is the Gibbs formation energy, $x$ is the vacancy level, $E_{\text{LaNiO$_{3-x}$}}$ is the total energy of LaNiO$_{3-x}$, $E_{\text{O}_2}$ is the total energy of the O$_2$ molecule, and $\mu_O$ is the oxygen chemical potential depending on pressure and temperature. Here, we neglect the phonon and entropy contributions of LaNiO$_{3-x}$ to the Gibbs formation energy at finite temperatures. In experiments, the thermodynamic stability condition of oxygen vacancies in given materials can depend on the applied oxygen pressure $P$ and temperature $T$. We assume that the oxygen molecule forms an ideal-gas-like reservoir during the experimental sample growth, therefore its chemical potential can be given by

$$\mu_O(T, P) = \mu_O(T, P^0) + \frac{1}{2} k_B T \ln \left( \frac{P}{P^0} \right) \quad (2)$$

where $P^0$ is the ambient pressure. The $\mu_O(T, P^0)$ values are taken from Ref. We plot $E_{\text{form}}$ as a function of $\mu_O$ (related to the applied pressure) at 920K using the LaNiO$_{3-x}$ structures obtained from DFT+U (Fig. 2a) and DFT (Fig. 2b). We compute the ground-state energy of LaNiO$_{3-x}$ using first-principles (DFT or DFT+U) by relaxing structures with the different magnetic orders (PM, FM and AFM) and choosing the lowest energy among different magnetic states. Our results suggest that, for the oxygen-rich region, when the oxygen pressure higher than 50Pa (corresponding to $\mu_o > -1.3$ eV), LaNiO$_3$ is the most stable structure compared to other vacancy structures with the
The Ni... that the small bump below the Fermi energy has mostly occupied DOS also shows a broad
2-t mostly contributed from the orbitals. O 2p orbitals are also mixed with these orbitals. O 2p peaks are distributed broadly below -2 eV. The unoccupied DOS also shows a broad \( e_g \) peak with a strong mixture with O 2p spectra due to the covalent bonding between Ni and O ions. As a result, the hole density per the O ion is 0.26 and the occupancy of the Ni 3d orbital becomes \( \sim 7.8 \) (See Table V).

The absence of apical oxygens in LaNiO\(_2\) changes electronic structures significantly compared to LaNiO\(_3\). First, the apical oxygen vacancy breaks the symmetry of the Ni-O octahedron and split the on-site orbital energies within \( e_g \) and \( t_{2g} \) manifolds as the local geometry of the Ni-O bonding becomes a square-planar symmetry. As a result, two \( e_g \) orbitals in Ni\(_{sp}\) become non-degenerate and the \( d_{z^2} \) orbital is lower in energy than the \( d_{x^2-y^2} \) orbital. Second, the removal of the apical oxygen ions from the Ni-O octahedron means that two electrons are effectively donated to the remaining the Ni-O square plane. The donation of two electrons from the apical oxygen changes the oxidation state of Ni\(^{3+}\) in LaNiO\(_3\) to Ni\(^{1+}\) in LaNiO\(_2\). Due to this electron transfer, \( d \) occupancy in Ni\(_{sp}\) becomes close to 9.1 while the hole per O ion is also reduced to 0.06 (See Table V). As a result, the \( d_{z^2} \) orbital tends to be fully filled while the \( d_{x^2-y^2} \) orbital is almost half-filled enhancing the electronic correlation effect.

Our DMFT DOS in LaNiO\(_2\) is also consistent with the experimental XAS measurement showing the strong reduction of the unoccupied O 2p spectra compared to the LaNiO\(_3\) case. Our unoccupied O 2p DOS (blue dashed line in Fig. 3) is also much reduced and the occupied O 2p peak in LaNiO\(_2\) is located further below the Fermi energy due to the reduced hole density in the O ion and the decreased Ni-O hybridization compared to LaNiO\(_3\). Due to this much reduced Ni-O hybridization and the \( d_{z^2} \) orbital occupancy close to the half-filling, the ground-state of LaNiO\(_2\) becomes close to the Mott insulating metal as reflected in the strong reduction of the \( d_{x^2-y^2} \) spectra near the Fermi energy which is also consistent with the experimental XAS measurement. This incoherent metallic state due to the strong correlation effect is also reflected in the large scattering rate (the imaginary part of the self-energy at the zero frequency in Fig. 5b) and consistent with the poor conductivity measured experimentally in LaNiO\(_2\). Our DFT band structure calculation reveals that some La 5d bands are also crossing below the Fermi energy (see Supplemental Material) although we do not include this hybridization effect of the La 5d orbital as we construct the Wannier functions for only Ni 3d and O 2p orbitals. Although treating the effect of this La 5d orbital on the DMFT correlation is beyond the scope of our paper, previous DMFT calculation in the similar NdNiO\(_2\) material argues that the Nd 5d band acts as a charge reservoir without significant hybridization with the Ni 3d orbita.

In Fig. 3c and 3d, we also plot the orbital-resolved DOS for both LaNiO\(_3\) and LaNiO\(_2\) obtained using DFT+U. We impose the PM spin order for both materials, consistently with the experiment as listed in Table I. In both materials, the DFT+U calculations also exhibit qualitatively similar features as the DFT+DMFT spectra. In

C. Correlated density of states

In this section, we study the correlated density of states (DOS) for the vacancy-ordered structure in LaNiO\(_{2.5}\) as well as stoichiometric LaNiO\(_3\) and LaNiO\(_2\) using both DFT+DMFT and DFT+U to treat correlations beyond DFT. First, we compare the DOS for stoichiometric LaNiO\(_3\) (\( x=0 \); Fig. 3a) and LaNiO\(_2\) (\( x=1 \); Fig. 3b) computed using DFT+DMFT. The ground-state of LaNiO\(_3\) computed using DFT+DMFT is the Fermi-liquid metal, which is consistent with the experimental measurement. The overall peak positions computed in DFT+DMFT are also consistent with the experimental PES peak positions. Our orbital-resolved DFT+DMFT DOS reveals that the small bump below the Fermi energy has mostly contributed from the \( t_{2g} \) character while the \( e_g \) character and the sharp peak near -0.7 eV is mostly contributed from the \( t_{2g} \) character. O 2p orbitals are also distributed below -2 eV. The unoccupied DOS also shows a broad \( e_g \) peak with a strong
LaNiO$_3$, the $t_{2g}$ peak is located slightly below the experimental peak at -0.7eV and the it is somewhat strongly hybridized with O $p$ orbitals. Consistently with DMFT, the unoccupied O 2$p$ DOS becomes much reduced in LaNiO$_3$ and $d_{x^2-y^2}$ orbital is also nearly half filled. However, the DFT+U spectra have still large DOS intensity at Fermi level and the O 2$p$ peak is relatively close to the Fermi energy compared to DMFT.

Now we turn to the LaNiO$_{2.5}$ case with the oxygen vacancy ordering. We performed both DFT+DMFT and DFT+U calculations to study the correlated electronic structure beyond DFT treating the realistic oxygen vacancy structure (Fig.4b-e). DFT+U was performed with the $G$-type AFM ordering (the lowest-energy magnetic structure; see Table II) and DFT+DMFT was performed with the paramagnetic spin symmetry. In this structure, the six-coordinated Ni-O octahedron (Ni$_o$) and the four-coordinated Ni-O square-plane (Ni$_{sp}$) are alternating in the $x - y$ plane as two apical oxygen ions are removed from the half of octahedra in LaNiO$_3$ (see Fig.4a). Our structural relaxation calculation shows that the Ni-O octahedron is distorted as the in-plane Ni-O bond length is larger than the out-of-plane bond (see Table II). However, the orbital energy difference between two $e_g$ orbitals is only 0.05eV, which is much smaller than $e_{g}$-$t_{2g}$ splitting of 0.5eV. In Ni$_{sp}$, the energy splitting between $d_{z^2}$ and $d_{x^2-y^2}$ is as large as 0.5eV.

As shown in Fig.4b-e, both DFT+DMFT and DFT+U predict the ground state of LaNiO$_{2.5}$ to be insulating consistently with experiments. This is in sharp contrast with the DFT DOS predicting the ground state to be metallic as DFT underestimates correlations (see Supplemental Material). DFT+DMFT DOS opens a spectral gap of 0.3 eV resulting in the PM insulating state while the band gap computed in DFT+U with AFM becomes much larger (~1.5 eV). Our DFT+DMFT calculation can also reveal that the two-peak structure of the unoccupied spectra measured in experiment originates from the two nonequivalent Ni ions in LaNiO$_{2.5}$. The Ni$_o$ ion (Fig.4b) develops a spectral Mott gap in the middle of the almost degenerate $e_g$ orbitals and the broad unoccupied peak near 2eV above the Fermi energy emerges as the upper Hubbard band due to the localized nature of Ni$_o$ $e_g$ orbitals and the broad unoccupied peak near 2eV above the Fermi energy.

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FIG. 5: Imaginary part of self-energies $Im \Sigma(\omega)$ computed for Ni $d_{x^2}$ and $d_{x^2-y^2}$ orbitals in (a) LaNiO$_3$, (b) LaNiO$_2$, and LaNiO$_{2.5}$ for two nonequivalent Ni ions, (c) Ni$_o$ and (d) Ni$_{sp}$ respectively.

(Fig. 5a) and LaNiO$_2$ (Fig. 5b) are also compared. The self-energies of $e_g$ orbitals in LaNiO$_3$ are degenerate and show the Fermi-liquid behavior ($Im \Sigma \sim \omega^2$) at the low frequency, consistently with the metallic ground state. In LaNiO$_2$, the $d_{x^2-y^2}$ orbital develop correlations as the self-energy develops a pole near the Fermi energy with the large scattering rate at $\omega = 0$. In LaNiO$_{2.5}$, both Ni$_o$ $e_g$ orbitals have strong correlations at the Fermi energy as self energy curves have poles right near $\omega=0$ while Ni$_{sp}$ in LaNiO$_{2.5}$ exhibits a flat curve. Since Ni$_o$ $e_g$ orbitals in LaNiO$_{2.5}$ are also nearly half filled (see Fig. 4 energy diagram), this indicates a Mott type insulator in Ni$_o$, while the Ni$_{sp}$ with oxygen vacancies behave similarly as the band insulator as only one $e_g$ orbital is fully filled and the other $e_g$ orbital is almost unoccupied (see Fig. 4 energy diagram). This Mott insulating behavior occurs at the half of lattice sites selectivity (in this case for Ni$_o$ sites), therefore it can be understood as the “site-selective” Mott transition. This site-selective Mott insulating phase is also accompanied by the substantial Ni-O bond disproportionation of 0.22Å between Ni$_o$ and Ni$_{sp}$ as obtained in the DFT+U relaxation calculation (see Table II) since the Mott insulating site is expanded to reduce the hybridization between Ni and neighboring O ions. In DFT+U, this mechanism occurs as the spin-state ordering since the Mott insulating site becomes a high-spin state while the band insulating site exhibits a low-spin state. The similar mechanism also occurs in rare-earth nickelates with smaller rare-earth ions such as LuNiO$_3$, however the band insulating site in this case forms an octahedron and $e_g$ orbitals in this site are still half-filled creating a singlet state with surrounding O holes.

In DMFT calculation, one can also measure the correlation strength from the obtained quasi-particle renormalization factor $Z$ defined as

$$Z = \left(1 - \frac{\partial \Sigma}{\partial \omega} |_{\omega=0}\right)^{-1}$$

which gives the inverse of the effective mass renormalization factor ($m^*/m = Z^{-1}$). The Ni $e_g$ band of LaNiO$_3$ has an effective mass factor of 1.7. For LaNiO$_2$, electronic correlation is further enhanced than LaNiO$_3$ and the quasi-particle band of the $d_{x^2-y^2}$ orbital is strongly renormalized with a factor of 8.9. In LaNiO$_{2.5}$, the $e_g$ orbitals of Ni$_{sp}$ are almost uncorrelated, with effective mass factor of ~1. However, the $e_g$ orbitals in Ni$_o$ have nearly the infinite effective mass, as the Mott insulating state develops.

Oxygen vacancy also changes the Ni oxidation state and increases the electron occupation in the Ni-O manifold effectively as two electrons are donated from the removed oxygen ion. Table V shows the occupation number for Ni 3d and O 2p orbitals in each structure obtained from DFT+DMFT. As the Ni oxidation state changes from Ni$^{3+}$ in LaNiO$_3$ to Ni$^{1+}$ in LaNiO$_2$, the $d-$orbital occupancy increases from 7.8 to 9.12 and the hole occupancy in the O ion decreases from 0.26 to 0.06. In LaNiO$_{2.5}$, the average Ni oxidation state is Ni$^{2+}$. However, it is not clear whether the electron transfer due to oxygen vacancy will occur mostly to Ni$_{sp}$ resulting in charge ordering between Ni$^{3+}$ in the Ni$_o$ ion and Ni$^{1+}$ in the Ni$_{sp}$ ion or both Ni$_o$ and Ni$_{sp}$ will have the similar Ni$^{2+}$ configuration without charge ordering. Our DFT+DMFT calculation shows that Ni$_o$ is close to Ni$^{2+}$ as the $e_g$ orbitals in Ni$_o$ are almost half filled (~2.13) and the $e_g$ occupancy in Ni$_{sp}$ is slightly more occupied than the half-filling leaving some holes per the O site (~0.15). This hole state in O is rather strongly hybridized with the Ni$_{sp}$ $e_g$ orbital as shown in the previous DOS result. Therefore, the site-selective Mott transition in LaNiO$_{2.5}$ also leads to small charge ordering between Ni$_o$ and Ni$_{sp}$ ions due to different hybridizations with O ions.

TABLE V: Occupations of Ni 3d and O 2p orbitals in LaNiO$_{3-x}$ obtained from DFT+DMFT.

| LaNiO$_{3-x}$ | Ni$_o$ | Ni$_{sp}$ | O$_{avg}$ |
|---------------|--------|-----------|-----------|
| LaNiO$_3$    | 7.79   | N/A       | 5.74      |
| LaNiO$_2$    | 8.13   | 8.63      | 5.85      |
| LaNiO$_{2.5}$| N/A    | 9.12      | 5.94      |

E. Rigid band shift approximation in LaNiO$_{3-x}$

Our DFT+DMFT calculation in LaNiO$_{2.5}$ shows that the paramagnetic insulating phase in LaNiO$_{2.5}$ originates from the change of Ni oxidation states as well as the oxygen vacancy ordering structure which induces both the
local symmetry change of Ni ions and different hybridization of Ni ions with surrounding O ions. To investigate the effect of the oxygen vacancy ordering structure on electronic correlations, we apply the rigid band shift approximation to LaNiO$_3$ within DFT+DMFT to impose the effect of the Ni oxidation state change alone. In this approximation, we use the same Wannier band structure obtained from LaNiO$_3$ at different vacancy levels while the effect of different Ni oxidation states is adopted by shifting the Fermi level to modify the total number of electrons within DMFT calculations accordingly.

Fig. 6(a–e) shows the DOS of different Ni oxidation states due to the change of vacancy level \( x \), namely Ni$^{3+}$ for \( x=0 \) and Ni$^{1+}$ for \( x=1 \). As the oxidation number changes from Ni$^{3+}$ to Ni$^{1+}$, O $p$ and Ni $t_{2g}$ states move further below the Fermi energy while keep the shape mostly unchanged. This trend is also consistent with the experiment data depicted as the shaded region. The Ni $e_g$ states near the Fermi energy also do not change significantly as the Fermi level shifts higher in energy for the smaller oxidation state. The Ni$^{2+}$ state corresponding to LaNiO$_2.5$ still exhibits the ground-state metallic state without developing a Mott state although the $e_g$ occupancy becomes close to the half-filling. In Fig. 6(f), we plot the mass renormalization factor $m^*/m$ and the corresponding Ni $d$ occupancies as a function of Ni oxidation states. While the $d$ occupancies change linearly, the effective mass becomes maximum only when the $d$ occupancy becomes close to 8.0 meaning the half-filled $e_g$ occupancy although the mass renormalization remains in range of 1.5–2.5. Therefore, the strong correlation effect occurring in the oxygen vacancy structure can not be captured by the Ni oxidation change alone within the rigid band shift approximation.

**IV. CONCLUSION**

In conclusion, we performed first principles calculations in LaNiO$_3$ with oxygen vacancies (LaNiO$_{3-x}$ with \( x=0, 0.25, 0.5, 0.75, \) and 1). Experimentally, the metal-to-insulator transition occurs as the oxygen vacancy level \( x \) approaches to 0.5 and the ground state is AFM (AFM becomes PM at higher temperature). We find that the vacancy ordering structure of alternating NiO$_6$ octahedra and NiO$_4$ square planes (with apical oxygen vacancies) becomes thermodynamically stable in LaNiO$_{2.5}$ when the oxygen pressure is lowered than the typical growth condition of LaNiO$_3$. DFT+U converges to the correct AFM magnetic order in LaNiO$_{2.5}$ while DFT favors FM implying that the electronic correlation effect can be important for oxygen vacancy structures. Our DFT+DMFT calculation in LaNiO$_{2.5}$ shows that the PM ground state is insulating and the nature of this insulating state is site-selective Mott phase in which the octahedral Ni ion develops a Mott state with strong electron correlations and the square-planar Ni ion becomes a band insulator with the negligible self-energy. We also explain the nature of the two-peak structure in unoccupied spectra measured in O1s XAS experiments of LaNiO$_{3-x}$. The lower energy peak in XAS originates from the square-planar Ni state strongly hybridized with O ions while the higher energy peak is resulted from the broad spectra of the localized $e_g$ orbitals in strongly correlated octahedral Ni ion. LaNiO$_2$ with the complete apical oxygen vacancies becomes also
strongly correlated as it reduces the Ni-O hybridization and lifts the degeneracy between $e_g$ orbitals, as a result, the ground state becomes close to the Mott state although it is still metallic. The change of Ni oxidation states alone within the rigid band shift approximation can not capture the strongly correlated insulating phase occurring in the oxygen vacancy structure of LaNiO$_3$ implying that it is important to treat realistic oxygen vacancy structures of materials using first-principles to account for electronic correlation effects induced by oxygen vacancies.

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SUPPLEMENTAL MATERIALS FOR OXYGEN VACANCY INDUCED SITE-SELECTIVE MOTT TRANSITION IN LANIO₃

A. DFT and DFT+U density of states

In Fig. 7, we list the density of states (DOS) for LaNiO₃₋ₓ with x=0, 0.25, 0.5, 0.75, and 1 computed using DFT and DFT+U with non-magnetic, ferromagnetic and G-type antiferromagnetic configurations. For LaNiO₃, LaNiO₂.75 and LaNiO₂.5 cases, we compare the orbital-resolved DOS with experimental photoemission spectroscopy (PES) spectra as depicted in the shaded region. In all calculations, as the oxygen vacancy level x increases, the La state moves down in energy close to the Fermi energy while the Ni state is slightly shifted below the Fermi energy. The Ni-O hybridization becomes also weaker as the vacancy level evolves. The ground-states of all DFT calculations become metallic as DFT underestimates correlation effects. In DFT+U, ferromagnetic and G-type antiferromagnetic ground states in LaNiO₂.5 become insulator consistently with the experimental transport property although the non-magnetic ground state is still metallic as the correlation effect is also underestimated.

B. DFT+DMFT calculation details

The overall procedure of DFT+DMFT as implemented in the DMFTwDFT package is as follows. First, we perform non-magnetic DFT calculations for each structure. Then, we adopt the Wannier90 package to obtain maximally localized Wannier functions (MLWFs) as localized orbitals for DMFT. To construct the Wannier orbitals, we take an energy window from -9 eV to +5 eV, with respect to Fermi energies, which basically contains all Ni 3d and O 2p orbitals. It is also important that the interpolated band structure obtained from MLWFs matches to the original DFT band structure. In Fig. 8, we plot Wannier band structures for LaNiO₃, LaNiO₂.5 and LaNiO₂ and compare to DFT band structures. For LaNiO₃, the Wannier bands match to the DFT bands almost perfectly capturing the original band structure in DFT. For LaNiO₂, Wannier bands almost overlap with DFT bands except some bands at G and A points near the Fermi energy which are mostly La bands. This is because we construct the MLWFs of only Ni 3d and O 2p orbitals. For LaNiO₂.5, Wannier bands almost match to the DFT bands near Fermi level, which are mostly Ni characters. There are also some DFT bands between 0 to 2.5 eV derived from La bands in which the Wannier bands do not have any counterparts.

From the obtained Wannier subspace, we perform the DMFT self-consistent calculation using the continuous-time quantum Monte Carlo as an impurity solver. We use 18×18×18 k-points which are denser than the DFT k-points while doing the DMFT calculations. To minimize the off-diagonal component of hybridization functions in DMFT, we adopt the rotated axis for constructing MLWFs which is aligned to the bonding direction of the local Ni octahedron sites. To avoid the double counting of the Coulomb interaction taken in DFT+DMFT, we also used the modified double counting correction energy (DC_type = 1 in the DMFTwDFT package) with the parameter α = 0.2, which is given by

\[ E^{DC} = \frac{(U - \alpha)}{2} \cdot N_d \cdot (N_d - 1) - \frac{J}{4} \cdot N_d \cdot (N_d - 2) \]  \hspace{1cm} (4)

where U is the Hubbard interaction, J is the Hund’s coupling, and N_d is the d-occupancy.

C. Total energies of LaNiO₃₋ₓ

In Table VI, we list total energies of LaNiO₃, LaNiO₂.75, LaNiO₂.5, LaNiO₂.25, and LaNiO₂ obtained from DFT and DFT+U calculations by relaxing structures with different magnetism including PM, FM, and G-type AFM. The energy difference between FM and AFM for each structure was given and explained in the main text.
FIG. 7: Orbital-resolved density of states calculated using the DFT method for LaNiO$_3$, LaNiO$_{2.75}$, LaNiO$_{2.5}$, LaNiO$_{2.25}$, and LaNiO$_2$ with (a) non-magnetic, (b) ferromagnetic, and (c) antiferromagnetic orderings, as well as using the DFT+U method with (d) non-magnetic, (e) ferromagnetic, and (f) antiferromagnetic orderings. The shaded region is taken from previous experimental work. Sub-figures with * in label indicates the ground state converged to zero magnetic moment.
FIG. 8: Comparison of the Wannier band structures of Ni 3d and O 2p orbitals with the DFT band structures for (a) LaNiO$_3$, (b) LaNiO$_{2.75}$, and (c) LaNiO$_2$.

TABLE VI: Total energies [eV] of LaNiO$_3$, LaNiO$_{2.75}$, LaNiO$_{2.5}$, LaNiO$_{2.25}$, and LaNiO$_2$

|        | PM       | FM       | AFM      | PM       | DFT+U    | AFM       |
|--------|----------|----------|----------|----------|----------|-----------|
| LaNiO$_3$ | -36.041  | -36.041  | -36.041  | -33.852  | -34.175  | -33.834   |
| LaNiO$_{2.75}$ | -34.437  | -34.442  | -34.435  | -32.160  | -32.650  | -32.610   |
| LaNiO$_{2.5}$  | -32.678  | -32.723  | -32.713  | -30.460  | -31.098  | -31.139   |
| LaNiO$_{2.25}$ | -30.950  | -30.953  | -30.951  | -28.664  | -29.124  | -29.056   |
| LaNiO$_2$     | -29.233  | -29.235  | -29.213  | -26.842  | -27.396  | -27.447   |

* Relaxation converged to 0 magnetic momentum.