Charge and orbital order in RNiO$_3$ (R=Nd,Y) by LSDA+U method

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Electronic structures of NdNiO$_3$ and YNiO$_3$ are calculated by using LSDA+U method with rotational invariance. The Jahn-Teller distortion is not allowed under the observed magnetic ordering. No orbital order on Ni sites cannot be observed in the calculation of both systems but different types of charge ordering. In a small distorting system NdNiO$_3$, all Ni ions are trivalent and oxygen sites have a particular ordering, both in charge and orbital. In a large distorting system YNiO$_3$, the charge disproportionation occurs, 2Ni$^{3+} \rightarrow$ Ni$^{2+}$+Ni$^{4+}$. Therefore, the charge ordering stabilizes the asymmetry of the arrangement of Ni magnetic moments in both systems.

Perovskite transition metal oxides are now of high interest because of the large variety and the possible controllability of their physical properties. Perovskite nickelates RNiO$_3$ (R = an trivalent rare earth or Y ions) can be classified into three different categories, according to their tolerance factor ($t = d_{R-O}/\sqrt{2} d_{Ni-O}$). One is those whose tolerance factor is much smaller ($t < 0.91$) and has a larger distortion, such as LuNiO$_3$ or YNiO$_3$. They are antiferromagnetic insulators at low temperatures. This class of RNiO$_3$ undergoes transition to paramagnetic insulator at the Neel temperature $T_N$ and also has another phase transition from paramagnetic insulator to paramagnetic metal (M-I transition) at very high transition temperature. Second is those whose tolerance factor is intermediate ($0.91 < t < 0.93$), such as NdNiO$_3$ or PrNiO$_3$. These materials are also antiferromagnetic insulators at low temperatures and above $T_N$ they are paramagnetic metals. Third is LaNiO$_3$ where $t = 0.94$ and is paramagnetic metal.

Low temperature phase of above mentioned first and second classes of RNiO$_3$ have the unique magnetic structures. Its magnetic diffraction peak is characterized by the propagation vector $\vec{k} = (1/2, 0, 1/2)$ and the magnetic unit cell is identified as the $2 \times 1 \times 2$ supercell of the crystallographic lattice. The magnetic order is specified to be alternating ferromagnetic (FM) and anti-ferromagnetic (AFM) couplings $\cdots$Ni$^{\uparrow}$ FM O $\rightarrow$ Ni$^{\uparrow}$ AFM O $\rightarrow$ Ni$^{\downarrow}$ FM O $\rightarrow$ Ni$^{\downarrow}$ AFM O $\rightarrow$ Ni$^{\uparrow}$ $\cdots$ along three crystallographic directions.

On the contrary to the asymmetric arrangement of magnetic bonds (FM/AFM) around each nickel site, Ni-O distances around each Ni ion are almost equal to each other. For instance, the difference between the longest and the shortest Ni-O bonds in one NiO$_6$ octahedron is at most 2% in RNiO$_3$. The Jahn-Teller distortion is absent in RNiO$_3$, even in the largely distorted system YNiO$_3$, whose tolerance factor is 0.88. Experimentally there is only one crystallographic site for Ni ions in NdNiO$_3$ and two different sites for Ni ions in YNiO$_3$. Therefore, one can expect trivalent ions Ni$^{3+}$ in NdNiO$_3$. On the contrary, Ni ions in YNiO$_3$ are divalent and quadrivalent, i.e. the charge disproportionation 2Ni$^{3+} \rightarrow$ Ni$^{2+}$+Ni$^{4+}$ occurs.

In this letter, we study the electronic properties of the AFM insulating phase of two perovskite nickelates, NdNiO$_3$ and YNiO$_3$, which are typical ones of above mentioned two respective classes. We use the LSDA+U method with the rotational invariance in conjunction with the LMTO-ASA method. The LSDA+U method counts the electron-electron interaction between localized orbitals by the Hartree-Fock type interaction term. The ionic positions and lattice parameters used in the present calculations are imported from the diffraction experiments. The unit cell here is the $2 \times 1 \times 2$ crystallographic supercell containing 16 Nd or Y ions, 16 Ni ions, and 48 O ions and, in addition, 32 empty spheres, totally 112 atomic spheres. Sixty-four k-points in the Brillouin zone are sampled in the calculation of the density of states. NdNiO$_3$ is antiferromagnetic up to $T_N = 200$K, but the Nd spin moment vanishes at about 30K. Therefore, three 4f electrons of Nd ion are counted in the frozen core. We also calculated the electronic structure of NdNiO$_3$ with 4f electrons in valence states, and the results show no significant difference. The Coulomb and exchange parameters $U$ and $J$ of Ni ions are fixed to be 7.0 eV and 0.88 eV, respectively, through all the LSDA+U calculations. These values are consistent with photoemission experiments and the results of the LSDA calculations. Calculated results are not changed much over a large range of values of $U$ and $J$.

The crystallographic space groups of NdNiO$_3$ and YNiO$_3$ are orthorhombic Pbnm and monoclinic P2$_1$/n, respectively. The group theoretical analysis shows that, using the projection operator method, the Jahn-Teller distortion of one NiO$_6$ octahedron can not be transferred over the whole enlarged $2 \times 1 \times 2$ supercell with $\vec{k} = (1/2, 0, 1/2)$. Therefore, the Jahn-Teller distortion actually cannot appear in the observed spin ordered state.

NdNiO$_3$: There are two possible spin configurations
in NdNiO$_3$ satisfying the observed transfer vectors $\vec{k} = (1/2, 0, 1/2)$. One is that the spin magnetic moments align ferromagnetically on the (101) plane and the planes are stacked with a doubled period as $\uparrow\uparrow\downarrow|\uparrow\downarrow\downarrow| \cdots$, whose magnetic space group is monoclinic $Pb\alpha$.\[11\] This spin configuration is assumed in the present letter. Another possible spin configuration with $\uparrow\downarrow\downarrow\downarrow$ spin order could be the doubled period checkerboard stacking along crystallographic $y$-axis, and the magnetic space group is orthorhombic $Cc\alpha mc2_1$.\[11\] The state of $Cc\alpha mc2_1$ shows orbital ordering of $e_g$ states on Ni sites, but the resultant calculated total energy is higher by 0.18 eV per $2 \times 1 \times 2$ cell than that of $Pb\alpha$. Because there is no possibility of subsidiary Jahn-Teller distortion to lower the total energy, $Cc\alpha mc2_1$ could not be the symmetry to be considered. The total energy is also calculated in a fictitious antiferromagnetic state of $Pb'nnm'$ whose magnetic unit cell is identical to the crystallographic one and is higher by 2.0 eV per $1 \times 1 \times 1$ cell.

FIG. 1. Projected density of states of trivalent nickel Ni$^{3+}$ in NdNiO$_3$. The energy zeroth is set at the top of the occupied states $E_F$. The local $z$ axis directs from Ni to one of oxygen atoms with the shortest Ni-O distance, and the local $x$ and $y$ axes to the appropriate O atoms.

Figure 1 shows the projected density of states on the Ni 3d orbitals in NdNiO$_3$. The system is insulator with a gap $E_g = 0.11$ eV. Each nickel ion has the local magnetic moment $\pm 1.1 \mu_B$ within the atomic sphere of a radius 2.51 au, contrary to the observed value of $\pm 0.9 \mu_B$.\[8\] It should be noticed that the local magnetic moment cannot be uniquely defined. Furthermore, NdNiO$_3$ is not a simple antiferromagnetic insulator but a dynamical effect is essential, which may be an origin of this discrepancy.\[2\] There is no distinctive variation in partial spin density of states of Ni site in each magnetic sublattice. An $e_g$ band lies on the energy range $E_F - 0.6$ eV $\sim E_F + 1.2$ eV. The numbers of states in the energy range $E_F - 0.6$ eV $\sim E_F$ and $E_F + 0.1$ eV $\sim E_F + 1.2$ eV are 16, respectively, which are the one occupied and one vacant $e_g$ states per Ni ion. Actually, these $e_g$ orbitals extend over surrounding oxygen sites from Ni ions due to strong hybridization between Ni $e_g$ and O $p$ orbitals. The extended occupied $e_g$ orbital has a 60% weight on $p$ orbitals on surrounding six oxygens, a 10% weight on an individual oxygen. Therefore, one would establish a model where one occupied $e_g$ state with majority spin locates at the top of the valence bands, and it hybridizes strongly with the $p$ states on nearby O ions. This is the molecular orbital $\sigma^*$ state.\[13\] Then one can assign all nickel ions in NdNiO$_3$ to be trivalent Ni$^{3+}$ ($t_{2g}^6e_g^1$), even though the Ni ion is not truly ionized by +3 charge. In the projected density of states of Ni site, one observes a large amount of $e_g$ states at the bottom of the $d$ bands, which are the bonding states between Ni $d$ and O $p$, corresponding to the $\sigma$ states in the molecular orbital picture.\[15\]

FIG. 2. Isometric surface of the spin density $\rho_+ - \rho_-$ $= \pm 0.01$ states/(atomic unit)$^3$ in the energy range $E_F - 0.6$ eV $\sim E_F$ in a thin slab parallel to (001) plane. Yellow and blue surfaces indicate the plus and minus spin densities, respectively. Black solid lines stand for Ni-O bonds and red lines unit cell.

The $e_g$ band in the range $E_F - 0.6$ eV $\sim E_F$ does not show any orbital ordering. In fact, off-diagonal elements within the $e_g$ subblock of the occupation matrix $\{n_{m'm}\}$ are zero and the diagonal elements are identical. The absence of the orbital ordering may be consistent with the fact that the [101] axis has three-fold rotational symmetry in the present spin configuration, once the distortion is neglected. Due to this pseudo three-fold rotational symmetry, the basis orbitals of $E_g$ representation of the trigonal group $D_3d$ is a good basis set and those derived from $e_g$ orbitals are $\varphi_{+z} = \frac{1}{\sqrt{2}}(\varphi_{3z^2-r^2} + i\varphi_{x^2+y^2})$ and $\varphi_{-z} = \frac{1}{\sqrt{2}}(\varphi_{3z^2-r^2} - i\varphi_{x^2+y^2})$. Therefore, there is no difference between the occupancies of $\varphi_{3z^2-r^2}$ and $\varphi_{x^2+y^2}$.

Figures 2 is the spatial profiles of spin densities $\rho_+ - \rho_-$ in the energy range $E_F - 0.6$ eV $\sim E_F$ ($\sigma^*$ state). Only one spin component of O $p$ orbitals on the FM bond is bridging between two Ni $e_g$ orbitals, while both spin components on the AFM bond couple with Ni $e_g$ orbitals of respective spins. Consequently, oxygen ions on the AFM bond have more charge in this energy range than oxygen on the FM bond. This is the realization of oxygen-site charge-ordered state discussed by Mizokawa et al. in the framework of the Hartree-Fock calculation.\[12\] However, the charge difference between oxygen sites of Ni$^{3+}$-O-Ni$^{3+}$ and Ni$^{3+}$-O-Ni$^{3+}$ in $\sigma^*$ states is mostly compensated by hybridized $\sigma$ state at lower energies. Besides, all oxygen ions have no local magnetic moment.

More significant results seen in Fig. 2 may be the $p$ orbital ordering on oxygen sites. The magnetic space group is $Pb\alpha$ and its unitary part is $Pa$. The unit cell and lattice primitive vectors are not identical to those in $Pbmnm$. The spin density in Fig. 2 is consistent with this magnetic group $Pb\alpha$, neither higher nor lower than this. The symmetry lowering of the unitary part $Pa$ is the origin of the opening the band gap at $E_F$ in the majority spin band, despite to the absence of the orbital ordering on Ni sites (i.e. symmetry driven band gap). Therefore, one can conclude that the origin of the insulator phase at low temperatures in NdNiO$_3$ is the characteristic spin density on the oxygen sites or, equivalently, the orbital ordering there. The energy gap $E_g = 0.11$ eV is due to the symmetry of charge order. In fictitious ideal cubic structure without distortion or tilting of NiO$_6$ octahedra, the system becomes metal whose valence and conduction
bands touch at points with each other. The structure of \( \sigma^* \) bands is insensitive to the value of \( U \). The value of the band gap is unchanged down to \( U = 4 \) eV. This is because the gap is driven by the symmetry.

**YNiO\(_3\):** One should expect larger distortion in YNiO\(_3\) because YNiO\(_3\) is the typical system with the small tolerance factor. There are two different crystallographic Ni sites, and the distances from each Ni ion to surrounding O ion are different by 3–4\% from one type of Ni ion to the other type. Calculated self-consistent solution is that with the apparent charge disproportionation and no orbital polarization. Since Ni\(^{4+}\) site has no spin magnetic moment, the two spin configurations discussed in NdNiO\(_3\) become identical and the spin configuration of YNiO\(_3\) is uniquely determined. The magnetic space group is \( \text{P} \text{2}_1 \text{2}_1 \text{a} \) if the spins of Ni\(^{4+}\) ions are non vanishing and, on the contrary, \( \text{P} \text{2}_1 \text{2}_1 / a \) if the spins of Ni\(^{4+}\) ions are zero. The latter symmetry \( \text{P} \text{2}_1 \text{2}_1 / a \) is actually the case.

Figure 3 shows the projected density of states at Ni ion sites. The system is insulator with a gap \( E_g = 1.03 \text{ eV} \). The resultant magnetic moments for half of Ni ions are \( \pm 1.5 \mu_B \) within the atomic sphere of a radius 2.52 au, namely divalent ions Ni\(^{2+}\) \((t_{2g}^6 e_{g}^2)\), of larger NiO\(_6\) octahedron and zero for another half of Ni ions within the atomic sphere of a radius 2.51 au, namely quadrivalent Ni\(^{4+}\) \((t_{2g}^5 e_{g})\), of smaller octahedron. The experimentally observed magnetic moments are \( \pm 1.4 \mu_B \) for Ni\(^{2+}\) ions and \( \pm 0.7 \mu_B \) for Ni\(^{4+}\) ions. The discrepancy may be due to a possible non-collinear spin order. The number of states in the energy range \( E_F - 0.47 \text{ eV} \sim E_F \) eV is 16 and dominant weight on Ni\(^{2+}\). Because the number of Ni\(^{2+}\) in the \( 2 \times 1 \times 2 \) cell is 8, these states are assigned as two \( e_g \) states mainly on Ni\(^{2+}\) and surrounding oxygens. The \( e_g \) orbitals of Ni\(^{4+}\) is lifted in the higher energy range \( (> E_F + 1 \text{ eV}) \) without spin polarization.

A large amount of \( e_g \) orbitals in Ni\(^{2+}\) ions locates at the bottom of the d bands , in the range \( E_F - 6.7 \text{ eV} \sim E_F - 5.8 \text{ eV} \) for Ni\(^{2+}\), and in the range \( E_F - 5 \text{ eV} \sim E_F - 4 \text{ eV} \) for Ni\(^{4+}\), stabilizes the bonding between Ni\(^{4+}\) ions and oxygen ions. From these facts, one can establish a model that deep \( \sigma \) molecular orbitals (one per both Ni\(^{2+}\) and Ni\(^{4+}\)) stabilize the system, and other two \( e_g \) states \((\sigma^* \text{ states})\) per one Ni\(^{2+}\) ion located at \( E_F - 0.47 \text{ eV} \sim E_F \).

**FIG. 3.** Projected density of states of (a) divalent Ni\(^{2+}\) and (b) quadrivalent Ni\(^{4+}\) in YNiO\(_3\). The energy zeroth is set at the top of the occupied states \( E_F \). The local coordinate axes are chosen in the same manner for those in Fig. 1.

The charge disproportionation is mainly due to the crystal field effect. The low spin state in Ni\(^{4+}\) or Ni\(^{3+}\) ion is energetically unstable in small \( Dq \) case and the ground state multiplet of Ni\(^{2+}\) is \( 3\Delta_2 \) \((t_{2g}^6 e_{g}^2)\) for all arbitrary values of \( Dq \). Therefore, the small tolerance factor causes two different Ni sites, compressed Ni\(^{4+}\) (large \( Dq \)) and dilated Ni\(^{2+}\) (small \( Dq \)), rather than uniformly dilated Ni\(^{3+}\) ionic states. The standard values of \( Dq / B \) (\( B \) is the Racah parameter) for Ni\(^{2+}\) is presumably around 1.0. Once one estimate the crystal field effects from the Ni-O bond lengths \( d_{\text{Ni-O}} \), the difference of 10\( Dq \) on two Ni ion sites is presumably about 20\%.

Two narrow \( e_g \) bands can be seen in the energy range \( E_F - 0.47 \text{ eV} \sim E_F - 0.23 \text{ eV} \) and \( E_F - 0.23 \text{ eV} \sim E_F \) in Fig. 3. Two Ni\(^{2+}\) \( e_g \) states are spatially extending over wide area and not only hybridizing with the nearest neighbor O ions but also extending over the nearest Ni\(^{4+}\) ions. This situation is well depicted in the spin density. Figure 4 shows the isometric surfaces of the spin density in the range of \( E_F - 0.47 \text{ eV} \sim E_F - 0.23 \text{ eV} \). The d-wavefunctions on Ni\(^{2+}\) are extending over the (101) plane, and antiferromagnetically coupled with other Ni\(^{2+}\) ions. Charge in each Ni ion is compensated in YNiO\(_3\) as in NdNiO\(_3\) and the difference between total charges in the muffin tin spheres on Ni\(^{2+}\) and Ni\(^{4+}\) sites is very small, equals to 0.03. This variation is the same order as that of oxygen ions in NdNiO\(_3\). However, charge disproportionation is coupled with the lattice distortion, where larger oxygen octahedron is surrounding Ni\(^{2+}\), and stabilizes the lattice system in YNiO\(_3\). Therefore, diffraction experiment can detect the charge ordering in the yttrium system easier than in the neodymium system.

**FIG. 4.** Isometric surface of spin density \( \rho_F - \rho_\uparrow \) = \( \pm 0.002 \text{ states}/(\text{atomic unit})^3 \) in the energy range of an \( e_g \) band \((E_F - 0.47 \text{ eV} \sim E_F - 0.23 \text{ eV})\) in a thin slab parallel to (101) plane. Yellow surface means the sign of the spin density is plus, blue one means minus.

In conclusion, we have studied two typical antiferromagnetic insulating phase of RNiO\(_3\), NdNiO\(_3\) and YNiO\(_3\), by using the LSDA+U method. A possibility of the Jahn-Teller distortion is excluded by the group theoretical consideration. No orbital order on Ni sites is observed in both systems, but two different types of ordering are observed. In small distorting RNIo\(_3\) such as NdNiO\(_3\), oxygen sites shows the orbital ordering and this is the origin of the gap opening in NdNiO\(_3\). In large distorting RNIo\(_3\) such as YNiO\(_3\), the charge disproportionation \( 2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+} \) occurs. The charge ordering mechanism can explain the stabilization of the asymmetric alignment of the local magnetic moments around each nickel site in both systems.

We may add the final comment about effects of electron-electron correlation in RNIo\(_3\). The widths of the calculated \( e_g \) bands \( D \) by the LDA are 2.82 eV(YNiO\(_3\)), 2.87 eV(NdNiO\(_3\)), and 3.18 eV(LaNiO\(_3\)). Then, the ratio of \( U / D \) may be estimated as \( 1 : 0.98 : 0.89 \), assuming the value of the Coulomb repulsion \( U \) is common for all, and one can see a large reduction of \( U / D \) in LaNiO\(_3\), which may be the key parameter for the difference of
the ground states of these perovskite nickelates. NdNiO$_3$ shows the anomalous M-I transition. LaNiO$_3$ is presumably an anomalous metal of strongly correlated electrons and could not be treated within the framework of the LSDA+U method.

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