Charge and Spin Order in RNiO₃ (R=Nd, Y) by LSDA+U Method

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Electronic structures of NdNiO₃ and YNiO₃ are calculated by using the LSDA+U method with rotational invariance. No orbital order on Ni sites is observed in the calculations for the two systems. Different types of charge ordering are found in the two systems. In a small distorted system NdNiO₃, all nickel ions are trivalent, while oxygen sites show charge ordering and spin density polarization in the energy range of Ni e_{g} \sigma^{*} band. In a large distorted system YNiO₃, charge disproportionation occurs. Therefore, the charge ordering stabilizes the asymmetry of the arrangement of Ni magnetic moments in both systems.

KEYWORDS: perovskite nickelates, charge order, spin order, LSDA+U

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Perovskite transition metal oxides are currently of high interest because of the large variety and the possible controllability of their physical properties. Perovskite nickelates RNiO₃ (R = a trivalent rare earth or Y ion) can be classified into three different categories, according to their tolerance factor (t = d_{R−O}/2d_{Ni−O}). One category is for compounds whose tolerance factor is very small (t < 0.91) and that have a large distortion, such as LaNiO₃ or YNiO₃. They are antiferromagnetic insulators at low temperatures. This class of RNiO₃ undergoes transition to a paramagnetic insulator at the Neel temperature T_N. Contrary to the asymmetric arrangement of magnetic bonds (FM/AFM) around each nickel site, Ni−O distances around each Ni ion are almost equal. For instance, the difference between the longest and the shortest Ni−O bonds in one NiO₆ octahedron is at most 2% in RNiO₃. The Jahn–Teller distortion of ab initio LSDA calculations is absent in RNiO₃, even in the large distorted system YNiO₃, whose tolerance factor is 0.88. Experimentally, there is only one crystallographic space group for Ni ions in NdNiO₃ and YNiO₃. There are two possible spin configurations in NdNiO₃ satisfying the observed vector \( k = (1/2, 0, 1/2) \). One is that the spin magnetic moments align ferromagnetically on the (10I) plane and the planes are stacked with a doubled period as \( \uparrow \downarrow \downarrow \uparrow \downarrow \downarrow \cdots \cdots \). These are antiferromagnetic insulators at low temperatures and above T_N they are paramagnetic metals. Third is LaNiO₃ where t = 0.94; it is a paramagnetic metal.

The low-temperature phase of above-mentioned first and second classes of RNiO₃ exhibits unique magnetic structures. Its magnetic diffraction peak is characterized by the propagation vector \( k = (1/2, 0, 1/2) \) 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 antiferromagnetic (AFM) couplings \( \ldots \text{Ni}^{3+}−\text{O}−\text{Ni}^{2+} \rightarrow \ldots \) along three crystallographic directions.

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The state of \( C_{6}'mc \) shows orbital ordering of \( e_g \) states on Ni sites, but the resultant total energy in the present calculation is higher by 0.18 eV per \( 2 \times 1 \times 2 \) cell than that of \( P_{b2a} \). Because there is no possibility of subsidiary Jahn–Teller distortion to lower the total energy, \( C_{6}'mc \) may not be the symmetry to be considered. The total energy is also calculated in a fictitious antiferromagnetic state of \( Pbmn' \) whose magnetic unit cell is identical to the crystallographic one and is higher by 2.0 eV per \( 1 \times 1 \times 1 \) cell.

Figure 1 shows the projected density of states on the Ni 3d orbitals in NdNiO\(_3\). The system is an 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 Å, in contrast to the observed value of \( \pm 0.9 \mu_B \).\(^{31}\) It should be noted 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 the reason for this discrepancy.\(^{50}\)

There is no distinctive variation in partial spin density of states of Ni site in each magnetic sublattice. An \( e_g \) band lies in the energy range \( E_F - 0.6 \) eV ~ \( E_F + 1.2 \) eV. The states with the energy range \( E_F - 0.6 \) eV ~ \( E_F \) consist of occupied \( e_g \) states, one state per Ni ion and totally 16, and those in the energy range \( E_F + 0.1 \) eV ~ \( E_F + 1.2 \) eV consist of vacant \( e_g \) states, one state per Ni ion and totally 16. In fact, 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 60% weight on O p orbitals of the surrounding six oxygens, and 10% weight on one 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.\(^{32}\) Then one can assign all nickel ions in NdNiO\(_3\) to be trivalent Ni\(^{3+}\) (\( t^2 \_{2g} \) \( e^1 \)), even though the Ni ion is not truly ionized by +3 charge. In the projected density of states of the Ni ion site, one observes a large number 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.\(^{12}\)

The \( e_g \) band in the range \( E_F - 0.6 \) eV ~ \( E_F \) does not show any orbital ordering. In fact, off-diagonal elements within the \( e_g \) subblock of the occupation matrix \([n_{\text{occ}}]\) are zero and the diagonal elements are identical. The [111] axis of the perovskite cubic lattice would be perpendicular to the (101) plane of the present lattice (\( P_{b2a} \) structure). This [111] axis of the cubic lattice corresponds to the [011] axis of the present lattice. The absence of the orbital ordering is due to the fact that the [011] axis of the present lattice has threefold rotational symmetry in the ideal cubic lattice.\(^{13} \) Due to this pseudo threefold rotational symmetry, the basis orbitals of \( E_g \) representation of the trigonal group \( D_2h \) is a good basis set and those derived from \( e_g \) orbitals are \( \phi_{a+} = -\frac{1}{\sqrt{3}} (\phi_{3z^2-r^2} + i\phi_{2z^2-r^2}) \) and \( \phi_{a-} = \frac{1}{\sqrt{2}} (\phi_{3z^2-r^2} - i\phi_{2z^2-r^2}) \). Therefore, there is no difference between the occupancies of \( \phi_{3z^2-r^2} \) and \( \phi_{2z^2-r^2} \).

Figure 2 is the spatial profile of spin densities \( \rho_1 - \rho_1 \) in the energy range \( E_F - 0.6 \) eV ~ \( E_F \) (\( \sigma^* \) state). Only one spin component of O p orbitals on the FM bond bridges the 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 the oxygen-site charge-ordered state which was discussed by Mizokawa et al. in the framework of the Hartree–Fock calculation.\(^{14}\) 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 low energies. Moreover, no oxygen ion has local magnetic moment.

The magnetic space group is \( P_{b2a} \) and its unitary part is \( Pa \). The unit cell and lattice primitive vectors are not identical to those in the crystallographic space group \( Pbnm \). The former has orthorhombic symmetry while the latter has monoclinic symmetry. One glide reflection in \( Pbnm \) transfers the atomic site \( A_1 \) to \( A_2 \) in Fig. 2. However this operation or that accompanied by the time-reversal operator is not an element in the magnetic space group \( P_{b2a} \). Therefore, the spin-density polarizations around \( A_1 \) and \( A_2 \) are inequivalent. The symmetry lowering of the unitary part \( Pa \), associated with \( U \), is the origin of the opening of the band gap at \( E_F \) in the
majority spin band, despite the absence of the orbital ordering on Ni sites (i.e., symmetry driven band gap). Therefore, one can conclude that the origin of the insulating phase at low temperatures in NdNiO$_3$ is the characteristic spin density on the oxygen sites. In fictitious ideal cubic structure without distortion or tilting of NiO$_6$ octahedra, the system becomes metal wherein valence and conduction bands touch at a few isolated k-points with each other. The choice of the value of $U$ does not affect the structure of the $\sigma^+$ bands. The value of the band gap is unchanged down to $U = 4 \text{eV}$. This is because the gap is driven by symmetry under the finite $U$.

YNiO$_3$: One should expect large 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 another. The calculated self-consistent solution is that with the apparent occupied states. The number of states in the energy bands can be seen in the energy ranges $E_F - 0.47 \text{eV} \sim E_F - 0.23 \text{eV}$ and $E_F - 0.23 \text{eV} \sim E_F$. Two narrow $e_g$ bands can be seen in the energy ranges $E_F - 0.47 \text{eV} \sim E_F - 0.23 \text{eV}$ and $E_F - 0.23 \text{eV} \sim E_F$. 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 the small $Dq$ case and the ground state multiplet of Ni$^{3+}$ is $3A_2$ ($t_{2g}^2e_g^2$) for all arbitrary values of $Dq$. Therefore, the small tolerance factor causes two different Ni sites, compressed Ni$^{3+}$ (large $Dq$) and dilated Ni$^{3+}$ (small $Dq$), rather than uniformly dilated Ni$^{3+}$ ionic states. The standard value of $Dq/B$ (B is the Racah parameter) for Ni$^{3+}$ is presumably around 1.0. Once one estimates the crystal field effects from the Ni–O bond lengths $d_{Ni-O}$, the difference of $10Dq$ on two Ni ion sites is presumably about 20%.

Two narrow $e_g$ bands can be seen in the energy range $E_F - 0.47 \text{eV} \sim E_F - 0.23 \text{eV}$. The 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 large oxygen octahedron is surrounding Ni\(^{2+}\), and stabilizes the lattice system in YNiO\(_3\). Therefore, a diffraction experiment can detect the charge ordering in the yttrium system easier than in the neodymium system.

In conclusion, we have studied two typical antiferromagnetic insulating phases of RNiO\(_3\), NdNiO\(_3\) and YNiO\(_3\), by using the LSDA+U method. The possibility of the Jahn–Teller distortion is excluded by the group theoretical consideration in ref. 10. No orbital order on Ni sites is observed in either of the two systems, but two different types of ordering are observed. In small-distortion RNiO\(_3\) such as NdNiO\(_3\), oxygen sites show the charge ordering and spin density polarization, and this is the origin of the gap opening in NdNiO\(_3\). In large-distortion RNiO\(_3\) such as YNiO\(_3\), 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 add a final comment on the 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\(_3\)). Therefore, the ratio of \(U/D\) can be estimated to be 1:0.98:0.89, assuming the value of the Coulomb repulsion \(U\) is common for all. 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, \(^{65}\) LaNiO\(_3\) is presumably an anomalous metal of strongly correlated electrons\(^{17}\) and could not be treated within the framework of the LSDA+U method.

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13) The unit cell of the crystallographic \(Pbnm\) structure can be obtained from the simple cubic perovskite structure as follows; (i) rotate by \(\frac{\pi}{2}\) around the [001] axis, (ii) make the \(\sqrt{2} \times \sqrt{2} \times 2\) supercell with the distortions. The [110] axis of the cubic lattice is parallel to the \(a\)–axis of the \(Pbnm\) structure. The unit cell of the \(Pbnm\) structure corresponds to the \(2\sqrt{2} \times \sqrt{2} \times 2\) supercell of the cubic cell, as in Fig. 2.
16) The value of 10Dq, the parameter of the crystal field, is proportional to \(d_{\text{eff}}\).