Effect of charge doping on the electronic structure, orbital polarization, and structural distortion in nickelate superlattice

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Abstract

Using first-principles density functional theory calculations, we investigated the effect of charge doping in a LaNiO$_3$/SrTiO$_3$ superlattice. The detailed analysis based on two different simulation methods for doping clearly shows that the electronic and structural properties change in a systematic way that the orbital polarization (i.e. relative occupation of two Ni-$e_g$ orbitals) is reduced and the Ni to apical oxygen distance enlarged as the number of doped electrons increases. Also, the rotation angles of the NiO$_6$/TiO$_6$ octahedra strongly and systematically depend on the doping so that the angle $\gamma$ gradually decreases whereas the $\alpha$ and $\beta$ increase as a function of electron doping. Further analysis shows that the electron (hole) doping can play a similar role with the compressive (tensile) strain for the octahedral rotations. Our results not only suggest a possible way to control the orbital and structural property by means of charge doping, but also provide useful information to understand the experiments under various doping situations such as oxygen vacancy.

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I. INTRODUCTION

Recent advances in the atomic-scale growth technique of transition metal oxide (TMO) heterostructures have created considerable research interest [1, 2]. In TMO, multiple degrees of freedom (i.e., charge, spin, orbital, lattice) are coupled to each other, often creating novel material characteristics such as high-temperature superconductivity and colossal magneto resistance [3]. By making artificial heterostructures of TMO, it is possible to control those degrees of freedom and band structures, and therefore create or design new ‘correlated electron’ properties. Previous TMO superlattice studies [4–8] have shown that many unexpected material phenomena can be realized at the TMO heterointerface, such as magnetism and superconductivity [9–13].

Combined with other degrees of freedom in TMO, charge doping can play a significant role in determining material properties. Sometimes extra charges are introduced in an unexpected and uncontrolled way. For example, oxygen vacancy often drives a TMO system to have fairly different material characteristics (e.g., an insulating material to be metallic) [14–16]. Cation inter-mixing can also be important as it introduces a different local ionic potential to the nearby atoms (e.g., inter-mixing of Sr$^{2+}$ and La$^{3+}$). On the other hand, it is also possible to control the amount of extra charges by chemical doping or electric field, for example. Considering all these possibilities, it is important to understand the effect of charge doping in TMO heterostructures. In particular, the relation between rotation of metal-oxygen octahedra and charge doping has never been investigated in a systematic way.

In this paper, we examine the effect of doping on nickelate superlattices which are being actively studied nowadays [17–31]. Taking LaNiO$_3$/SrTiO$_3$ as a prototype example [28–31], we performed first-principles density functional theory (DFT) calculations and examined the electronic structure, orbital polarization, magnetism, and structural distortion as a function of doping. To simulate charge doping, two different approaches were adapted, namely, the rigid band shift method and the supercell calculation with a couple of Sr$^{2+}$/La$^{3+}$ ratios. The systematic changes are found in these physical properties: As the number of extra electrons increases, the orbital polarization (i.e., the relative occupation of $d_{x^2−y^2}$ to $d_{3z^2−r^2}$) is reduced, and the Ni to apical oxygen distance enhanced. The octahedra rotation angles also exhibit a systematic dependence on charge doping. Our results suggest a possibility to control the structural property as well as the electronic structure by doping, and provides useful
information to understand the experiments under the various types of doping situations.

After presenting computation details in Sec. II, we discuss the doping effect with no oxygen octahedral rotation in Sec. III. In Sec. IV, the possible NiO$_6$ and TiO$_6$ cage rotations are taken into account. After discussing further issues in Sec. V, a summary is given in Sec. VI. In the appendix, we briefly discuss the electronic structure changes as a function of doping, which provides an electronic origin of the systematic changes found in the other physical quantities.

II. COMPUTATION DETAILS

For the band structure calculations, we used DFT within local spin density approximation (LSDA) \cite{32} and the projector-augmented wave (PAW) method \cite{33} as implemented in the Vienna \textit{ab initio} simulation package \cite{34}. We adopted a plane-wave energy cutoff of 400 eV with a 5 $\times$ 7 $\times$ 7 \textit{k}-point sampling on the Monkhorst-Pack grid. To incorporate the effect of correlations, the so-called simplified version of rotationally invariant LSDA+$U$ as suggested by Dudarev \textit{et al.} \cite{35} was used with the effective $U \equiv U - J$ varying from 0 to 5 eV while we mainly present the $U=3$ eV results considering the literature values\cite{21, 22, 27}. Structural optimization was performed with a force criterion of 1 meV/Å. During this process, a ferromagnetic order, suggested to be the ground state in recent DFT calculations\cite{21, 22, 27}, was set as the initial magnetic configuration. However, we also note the unresolved issue regarding the spin ground state predicted by DFT-based methods \cite{21, 25, 27}.

Fig. 1 shows the unit cell structure of the (LaNiO$_3$)$_1/(SrTiO_3)_1$ superlattice used in this study. As shown in Fig. 1(a), we chose $\sqrt{2} \times \sqrt{2}$ supercell with La-Sr intersite mixing in which tetragonal symmetry is preserved. For the in-plane and out-of-plane lattice constant, we used the fixed value of 3.905 $\times$ $\sqrt{2}$ and 7.732 Å. These values correspond to the lattice constant of bulk SrTiO$_3$ and the sum of bulk lattice constant of SrTiO$_3$ and LaNiO$_3$, respectively. To investigate the influence of excess electron/hole doping we mainly used the rigid band shift method, in which the dopped charges are compensated with the uniform background with the opposite sign. Five different charge dopings have been considered: $\pm 0.50$, $\pm 0.25$, 0.00 electrons per Ni atom (hereafter denoted as $\pm 0.50e$/Ni-, $\pm 0.25e$/Ni-, 0.00e/Ni-cell, respectively). A different type of doping is also considered by changing the Sr/La ratio. Since our unit cells contain four $A$-site cations, $\pm 0.5e$ of chemical doping can be simulated with
the case of \((\text{La}_{0.5}\text{NiO}_3)_{1}/(\text{Sr}_{1.5}\text{TiO}_3)_{1}\), and \((\text{La}_{1.5}\text{NiO}_3)_{1}/(\text{Sr}_{0.5}\text{TiO}_3)_{1}\) as shown in Fig. 1(c) and (d) respectively. These two will be denoted as \(\text{LaSr}_3\)- and \(\text{La}_3\text{Sr}\)-cell, respectively, hereafter. Note that, \(\text{LaSr}_3\)- and \(\text{La}_3\text{Sr}\)-cell calculations correspond to the \(-0.50\epsilon/\text{Ni}\) and \(+0.50\epsilon/\text{Ni}\)-cell, respectively, in terms of electron doping.

The orbital polarization, representing the relative occupations in the two Ni-\(e_g\) orbitals, can be defined as \[P_{e_g} = \frac{n_{d_{x^2-y^2}} - n_{d_{3z^2-r^2}}}{n_{d_{x^2-y^2}} + n_{d_{3z^2-r^2}}},\] (1)

\[n_i = \int_{\epsilon_b}^{\epsilon_F} f_i(\epsilon)d\epsilon,\] (2)

where we choose \(\epsilon_b = -3.5\) eV (with the Fermi energy \(\epsilon_F = 0\)) to capture the occupations on the valence \(d\)-orbital complexes. We found that our conclusions were unchanged even when we used the values of \(\epsilon_b\) down to \(-10\) eV.

III. RESULTS WITHOUT OCTAHEDRAL ROTATION

In this section, we present the calculation results that are obtained from the structures with no rotational distortion. In these calculations, due to the high symmetry of the initial geometry, the undistorted structures are maintained after the relaxation process. The results are meaningful to understand the system in further details and can be relevant to the experimental situation in which the rotational distortion modes are suppressed for some reason, such as substrate strain, although a recent study of LNO/STO indicates the possible rotations \[30\].

A. Structural changes

Fig. 2 (a)-(e) summarizes the structural change induced by doping. The main features are as follows: (i) The distance between Ni and apical oxygen \((d_{\text{Ni}-\text{O}_{\text{ap}}})\) increases as the number of doped electrons increases. As clearly shown in Fig. 2(e), this increasing trend is evident for both \(U = 0\) and \(3\) eV. It is also noted that both the \(\text{LaSr}_3/\text{La}_3\text{Sr}\)-cell and rigid band shift calculations predict the consistent results regarding this increasing trend. In the case of \(\text{LaSr}_3/\text{La}_3\text{Sr}\)-cell calculations, due to the lowered symmetry along the out-of-plane direction, two inequivalent \(d_{\text{Ni}-\text{O}_{\text{ap}}}\) distances are obtained, corresponding to two
The calculated values of $d_{\text{Ni-O} \text{ap}}$ by LaSr$_3$-/La$_3$Sr-cell deviate from the corresponding values of the rigid band shift by $\sim 0.01$–$0.04$ Å (compare the filled and open symbols at $\pm 0.5e$), which reflects the intrinsic difference between the two computation methods. (ii) As schematically shown in Fig. 2(a), La and Sr cations move toward the NiO$_2$ plane as more electrons are introduced. From the electrostatic point of view, the excess electrons mainly doped into Ni-$e_g$ orbitals create an attractive force for La$^{3+}$ and Sr$^{2+}$, which can be responsible for these movements. (iii) In LaSr$_3$-/La$_3$Sr-cell calculations, the lowered lattice symmetry allows the oxygen atoms in the NiO$_2$ plane to deviate from their original positions. The in-plane and out-of-plane oxygen displacements are illustrated in Fig. 2(c) and (d), respectively, and these displacements are $\sim 0.05$–$0.09$ Å.

The additional ionic movement caused by $U$ is found to be a few percent. That is, $d_{\text{Ni-O} \text{ap}}$ is slightly enhanced further by $U$. As shown in the inset of Fig. 2(e), $d_{\text{Ni-O} \text{ap}}$ in the case of $+0.50e$/Ni can be increased up to $\sim 2\%$. It is interesting to note that, at a fixed doping level of $+0.5e$/Ni, $d_{\text{Ni-O} \text{ap}}$ gradually increases as $U$ increases (with some deviation at 5 eV). This feature is presumably attributed to the $U$-dependence of $d_{3z^2-r^2}$-orbital occupations which will be discussed further in the following subsection.

**B. Electronic structure, orbital polarization, and magnetism**

First we note that the doped charges reside mostly in the Ni-$e_g$ bands and the empty Ti-$t_{2g}$ is located well above $\sim 2$ eV. In case of La$_3$Sr-/LaSr$_3$-cell calculations, it is found that a small fraction of Ti-$t_{2g}$ bands touches the Fermi level at $U=0$ and is pushed far away by $U_{\text{Ni}}$. From the shape of Ni-$e_g$ projected density of states (PDOS), schematically shown in Fig. 3(a), it is expected that a major portion of the doped charges will go into $d_{3z^2-r^2}$ orbitals and the orbital polarization changes accordingly (for the full details of the PDOS, see Fig. 6 in Appendix). As clearly seen in Fig. 3(b), the orbital polarization gradually decreases as the number of doped electron increases for both $U = 0$ and 3 eV. This feature is also confirmed by the La$_3$Sr-/LaSr$_3$-cell calculations (open symbols in Fig. 3(b)) and can be understood well from the PDOS features in Fig. 3(a). Notably, the calculated orbital polarization is similar for both cases despite the differences in the two computation methods. The PDOS calculated by the two computation methods are found to be quite similar as
shown in Appendix (Fig. 6).

This behavior of orbital polarization can be consistent with the result of $d_{\text{Ni-O}_{\text{ap}}}$ in the sense that the more occupations in $d_{3z^2-r^2}$ (i.e., the smaller $P_{e_g}$) corresponds to the longer $d_{\text{Ni-O}_{\text{ap}}}$ from the point of view of Coulomb repulsion between the apical oxygen $p_z$ and Ni-$d_{3z^2-r^2}$ electrons. Note that the lattice degree of freedom couples to the orbital occupancy and polarization so that by electron (hole) doping, $d_{\text{Ni-O}_{\text{ap}}}$ increases (decreases) and $P_{e_g}$ is enhanced (reduced). Another intriguing feature is the behavior of magnetization of $e_g$-orbitals upon doping shown in Fig. 3(c). While the paramagnetic solution is always stable in $U = 0$ calculations, in the intermediate strength of $2 < U \leq 3$ eV, Ni magnetic moment can be induced either in the electron-doped ($U = 2$ and 3 eV) or in the hole-doped regime ($U = 3$ eV). The schematic shape of PDOS suggests, in this range of $U$, that the Stoner mechanism may be responsible for the magnetism as the PDOS peaks of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ state get closer to the Fermi level. Note that, at higher $U=5$ eV such doping-dependent behavior disappears and the magnetization is gradually enhanced with more doped electrons.

IV. RESULTS WITH OCTAHEDRAL ROTATION

In this section, the rotational degree of freedom is taken into account. In combination with it, the doping effect on the structural, electronic, orbital, and magnetic properties is examined. As the starting configurations for the structural optimization, we adopted four different unit cells having ($a^0a^0c^-$)-, ($a^-a^-c^0$)-, and ($a^-a^-c^\pm$)-type rotations (following Glazer notation as defined in Ref. 22, 36, and 37, where the positive and negative signs mean the ferro- and antiferro-distortive rotation, respectively) and performed the relaxation calculations with the symmetry enforced. The structures obtained by this process are further optimized with the symmetry constraint turned off. Without the constraint, the oxygen cage shape can deviate from the ideal one. Therefore, we present the averaged values of the bond lengths and the rotation angles. Also, owing to the removal of the structural constraints, the Jahn-Teller- or breathing-type distortion of NiO$_6$ octahedra is obtained in some cases.
A. Structural changes

The rotation pattern of NiO$_6$ and TiO$_6$ octahedra also exhibits a systematic dependence on charge doping. Fig. 4(a) shows the evolution of NiO$_6$ rotation angles as a function of doping ($U = 0$ eV). In the case of uniform background doping (filled symbols), the antiferro-
distortive angle $\gamma$ (see the inset of Fig. 4(b)) is gradually reduced from $-6^\circ$ to $-2^\circ$ as the electron doping level increases while the angle $\alpha$ and $\beta$ are enhanced from $-2^\circ$ to $-4^\circ$. A similar feature is found in the LaSr$_3$/La$_3$Sr-cell calculation (open symbols) although the tendency is less clear because we have only two points. In the hole-doped region (from $-0.50e$ to $0.00e$), $\alpha$ and $\beta$ are basically unchanged while $\gamma$ exhibits the same decreasing feature as in the electron-doped region (from $0.00e$ to $0.50e$).

To understand this rotation pattern we performed the analysis on the distance between Ni and in-plane oxygen ($d_{\text{Ni}-\text{O}_{\text{in}}}$) relative to $d_{\text{Ni}-\text{O}_{\text{ap}}}$. As summarized in Fig. 5(a) it was found that the $d_{\text{Ni}-\text{O}_{\text{ap}}}/d_{\text{Ni}-\text{O}_{\text{in}}}$ ratio gradually increases as the electron doping level increases. In the sense that the larger $d_{\text{Ni}-\text{O}_{\text{ap}}}/d_{\text{Ni}-\text{O}_{\text{in}}}$ ratio corresponds to a more compressively strained situation, the electron (hole) doping plays a similar role with the compressive (tensile) strain. Therefore, the rotation pattern can be understood as an adaptation of the NiO$_6$ and TiO$_6$ octahedra in response to this effective strain that comes in due to the change of the $\langle d_{\text{Ni}-\text{O}_{\text{ap}}} \rangle/\langle d_{\text{Ni}-\text{O}_{\text{in}}} \rangle$-ratio under the fixed lattice constants, which is consistent with previous studies of $d^0$-perovskite systems under real strain[37]. Our results suggest that, due to the strong charge-orbital-lattice coupling, not only epitaxial strain but also doping can be used to control the octahedral rotation pattern in perovskite superlattices or thin films.

While the systematic trend of rotation is maintained in the finite $U$ calculations, the rotation angles are significantly enhanced as clearly seen in Fig. 4(b). Also, further structural changes are introduced. In the undoped case, the Jahn-Teller type distortion of NiO$_6$ is stabilized (Fig. 4(c)). The long ($a_l$) and short ($a_s$) Ni-O bond lengths are presented in Table 4. At the doping level between 0.0 and $+0.25e$/Ni, the structural transition from ($a^0a^0c^-$)- to ($a^-a^-c^+$)-phase and the breathing-type distortion is found to occur (Fig. 4(d)) so that the two Ni sites become inequivalent. The Ni-O bond lengths for these two different Ni-sites (denoted as Ni(1) and Ni(2)) are presented in Table 4. Simultaneously with the charge disproportionation, the $\langle d_{\text{Ni}-\text{O}_{\text{ap}}} \rangle/\langle d_{\text{Ni}-\text{O}_{\text{in}}} \rangle$-ratio is significantly enhanced for Ni(2) (see Fig. 5(a)). Owing to the large $d_{\text{Ni}-\text{O}_{\text{ap}}}$ for both Ni(1) and Ni(2), the ($a^0a^0c^-$)-type
rotational pattern becomes unstable and the tilting pattern of the \((a^-a^-c^+)-(a^-a^+\cdots\cdots-a^-c^-)\)-type is stabilized in response to the out-of-plane lattice mismatch and the ‘effective’ compressive strain.

**B. Electronic structure, orbital polarization, and magnetism**

The decreasing feature of \(P_{eg}\) discussed in Sec. III (without octahedral rotation) is found to be enhanced by rotational distortion. Fig. 5(b) summarizes our calculation results, where Ni(1) and Ni(2) are distinguished due to the charge disproportionation. \(P_{eg}\) decreases as the number of doped electron increases for both \(U=0\) and 3 eV, indicating that the extra electrons mainly occupy the \(d_{3z^2-r^2}\) orbital, rather than \(d_{x^2-y^2}\). This feature can also be found in PDOS (see Appendix, Fig. 8). While the general decreasing trend of \(P_{eg}\) is found for both Ni(1) and Ni(2), some deviation is also noted at the doping level higher than +0.25e (Fig. 5(b)). The PDOS analysis shows that, as more electrons are introduced, the Ni(2)-\(d_{x^2-y^2}\) occupation is reduced, while the two \(eg\) orbitals of Ni(1) are occupied with equal amounts of electrons (see Appendix, Fig. 8). This feature is also reflected in the \(\langle d_{Ni-O_{ap}}\rangle/\langle d_{Ni-O_{in}}\rangle\)-ratio (Fig. 5(a)), \(P_{eg}\) (Fig. 5(b)), and magnetizations (Fig. 5(c)).

Note that magnetism occurs even in \(U = 0\) eV, possibly due to the \(d_{x^2-y^2}\) bandwidth narrowing (see Appendix, Fig. 8) induced by the octahedral rotation. The spin order is antiferromagnetic at +0.50e. Not surprisingly, the finite \(U\) calculation also predicts the magnetic solution. As reported recently by Boris et al., LaNiO\(_3\)-based superlattices can have a local magnetic moment [17] while the ordering type is still not clearly resolved [21, 25, 27]. Our result seems to support the idea that the moment is related to the enhanced \(d_{3z^2-r^2}\) component at the Fermi level in the electron-doped case combined with the narrowed bandwidth. The fact that doping can induce the local magnetic moment add an interesting aspect to the discussion regarding the metal-insulator and magnetic transition in rare-earth nickelates [8, 38, 45].

**V. DISCUSSION**

The doping simulated by the rigid band shift cannot be same as what happens in real experimental situations such as oxygen vacancy. For example, oxygen vacancy not only introduces effective electron dopings, but also the distortion of local structure by disconnecting
TABLE I. The calculated bond lengths (in Å) between Ni and O in the Jahn-Teller and breathing type distorted structures ($U = 3$ eV). The same notations with Fig. 4 are used for $a_l$, $a_1$, $a_s$, $a_2$, $c$, $c_1$ and $c_2$.

| Structure   | Doping          | $a_l$ and $a_1$ | $a_s$ and $a_2$ | $c$ and $c_1$ | $c_2$ |
|-------------|-----------------|-----------------|-----------------|----------------|-------|
| Jahn-Teller | $\Delta e = 0.00 e$/Ni | 2.007±0.002     | 1.919±0.001     | 1.929±0.001    |       |
| Breathing   | $\Delta e = +0.25 e$/Ni | 1.991±0.009     | 1.951±0.007     | 1.976±0.007    | 1.978±0.008 |
|             | $\Delta e = +0.50 e$/Ni | 2.019±0.010     | 1.937±0.006     | 1.996±0.010    | 2.031±0.013 |
| La$_3$Sr    |                 | 2.017±0.007     | 1.938±0.006     | 1.995±0.005    | 2.031±0.008 |

the metal–oxygen–metal network. However, we note that the two different approaches, which incorporate the charge doping in our calculations, produce consistent results regarding the change of the electronic structure, orbital polarization and structural property. Also, the orbital polarization is insensitive to some degrees of structural difference. These findings strongly suggest that the overall conclusions presented in this study are quite relevant to various doping situations in experiments, in spite of the limitation of simulation methods.

We emphasize that our results can provide useful information to understand the experiment. For example, the further distortion of rotated oxygen octahedra caused by doping implies that more oxygen vacancies are not necessarily leading the system to be more metallic because further rotation can simultaneously make the system be less metallic due to the enlarged effective $U/t$ parameter. Also, our prediction of polarization dependence as a function of electron doping can be tested in experiments, for example by changing the oxygen partial pressure in the pulsed laser deposition process.

Similar doping-induced structural changes may happen in other oxide superlattices with $d$-orbital degrees of freedom, such as the LaTiO$_3$/LaAlO$_3$ system. One may also speculate the possibility of rich phases from the LaNiO$_3$/LaTiO$_3$ superlattices, where the two independent orbital degrees of freedom from the Ti-$t_{2g}$ and Ni-$e_g$ can interact through corner-sharing coupling of the NiO$_6$ and TiO$_6$ octahedra. Such materials as well as other relevant systems may have substantial importances to deserve further theoretical investigation.
VI. SUMMARY

The effect of charge doping on the electronic, orbital and structural properties in LaNiO$_3$/SrTiO$_3$ has been investigated using first-principles density functional theory calculation in which doping was simulated with two different methods, namely, rigid band shift and the supercell calculation. The results clearly show the systematic dependence of these physical properties on doping. As more electrons are introduced, the orbital polarization is gradually reduced and the Ni to apical oxygen distance increases. These features are found in both structural phases with and without octahedral rotations. Remarkably, the rotation angles of the NiO$_6$/TiO$_6$ octahedra are also found to strongly depend on doping so that the angle $\gamma$ gradually decreases, whereas $\alpha$ and $\beta$ increase as a function of electron doping. Further analysis shows that the electron (hole) doping can play a similar role with the compressive (tensile) strain for the octahedral rotations. Our results suggest a possible way to control the orbital and structural property by means of charge doping and provide useful information to understand the experiments under various doping situations, such as oxygen vacancy.

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Appendix A: Projected density of states (PDOS)

In this Appendix, we present the electronic structure change as a function of doping, which provides further information to understand the doping dependence of our system and is closely related to the other physical quantities discussed above.

Fig. 6 shows the PDOS in the structure with no octahedral rotation. First of all, we note that the electronic structure difference between rigid band shift and LaSr$_3$/La$_3$Sr-cell calculation is not significant. This point also holds for the results of rotated structures (Fig. 7 and Fig. 8). It is therefore consistent with our finding that two different approaches predict the same features regarding the orbital occupation and structural properties as discussed above. The overall shape of the Ni-$e_g$ PDOS is actually consistent with the schematic picture in Fig. 2(a), vindicating our discussion in Sec. III.B based on this picture.

Fig. 7 and 8 show the PDOS from the structures with octahedral rotations in which the Jahn-Teller or breathing type distortion is incorporated (main results discussed in Sec. IV). Compared to the rotation-free results, due to the rotations, additional splittings are introduced in the Ni-$e_g$ states as clearly shown in Fig. 8. Also, in the presence of $U$, electron doping induces charge disproportionation (see the fifth, sixth, and seventh rows of Fig. 8(b) and (c)). From the PDOS results and the data in Fig. 5, it can be suggested that Ni(1) and Ni(2) (Fig. 8(b) and (c)) move closer to the $d^8$- and $d^7$-configuration in the electron-doped regime, respectively.

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FIG. 1. (Color online) (a) The atomic structures used in the calculations. The black thin lines show the unit cell. (b)-(d) The arrangement of La and Sr ions are shown in (b) $(\text{LaNiO}_3)_1/(\text{SrTiO}_3)_1$, (c) $(\text{La}_{0.5}\text{NiO}_3)_1/(\text{Sr}_{1.5}\text{TiO}_3)_1$, (LaSr$_3$-cell) and (d) $(\text{La}_{1.5}\text{NiO}_3)_1/(\text{Sr}_{0.5}\text{TiO}_3)_1$ (La$_3$Sr-cell), respectively.
FIG. 2. (Color online) Schematic pictures illustrating the displacement of (a) La, Sr and (b) O atoms upon electron doping in the case of rigid band shift calculations. (c) In-plane and (d) out-of-plane displacement of the oxygen ions in the case of LaSr$_3$/La$_3$Sr-cells. (e) The calculated $d_{\text{Ni-Oap}}$ as a function of doping. The circles and squares represent the results of $U=0$ and 3 eV calculations, respectively. Filled and empty symbols correspond to the results from rigid band shift and LaSr$_3$/La$_3$Sr-cells, respectively. The inset shows the calculated $d_{\text{Ni-Oap}}$ as a function of $U$ in the case of $+0.50e$/Ni.
FIG. 3. (Color online) (a) Schematic PDOS of Ni $d_{x^2-y^2}$- and $d_{3z^2-r^2}$-orbital, (b) the calculated orbital polarization, and (c) the magnetic moment (per a Ni atom) as a function of doping. The filled and empty symbols correspond to the results from rigid band shift and LaSr$_3$/La$_3$Sr-cells, respectively.
FIG. 4. (Color online) (a)-(b) The calculated rotation angle changes for (a) \( U=0 \) and (b) \( 3 \) eV as a function of doping. The filled and open symbols represent rigid band shift and the LaSr\(_3\)/La\(_3\)Sr-cell calculation, respectively. The angle \( \alpha, \beta, \gamma \) are defined in the inset of (b). Following the Glazer notation, the positive and negative signs mean the ferro- and antiferro-distortive rotation, respectively. (c)-(d) Schematic figures illustrating (c) the Jahn-Teller-distorted structure (with no doping and \( U=3 \) eV) and (d) the breathing type distortion (\(+0.25\) and \(+0.50\) doping case with \( U=3.0 \) eV). In (c) the longer and shorter Ni-O bonds are denoted by \( a_l \) and \( a_s \), respectively, and the c-lattice parameter is unchanged. In (d), two inequivalent Ni sites are denoted as Ni(1) and Ni(2), respectively. In this case, the out-of-plane c-lattice parameters are also different and denoted as \( c_1 \) and \( c_2 \), corresponding to Ni(1) and Ni(2), respectively.
FIG. 5. (Color online) The calculation result of (a) $\langle d_{\text{Ni-Oap}} \rangle / \langle d_{\text{Ni-Oin}} \rangle$ ratio, (b) orbital polarization $P_{\text{eg}}$, and (c) Ni-magnetic moment as a function of electron doping. The filled and open symbols represent the rigid band shift and the LaSr$_3$/La$_3$Sr-cell calculation, respectively. Note that for the doping level higher than +0.25e, and with $U=3$ eV, there are two different Ni-sites due to the charge disproportionation.
FIG. 6. (Color online) The change of Ni-$d$ and Ti-$d$ PDOS as a function of doping. (a)-(b) Ni-$t_{2g}$, Ni-$e_g$, and Ti-$d$-orbitals are presented by blue, red, and light blue lines, respectively. (c)-(d) Ni-$d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states are represented by blue and red lines. (a) and (c) are the results with $U=0$ eV, and (b) and (d) with $U=3$ eV. The first and last rows show the results from LaSr$_3$- and La$_3$Sr-cell calculations, respectively. The second, third, and fourth rows correspond to rigid band shift calculation with $-0.50e$/Ni, $0.00e$/Ni, and $+0.50e$/Ni doping, respectively.
FIG. 7. (Color online) PDOS of the Ni-$t_{2g}$, Ni-$e_g$ and Ti-$d$ states in the presence of NiO$_6$ and TiO$_6$ octahedra rotations. (a) $U=0$ (b) $U=3$ for Ni(1), and (c) $U=3$ for Ni(2). The first to fifth (last) rows correspond to the results from the LaSr$_3$-cell, $-0.50e$/Ni, $0.00e$/Ni, and $+0.50e$/Ni, and La$_3$Sr-cell, respectively.
FIG. 8. (Color online) PDOS of the Ni-$d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states in the presence of NiO$_6$ and TiO$_6$ octahedra rotations. (a) $U=0$ (b) $U=3$ for Ni(1), and (c) $U=3$ for Ni(2). The first to fifth (last) rows correspond to the results from the LaSr$_3$-cell, $-0.50e$/Ni, 0.00e$/Ni, and $+0.50e$/Ni, and La$_3$Sr-cell, respectively.