

Electronic structure of possible nickelate analogs to the cuprates

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The electronic structure of various nickel oxides with nickel valence varying from 1+ to 3+ was investigated with the aim to find similarities and differences to the isoelectronic cuprates. Only if the Ni ions are forced into a planar coordination with the O ions can a $S=1/2$ magnetic insulator be realized with the difficult Ni^+ oxidation state and possibly doped with low spin ($S=0$) Ni^{2+} holes directly analogous to the superconducting cuprates. The more common Ni^{3+} oxidation state cannot be used to make a parent magnetic insulator as it forms rather as localized $S=1$ Ni^{2+} embedded in a sea of itinerant O holes. Strong coupling of these holes to the localized spins via $2p$ - $3d$ hybridization leads to a heavy-fermion system with a large Kondo temperature, which was confirmed experimentally for LaNiO_3 . [S0163-1829(99)03411-6]

I. INTRODUCTION

Although it is now more than a decade since the discovery of high-temperature superconductivity in the cuprates and over 50 examples are known, this fascinating phenomenon remains confined to a narrow group of compounds. All contain CuO_2 planes lightly doped away from a stoichiometric Cu^{2+} oxidation state mostly by hole doping. To date it has not proved possible to extend the phenomenon even to the neighboring nickelates. In this paper we will examine the electronic structures of the nickelates and compare and contrast these with that of the cuprates.

It is well known that generally nickelates prefer an octahedral coordination rather than the planar coordination of the cuprates. However, we will not attempt to predict stable structures *per se*. Rather we restrict ourselves to an examination of the electronic structure of nickelates, imposing either octahedral or planar structures. To this end we employ the LDA+U method.¹ This method allows orbital correlations driven by the strong intraatomic Coulomb interaction to be included in a LDA (local density approximation) calculation. Experience with the cuprates and transition metal compounds shows this to be a reliable method to predict the electronic structure.² For example, the antiferromagnetic insulating nature of the stoichiometric cuprates with a Cu^{2+} oxidation state and the paramagnetic insulating nature of $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ with a low-spin Cu^{3+} oxidation state are correctly reproduced.³ We believe the results reported here are reliable and offer insight into the electronic structure of Ni ions not only in the standard octahedral but also in rarer planar coordination.

In both nickelates and cuprates the antibonding e_g shell of the $3d$ complex is partly occupied with three electrons in Ni^+ and Cu^{2+} , two electrons in Ni^{2+} and Cu^{3+} , and one electron in Ni^{3+} and Cu^{4+} (if it exists). Thus the similarity between

nickelates and cuprates is close but as we shall see there are clear differences. Still the possibility to obtain a nickelate counterpart of the cuprate superconductors is not excluded although it is not easy. Without wishing to enter here into the debate on the origin of the high- T_c superconductivity, our criterion for a promising nickelate will be an explicit analogy to the high- T_c cuprates, i.e., planes of $S=\frac{1}{2}$ ions are lightly doped with mobile low spin $S=0$ ions. If such a nickelate system could be synthesized, then a real counterpart of the cuprates can be investigated for superconductivity. Another aim will be to investigate the nature of the Ni^{3+} oxidation state. At first sight one might reasonably expect that Ni^{3+} with one electron in the antibonding e_g shell should be an ideal Jahn-Teller ion. However, as discussed below, nickelates with a Ni^{3+} oxidation state generally are cubic and metallic or at least are only small gap insulators and are not well localized Mott insulators. Our results for a planar coordinated Ni^{3+} oxidation state show that even in this case the Jahn-Teller paradigm does not work and the Fermi energy enters the nonbonding O $2p$ orbitals, a configuration which is not a Jahn-Teller split $3d$ ion. This we will argue is part of the reason for the failure of the Jahn-Teller mechanism in the Ni^{3+} oxidation state.

The outline of the paper is as follows. At first we present the results of LDA+U calculations for the commonest oxidation, Ni^{2+} . The well known oxide, La_2NiO_4 has a planar structure and octahedral coordination for the Ni ion. Our calculations correctly reproduce the high-spin $S=1$, Ni^{2+} configuration of La_2NiO_4 . However, if we examine a planar local configuration, e.g., in a infinite layer compound SrNiO_2 which has only a square coordination of the Ni ion without apical O ions, then a low-spin $S=0$ Ni^{2+} configuration results. This configuration is directly analogous to the low-spin $S=0$ Cu^{3+} ion, i.e., it is also a Zhang-Rice singlet.

Next we examine a Ni^+ ion which has been reported in

planar coordination in the infinite layer compound LaNiO_2 . Note the synthesis of this compound is very difficult. Our LDA+U calculations give a stable solution with a $S = \frac{1}{2}$ Ni^{2+} ions in an ordered antiferromagnetic structure, directly analogous to the infinite layer cuprate insulator CaCuO_2 . These results offer hope that planar nickelates directly analogous to the high- T_c cuprates may be possible. We tried unsuccessfully to stabilize a Ni^{3+} configuration in an octahedral environment by substituting possible tetravalent ions (like Pb) for La^{3+} in La_2NiO_4 , but that proved to be impossible.

Lastly we consider Ni^{3+} ions. Many nickelates with this oxidation state are known. We chose to calculate the compounds LaNiO_3 and LaSrNiO_4 as three-dimensional and two-dimensional examples of Ni^{3+} ions in octahedral coordination. In neither case do we find stable $S = \frac{1}{2}$ Mott insulating states, although a Ni^{3+} ion with one electron in e_g shell might be considered as analogous to Ni^{2+} with one hole in e_g shell. As we shall discuss in more detail below, these Ni^{3+} compounds form Kondo metals with holes in the O $2p$ band which hybridize strongly with the $S = 13d^8$ state of Ni ion. Even if we force a planar configuration of oxygen atoms around a Ni ion as in an infinite layer compound KNiO_2 , a $S = \frac{1}{2}$ magnetic insulator does not form, rather the $2p$ states of the O holes change their character to nonbonding.

Finally we summarize our work in the concluding section.

II. THE CALCULATION METHOD

The main idea of the LDA+U method is that LDA gives a good approximation for the average Coulomb energy of d - d interactions E_{av} as a function of the total number of d -electrons $N = \sum_{m\sigma} n_{m\sigma}$ where $n_{m\sigma}$ is the occupancy of a particular $d_{m\sigma}$ orbital:

$$E_{\text{av}} = \frac{1}{2}UN(N-1) - \frac{1}{4}JN(N-2). \quad (1)$$

But LDA does not properly describe the full Coulomb and exchange interactions between d electrons in the same d shell. So Anisimov *et al.*¹ suggested to subtract E_{av} from the LDA total energy functional and to add orbital- and spin-dependent contributions to obtain the exact (within a mean-field approximation) formula:

$$E = E_{\text{LDA}} - E_{\text{av}} + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2} \sum_{m \neq m', m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}. \quad (2)$$

Taking the derivative with respect to $n_{m\sigma}$ gives the orbital-dependent one-electron potential:

$$V_{m\sigma}(\mathbf{r}) = V_{\text{LDA}}(\mathbf{r}) + \sum_{m'} (U_{mm'} - U_{\text{eff}}) n_{m'-\sigma} + \sum_{m' \neq m} (U_{mm'} - J_{mm'} - U_{\text{eff}}) n_{m\sigma} + U_{\text{eff}} \left(\frac{1}{2} - n_{m\sigma} \right) - \frac{1}{4}J, \quad (3)$$

with $U_{\text{eff}} = U - \frac{1}{2}J$. The Coulomb and exchange matrices $U_{mm'}$ and $J_{mm'}$ are expressed through the integrals over products of three spherical harmonics and screened Coulomb and exchange parameters U and J .⁴

A nontrivial problem is what value of the screened Coulomb interaction U to use. For insulators, such as late transition-metal oxides a good approximation is to calculate static screening of the d - d intrashell Coulomb interaction in a supercell LDA calculation.⁵ Such calculation for nickel oxides gave the following values: $U = 8$ eV and $J = 1$ eV. The calculation scheme was realized in the frame of LMTO (linear muffin-tin orbitals) method⁶ using Stuttgart TBLMTO-47 computer code.

III. THE OXIDATION STATE Ni^{2+}

Most Ni^{2+} ions form in octahedral coordination with equal or only relatively small variations in Ni-O bond lengths. A well known example is the compound La_2NiO_4 —the direct analog of the cuprate La_2CuO_4 . This structure can be viewed as layers of MeO_6 octahedra connected via apical oxygen atoms with coplanar La ions situated between the layers. In the nickelate however the octahedron is much less distorted than in the cuprate: 1.95 Å and 2.24 Å for Ni-O bond lengths in-plane and out-of-plane as compared with 1.89 Å and 2.43 Å for La_2CuO_4 .

The LDA+U calculation of the electronic structure of La_2NiO_4 resulted in an antiferromagnetic insulator as a ground state with a value of the magnetic moment per Ni ion of $1.55\mu_B$. The total and partial densities of states obtained in the calculations are presented in Fig. 1. As one can see, both minority spin e_g $3d$ orbitals of the Ni ion, in-plane $x^2 - y^2$ and out-of-plane $3z^2 - r^2$, are unoccupied resulting in the formal high-spin ($S = 1$) state of Ni^{2+} in La_2NiO_4 . However due to their hybridization with the oxygen $2p$ states the value of the magnetic moment of Ni is smaller than the integer ionic number. Since both orbitals are occupied by a majority spin electron, Ni^{2+} is not a Jahn-Teller ion, which explains the relatively small distortion of the NiO_6 octahedra in La_2NiO_4 .

In the presence of apical O ions, the high spin state of Ni^{2+} is stable, but Ni^{2+} as a $3d^8$ ion is electronically equivalent to Cu^{3+} which generally prefers a low-spin ($S = 0$) configuration. Indeed Azuma *et al.*⁷ have evidence that when Ni is substituted for Cu in the layered compound SrCu_2O_3 , the Ni impurity ion is in a low-spin configuration. So it is highly interesting to see what happens if we place Ni^{2+} ions in a planar coordination without apical O atoms. To this end we calculated the simplest (hypothetical) layered compound SrNiO_2 with the same crystal structure as the so-called “infinite layer” cuprate CaCuO_2 . This cuprate is the prototype of the undoped parents of all high- T_c cuprates, because it consists only of CuO_2 layers only with Ca ions between them. The transition metal ion in this structure has a fourfold coordination with four O ions, which is typical for Cu^{2+} compounds. The LDA+U calculation for CaCuO_2 (Ref. 1) gave an antiferromagnetic insulator with the Cu^{2+} ions in a $S = 1/2$ state and the single $3d$ hole sitting in the $x^2 - y^2$ orbital, which has lobes directed towards the four planar O ions. In the SrNiO_2 compound the Ni^{2+} ion has two $3d$ holes and there are two possible states: a high-spin ($S = 1$)

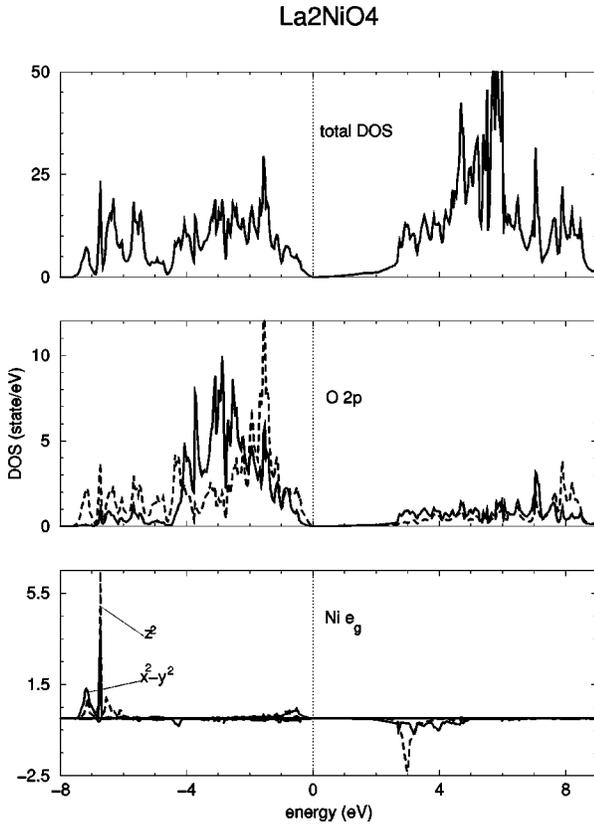


FIG. 1. The total and partial (O 2p and Ni e_g 3d) densities of states for La_2NiO_4 . Solid and dashed lines for O 2p correspond to apical and planar oxygen atoms.

one with holes in both in-plane x^2-y^2 and out-of-plane $3z^2-r^2$ minority spin 3d orbitals as in La_2NiO_4 or a low-spin ($S=0$) one with both holes in the in-plane x^2-y^2 orbitals. The results of our calculations showed not only that the low-spin solution is lowest in energy, but that the high-spin solution does not even exist (i.e., attempts to start the self-consistency procedure with a $S=1$ state of Ni^{2+} ion lead to a vanishing magnetic moment in the process of iteration). The ground state of SrNiO_2 is found to be a diamagnetic insulator (see Fig. 2), exactly analogous to the planar Cu^{3+} cuprate $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$.³

The conclusions from this section are clear. In the structure where apical O atoms are present, the high-spin ($S=1$) configuration of Ni^{2+} is favored and not the low-spin ($S=0$) configuration that the isoelectronic Cu^{3+} takes. However it is possible to stabilize the latter if the Ni^{2+} ions are forced into a strongly planar local environment, e.g. one without apical O atoms.

IV. THE OXIDATION STATE Ni^+

In contrast to Ni^{2+} , it is very difficult to stabilize this oxidation state.⁸ In the La_2NiO_4 structure one must substitute a tetravalent ion for La^{3+} but even then the calculation did not yield a stable Ni^+ ion. A difference in ionization of 3+ between the cations is apparently just too great. However in planar structures the situation is different and the layered compound LaNiO_2 with the same crystal structure as of CaCuO_2 has been reported.⁹ This encouraged us to calculate

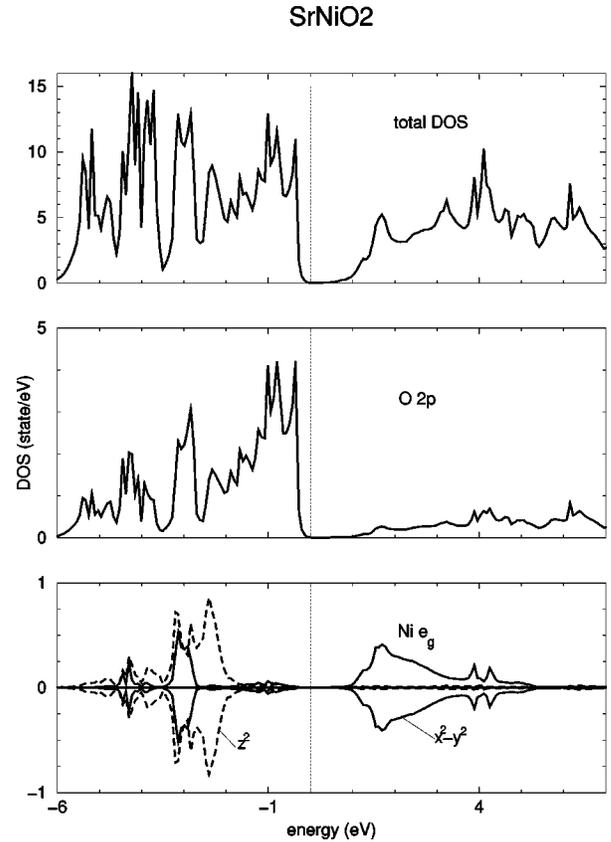


FIG. 2. The total and partial (O 2p and Ni e_g 3d) densities of states for SrNiO_2 .

its electronic structure. The results of the LDA+U calculation are shown in Fig. 3 and give a stable antiferromagnetic insulator very much like that of Cu^{2+} cuprate. Again the 2p states are completely filled and the only 3d hole of the Ni^+ ion is found in the minority spin x^2-y^2 orbital. This is exactly equivalent to the structure found in CaCuO_2 .¹

The conclusion is that a $S=\frac{1}{2}$ magnetic insulator based on the Ni^+ ion is theoretically possible which would be a direct nickelate analog to the insulating parents of the high- T_c cuprates. As discussed above, hole doping should lead to a low-spin ($S=0$) Ni^{2+} configuration. However, a necessary requirement is that the local environment is clearly planar.

V. THE OXIDATION STATE Ni^{3+}

Compounds with trivalent Ni^{3+} ions are well known, in contrast to the monovalent Ni^+ ions. At first sight there would seem to be a direct similarity between both oxidation states and Mott insulators with $S=\frac{1}{2}$ ions stabilized by Jahn-Teller distortions might have been expected due to the presence of 1 electron in the e_g shell. However this is not the case at all. For example, the alloy series $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ (Ref. 10) shows evidence for this Jahn-Teller effect in the lattice parameters only for $x < 0.5$ when the Ni^{3+} ions are relatively dilute. When they are concentrated as $x \rightarrow 1$, a metallic state with an essentially undistorted NiO_6 octahedron has been found. To understand this unexpected finding we have made a LDA+U calculation for $x=1$ (LaSrNiO_4), when all nickel ions are in a Ni^{3+} configuration.

The results are rather unusual. Instead of the insulator

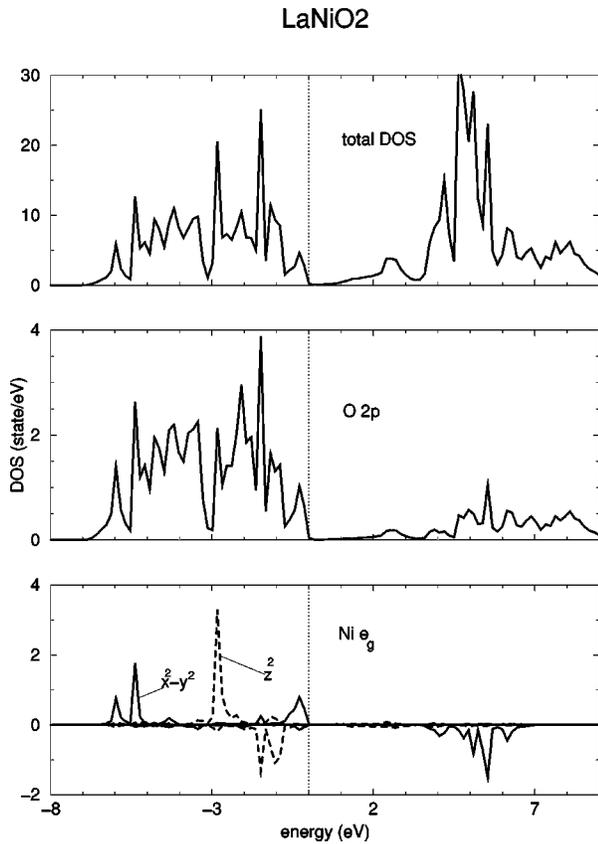


FIG. 3. The total and partial (O $2p$ and Ni e_g $3d$) densities of states for LaNiO_2 .

with $S = \frac{1}{2}$ ions, we obtained a metallic ground state with $S = 1$ Ni ions. The electronic structure (see Fig. 4) looks very much the same as that of undoped La_2NiO_4 (Fig. 1), but with the Fermi level has moved from the energy gap into the top of the valence band as in a rigid band approximation. The integrated density of states between the Fermi level and the top of valence band shows the one hole per formula unit has entered in $2p$ O states. In other words in going from Ni^{2+} to Ni^{3+} ion the additional hole does not enter one of the majority spin orbitals of the e_g shell but rather enters the oxygen $2p$ states. This result is in agreement with the Zaanen-Sawatzky-Allen¹¹ classification of the end of $3d$ row transition metal oxides as “charge-transfer” insulators different to the classic Mott insulators of the light transition metal oxides. In the latter the both top of the valence band and the bottom of conduction band are of $3d$ -orbital character, while in the former the top of the valence band is formed by the O $2p$ states. The lowest energy excitations in a classic Mott insulator correspond to transfer an electron from one d ion to another, while in charge transfer insulators it will be from oxygen $2p$ states to $3d$ orbitals of transition metal ion. With doping the holes are introduced into the O $2p$ band [experimentally confirmed by x-ray absorption spectroscopy for Li-doped NiO (Ref. 12)] which is much broader than the narrow band of localized $3d$ states. The result is the set of $S = 1$ Ni ions embedded in partially filled O $2p$ bands. From the partial densities of O $2p$ and Ni $3d$ states in Fig. 4, one can see that the Fermi level comes through the O $2p$ states having significant admixture of majority spin e_g orbitals.

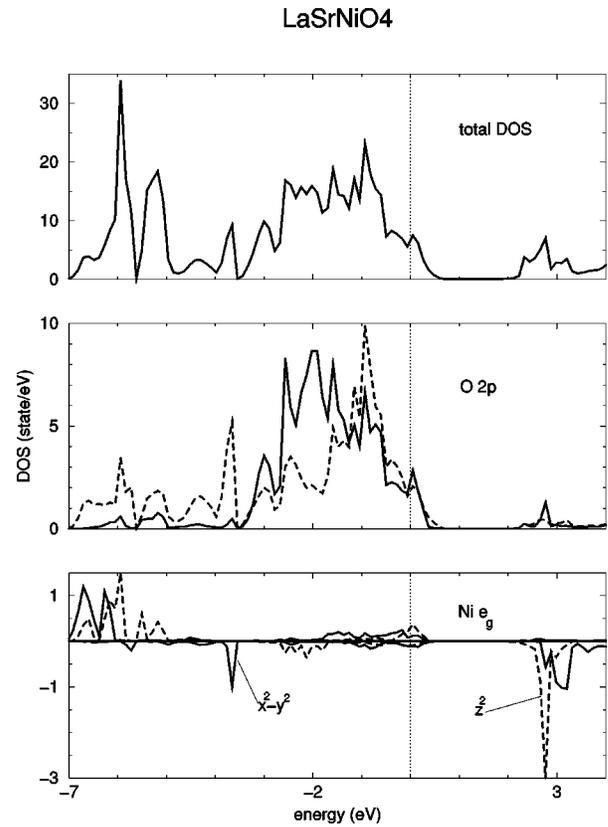


FIG. 4. The total and partial (O $2p$ and Ni e_g $3d$) densities of states for LaSrNiO_4 . Solid and dashed lines for O $2p$ correspond to apical and planar oxygen atoms.

That means that mobile O holes will be strongly antiferromagnetically coupled to the localized Ni spins and thus LaSrNiO_4 should be regarded as a heavy electron metal with a large Kondo temperature.

The perovskite LaNiO_3 is a three-dimensional Ni^{3+} nickelate. The main motive of the crystal structure are still NiO_6 octahedra but now they are connected via all vertices, not just via the planar ones. As a result the bands are broader and the electron states more itinerant (see Fig. 5). The electronic structure reminds us of LaSrNiO_4 but with nearly zero separation between the minority and majority Ni $3d$ bands and much broader features in the DOS. Experimentally, LaNiO_3 is a paramagnetic metal¹³ with clear signs of strong correlations, e.g. both the Pauli magnetic susceptibility, χ , and the linear coefficient of the specific heat, γ , are enhanced well above their electron gas values and electrical resistivity shows a strong T^2 dependence at low temperatures. These results confirm our interpretation of the Ni^{3+} oxides as heavy electron metals.

Given that the expected Jahn-Teller distortion does not occur when apical O atoms are present, it is clearly of great interest to know what would happen if a planar environment is imposed on the Ni^{3+} ions. As a possible example we consider a layered compound in the form of KNiO_2 without apical oxygen atoms (i.e., the same crystal structure as in CaCuO_2). The resulting electronic structure (see Fig. 6) strongly reminds us that of the diamagnetic insulator SrNiO_2 (Fig. 2) but with the important difference that now the Fermi level has moved into the valence band in accordance with a rigid band approximation. Further we find the top of the

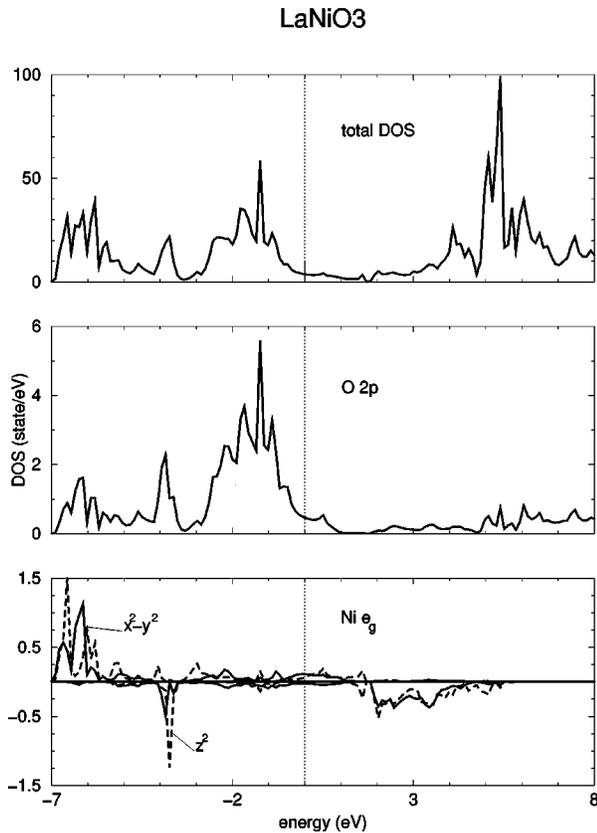


FIG. 5. The total and partial (O $2p$ and Ni e_g $3d$) densities of states for LaNiO_3 .

valence band is formed by nearly pure O $2p$ states with practically no admixture of Ni $3d$ orbitals and so the ground state must be viewed as a O $2p$ metal with holes in the valence band practically uncoupled from the Ni ions.

In conclusion the relative positions of the $3d$ and $2p$ levels in nickelates do not allow the stabilization of a magnetic insulator with a simple $S = \frac{1}{2}$ ionic configuration for the Ni^{3+} oxidation state, even when a planar local environment is imposed. This clearly rules out the possible use of trivalent nickelates as parent compounds analogous to divalent cuprates.

VI. CONCLUSION

The results of these LDA+U calculations to search for nickelate analogs of the high- T_c superconducting cuprates can be simply told. The most common pair of oxidation states $\text{Ni}^{2+}/\text{Ni}^{3+}$ are quite different to the cuprates and the only possibility that could work theoretically would be $\text{Ni}^+/\text{Ni}^{2+}$ but again only if a fourfold planar rather than a sixfold octahedral coordination can be enforced. This will be difficult to achieve as hardly any planar nickelates with these oxidation states are known. This is not surprising since no nickelate superconductors have been found to date, in spite of strenuous efforts. In this work we focussed on the simplest infinite layer planar structures LaNiO_2 and SrNiO_2 to obtain planar Ni^+ and Ni^{2+} . But there may be other ways. For example, if one could replace the apical O in LaSrNiO_4 with Cl ions to form $\text{LaSrNiO}_2\text{Cl}_2$ then at least in theory a mag-

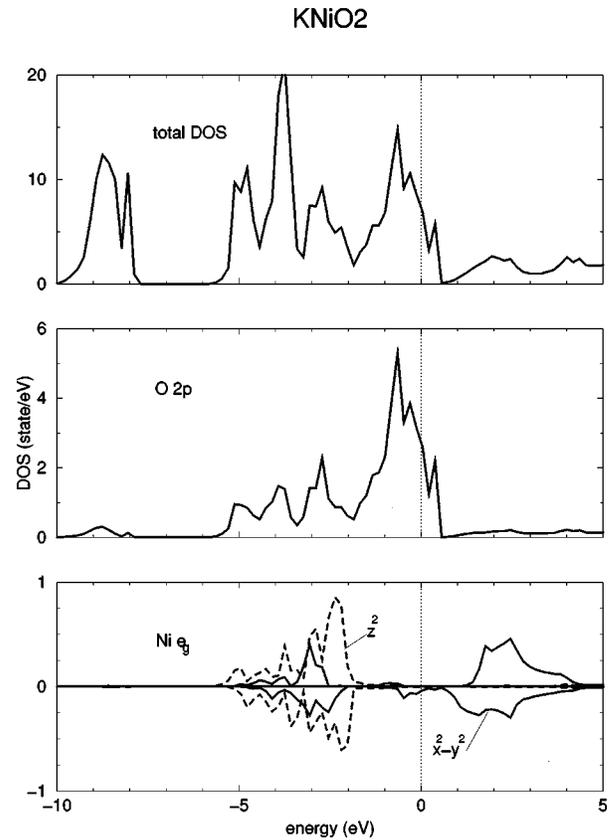


FIG. 6. The total and partial (O $2p$ and Ni e_g $3d$) densities of states for KNiO_2 .

netic insulating parent with Ni^+ oxidation state would result. It is of course much easier to calculate hypothetical structures rather than to synthesize them, but we hope at least these calculations can give some useful hints for what may be possible and that the search for a nickelate superconductor is not completely without hope.

Another result of these calculations is to shed light on the puzzle of why Ni^{3+} compounds with one electron in the e_g shell are not simple Jahn-Teller ions. Instead we find that a heavy fermion system with local $S = 1$ spins of Ni^{2+} ions in a sea of mobile oxygen holes is formed.

Finally we note that there are planar nickelates with a formal Ni^{3+} oxidation state but with a rhombohedral structure and triangular coordination of the NiO_6 octahedra, e.g. LiNiO_2 .¹⁴ In this case a magnetic insulating groundstate is found which has been interpreted as arising from the localization of the $2p$ O holes due to the Coulomb repulsion on the O sites. Again a simple local Jahn-Teller distortion of the NiO_6 does not occur but a complex behavior due to competing spin and orbital order is found.¹⁵ This case is also not promising as a possible trivalent parent compound.

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