Chapter 6

Charge disproportionation in YNiO$_3$ and CaFeO$_3$ crystals

Abstract

Periodic and embedded cluster approaches are used to investigate the charge disproportionation suggested for the low temperature phase of CaFeO$_3$ and YNiO$_3$ crystals. The analysis of the ground state charge distributions calculated within the periodic approach and from cluster wave functions clearly demonstrates that all TM ions have similar electron environments in the low temperature phase. The thermally induced transition leading to the two different crystallographic sites is characterized by a small change in the contribution of the ligand to metal charge transfer configurations and therewith a small change in the covalency of the TM–ligand bonding.

6.1 Introduction

In 3d perovskites with TM-3d$^4$ ($t_{2g}^2 e_g^1$) or TM-3d$^7$ ($t_{2g}^6 e_g^1$) electronic configurations, the lift of the degeneracy of TM states of $E_g$ symmetry causes an energetically favorable distortion of the octahedron formed by the oxygen ligands, giving rise to so-called Jahn Teller distortions. This type of distortion has been experimentally observed for LaMnO$_3$ crystals. An interesting alternative type of local distortion reported for CaFeO$_3$ and YNiO$_3$ crystals is the alternating compression and expansion of neighboring octahedra.

Mössbauer spectroscopy investigations on CaFeO$_3$ (with a TM nominal valency of 4+,
3d⁴) introduced the idea of charge disproportionation (CD) in the crystal based on the observation of two different Mössbauer isomer shift (See Chapter 3) for low temperature of 0.31 and -0.03 mm·s⁻¹ [14]. X-ray diffraction indicates the existence of two different metal sites [4] suggesting an alternative type of distortion compared to JT distortions. As mentioned in chapter 1, the two crystallographic sites in CaFeO₃ have been interpreted as being due to the co-existence of Fe⁴⁺δ and Fe⁴₋δ sites. The average Fe–O bond length in the small octahedra (1.872 Å) is still larger than the average bond length for which, under external pressure of 25 GPa, a high spin to low spin transition occurs.

The RNiO₃ crystals, R being trivalent rare earth ions (La to Lu) or Y, [127, 138–140] are also subject to this alternative type of distortion. They are studied as prototype materials with a bandwidth-controlled metal-insulator transition. The nominal valency of Ni is 3+ with a d-electron configuration t²⁶ e⁸ and spin S = 1/2. RNiO₃ (R=Y, Ho, Er, Lu) crystallizes in the orthorhombically distorted perovskite structure Pbnm. NiO₆ octahedra are very regular in the investigated Ni perovskites. A symmetry breaking of the orthorhombic Pbnm structure leading to monoclinic P2₁/n, with two different chemical sites for the Ni ions, is observed when temperature is decreased [5, 7]. In YNiO₃ the transformation occurs around T_CD = 582 K [5] and is similar to the transition observed in crystalline CaFeO₃ (see Table 1.1). The average Ni–O distances of the small and large octahedra are 1.916 Å and 2.009 Å, respectively. The pressure dependence of the infrared spectrum and X-ray synchrotron diffraction data of YNiO₃ show a pressure induced melting of the CD around 14 GPa [66]. A similar pressure-induced melting of the CD phase has been reported for CaFeO₃ around 17 GPa as can be seen, for example, in Figure 1.4.

These materials are thought to avoid, via the charge disproportionation mechanism, the TM-3d⁴ and 3d⁷ electronic configurations that could be at the origin of a JT type local distortion. Their alternative type of distortion, explained with a variation of the TM charge, is investigated in this chapter using periodic and embedded cluster approaches by careful analysis of the many-electron wave functions.

In this chapter we investigate the electronic structure of CaFeO₃ and YNiO₃ crystals in their low-temperature crystal structure. The main objective of these investigations is to
establish whether or not there are significant differences between the electron distributions around the TM ions in the center of large and small oxygen octahedra. One sign of different electron distributions could be significantly different weights of the leading electronic configurations as studied for example in Chapter 4. Is the low temperature electronic ground state similar to that of the high temperature structure or can it be better be associated with metal-to-metal charge transfer? Such questions cannot be answered by studying only one-center clusters, especially since the role of the oxygen ligands is much more complex than being simple closed shell spectators. Giving a balanced description of the two neighboring TM sites requires at least \([\text{TM}_2\text{O}_{11}]^{n+}\) clusters. However, in this cluster only one of the oxygen ligands has two TM neighbors, whereas in the crystal all oxygen ions have two TM neighbors. So a balanced description of oxygen holes in the oxygen versus holes on metal is not possible. A better cluster model has a center with four TM ions in a square arrangement and four bridging oxygen ions.

Inclusion of all nearest oxygen neighbors of the four TM ions leads to a \([\text{TM}_4\text{O}_{18}]^{n-}\) cluster. CASSCF calculations in such a cluster for the CaFeO\(_3\) crystal are not yet possible in practice, because of the large active space that is required: at least four active orbitals per center. For YNiO\(_3\), CASSCF calculations on a \([\text{Ni}_4\text{O}_{18}]^{24-}\) cluster were feasible and they are reported in this chapter. A schematic view of the cluster is shown in Figure 6.1. The results of embedded cluster calculations may be sensitive to the details of the embedding. Therefore, we also discuss periodic quantum chemical calculations, in which this issue does not play a role.

### 6.2 Details of calculations

#### 6.2.1 Periodic approach

Periodic quantum chemical calculations are nowadays the most common method to predict electronic structures and properties of crystals. Starting from the structural parameters, which are usually taken from X-ray and/or neutron diffractions, the electrical properties like
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The gap between the valence band and conduction band, can be calculated and compared to experiment.

The choice for methods based on density functional theory (DFT) to get the crystal properties is often made to reach a relatively good description at low computational efforts. However, within DFT simple LDA (Local Density Approximation) methods fail to describe such crystals adequately, mostly because electron correlation is not properly accounted for. These effects can be approximated by introducing empirical parameters, for example U in the LDA+U method [31]. Another way to improve DFT is to introduce Hartree-Fock (HF) exchange in the functional by using so-called hybrid functionals. We use in this work the hybrid functional referred to as B3LYP corresponding to the Becke formulation for the exchange part, mixed with 20 % of HF exchange, and a Lee Yang and Parr formulation for the correlation part of the functional. This hybrid functional has shown to give a good description of ionic crystals containing transition metal ions [30,86,141].

Periodic unrestricted Hartree-Fock and unrestricted hybrid Density Functional Theory calculations have been carried out with the CRYSTAL06 program package, [87] for which the Bloch functions are expressed as a linear combination of atom centered Gaussian type orbital (GTO) basis sets (see Chapter 2 for a detailed description). The Fe and Ni atomic basis sets contain contracted GTO’s obtained by contraction of the (20s12p5d) primitive Gaussian set resulting in a (5s4p2d) contracted basis set [142, 143]. The oxygen basis set corresponds to a (4s3p1d) contracted GTO basis obtained from a (14s6p) primitive set [144]. For Ca$^{2+}$ a (5s4p2d) basis was used [144] and finally a (5s4p3d) basis set was added for Y$^{3+}$ [145]. The cutoff threshold parameters ITOL for Coulomb and exchange integral evaluations have been set to the 7, 7, 7, 7 and 14 , respectively. The integration in reciprocal space has been carried out using a k-space grid parameter of 4 yielding 27 points in the irreducible Brillouin zone.
6.2. Details of calculations

6.2.2 Embedded cluster approach

The embedded cluster approach, considering $[\text{FeO}_6]^{8-}$ and $[\text{NiO}_6]^{9-}$ clusters, allows one to give a first approximation of the local electronic distribution around the TM including an accurate treatment of electron correlation. We also considered in this work a cluster containing four Ni ions, i.e. a $[\text{Ni}_4\text{O}_{18}]^{24-}$ cluster (see Fig. 6.1) to ensure a balanced description of the possible charge ordering effects for YNiO$_3$ in the charge disproportionated phase.

![Figure 6.1: $[\text{Ni}_4\text{O}_{18}]^{24-}$ cluster simulating part of the ab plane of an YNiO$_3$ crystal embedded in 18 Y$^{3+}$ and 16 Ni$^{3+}$ ions described with AIEMPs](image)

The ions directly surrounding the basic cluster, for which an all electron description
is used, are represented with *ab initio* Embedded Model Potentials (AIEMP) \[44,45\]. As suggested in Chapter 2 of the dissertation we add \((1s,1p)\) valence basis functions to the oxygen, iron and nickel ions \[49\], that are modeled with an AIEMP. In addition, the long-range electrostatic interactions are considered with a set of optimized point charges that reproduce the Madelung field in the cluster region arising from the rest of the crystal. The Madelung field in the cluster region is computed assuming \(\text{Fe}^{4+}, \text{Ni}^{3+}, \text{O}^{2-}, \text{Y}^{3+}\) and \(\text{Ca}^{2+}\) point ions for \(\text{CaFeO}_3\) and \(\text{YNiO}_3\) crystals. The choice is motivated for consistency with results presented in previous chapters.

The one-electron basis sets for the iron and nickel ions employed in embedded cluster study are derived from a \((21s, 15p, 10d, 6f)\) primitive basis set. \((14s, 9p, 4d)\) primitive basis sets are used for the oxygens. Following the atomic natural orbital (ANO-L) contraction of Roos and co-workers \[78\], we obtain a \((6s, 5p, 4d, 1f)\) contracted basis for Fe, Ni and a \((4s, 3p, 1d)\) contracted basis for O. We approximate the exact N-electron wave function of cluster electrons using the CASSCF method as discussed in chapter 2. The method exploits a division of the orbital space into inactive, active and virtual orbitals. We performed, as done from the beginning of this dissertation, CASSCF calculations including the 3d orbitals and a set of correlating 3d’ orbitals in the active space. Moreover, we included in the active space the bonding counterpart of the antibonding Fe-3d\((e_g)\) like orbitals. These bonding orbitals have mainly O-2p character. This leads to a CAS\((8,12)\)SCF for the \([\text{FeO}_6]^{8-}\) clusters and a CAS\((11,12)\)SCF for the \([\text{NiO}_6]^{9-}\) clusters. Using the CASSCF method, we perform a full CI in the active space and describe the remaining electrons using doubly occupied orbitals. The remaining dynamical correlation, which is mainly due to atomic effects, is considered with second order perturbation theory, using the CASSCF wave function as zero order wave function.

For the description of possible ordering of charges a \([\text{Ni}_4\text{O}_{18}]^{24-}\) cluster was considered. The \(\text{Ni} 3d(e_g)\) like orbitals are in the active space, while keeping the 3d\((t_{2g})\) orbitals doubly occupied. The resulting CAS\((4,8)\)SCF calculation for the \([\text{Ni}_4\text{O}_{18}]^{24-}\) cluster is used to determine the ground state for this four magnetic center cluster and also investigate the electronic charge distribution in a charge disproportionated phase. Prior to this study
we performed a set of calculations where the corresponding bonding O-2p\((e_g)\) orbitals are included in the active space, leading to a CAS(20,12)SCF to get a better estimation of the ligand to metal charge transfer in our reference wave function. This active space, which contains 20 active electrons is still not as accurate as that of the one-center cluster, where all Ni-3d and also the Ni-3d’ orbitals are included in the active space. Hence we cannot directly compare the analysis in terms of charge-transfer contributions of the one-center and four-center clusters since in the four-center cluster we do not include all the configurations to describe completely the charge transfer processes in the extended cluster.

The embedding of the \([\text{Ni}_4\text{O}_{18}]^{24-}\) is analogous to that of the \([\text{NiO}_6]^{9-}\) cluster, with the ions directly surrounding the cluster described by AIEMP and the Madelung field computed assuming Ni\(^{3+}\), O\(^{2-}\) and Y\(^{3+}\) point charges. The embedding was used for all electronic states of the cluster, i.e. also for the calculations in search of charge-ordered state. The motivation for not changing the magnitude of the embedding point charges is that the number of electrons in the vicinity of the TM nuclei varies much less than the formal ionic charge. See for example Table 3.3 and the discussion in Chapter 3.

6.3 Results

6.3.1 Periodic approach: Electronic structure

The results of periodic electronic structure calculations are often visualized with the aid of a band structure plot, which represents the evolution of the crystal orbital energies in the first Brillouin zone. The spin unrestricted HF (UHF) and spin unrestricted DFT (B3LYP) (abbreviated B3LYP in the following) band structures [146] show that the composition of the valence and conduction bands are completely different for the two methods. The B3LYP study gives a much richer band structure close to the Fermi level. Detailed information can also be obtained from the density of states (DOS) as a function of energy that are reported in Figures 6.2 and 6.3. The total DOS as well as the TM-3d and O-2p contributions to the DOS, the so-called Local density of states LDOS, are presented.
Structural parameters reported by Woodward et al. [4] and Alonso et al. [5] were used for the ferromagnetic (FM) spin alignment with total spin per unit cell equal to 16 for CaFeO$_3$ and equal to 4 for YNiO$_3$, respectively. The total density of states (DOS) obtained from UHF and B3LYP calculations show some similarity to the DOS reported for the LaMnO$_3$ crystal [30]. The difference between these crystals, which are characterized with different type of local distortions, is seen from the local density of states (LDOS). In the present case the TM-3d contributions are shown separately for the two distinct TM ions (TM(1) and TM(2)). These are found to be in a different energy range. Following tradition, spin-up densities of states are shown as positive densities, whereas spin-down densities are shown as negative densities. We note a higher spin-down density in Figures 6.2 and 6.3, for YNiO$_3$ as compared to CaFeO$_3$. This is of course due to the completely filled Ni t$_{2g}$ orbitals.

Comparing the results for both methods reveals rather large differences. All calculations predict the correct insulating character as could be anticipated from previous calculations on similar crystals [30, 141]. From the total DOS results, we see that the band gaps produced by UHF results are much larger than those of the corresponding B3LYP calculations. Such differences are well known since they have been observed in earlier \textit{ab initio} calculations considering Hartree-Fock and DFT with a hybrid functional (see for example the works on NiO by Moreira \textit{et. al.} [86], on LaMnO$_3$ by Muñoz \textit{et. al.} [30], and on several copper compounds by Moreira \textit{et. al.} [141]). For example, the calculated band gap of LaMnO$_3$ is calculated to be extremely sensitive to the treatment of the exchange and correlation. UHF predicts $\Delta=13$ eV, which is much larger than the observed $\Delta=1.7$ (see [30] and references therein). The band gap according to the LDA implementation of DFT for LaMnO$_3$ is 0.2 eV. The introduction of Fock exchange has a very large effect. The magnitude of the band gap predicted by different DFT methods varies with the amount of Fock exchange although not in a linear way. The B3LYP functionals predict values of $\Delta$ which are reasonably close to experiment, UHF and LDA represent extremes of an overestimation and underestimation of the band gap.

The UHF LDOS exhibit a very large contribution of the occupied oxygen states near the Fermi energy while the contribution of the TM-3d orbitals is negligible. The B3LYP
calculations show that the DOS near the Fermi energy is of mixed TM-3d and O-2p character as suggested by LDA+U calculations reported by Saha-Dasgupta et al. [31]. The B3LYP DOS show below the Fermi level a quasi-similar energy range for the TM and oxygen density of states, indicating stronger covalent bonding than in UHF results. The B3LYP calculated gap is also reduced compared to UHF leading to an insulating state with a gap of 0.8 eV for the ferromagnetic phase of CaFeO₃ crystal and a gap of 1.1 eV for the YNiO₃ crystal. YNiO₃ described with DFT (B3LYP) within the periodic approach, yields stronger overlap between Ni-3d and oxygen contributions to the total density of states compared to CaFeO₃.

Table 6.1 reports the Mulliken population analysis calculated for the TM ions using periodic approach. For CaFeO₃ and YNiO₃, the two chemically different TM ions are denoted by TM(1) and TM(2) where (1) denotes the TM ion site with smaller TM-O bond lengths with respect to the high temperature phase and (2) the TM site with larger TM-O bond lengths. The interpretation of Mulliken gross populations (MP) in terms of effective charges should be avoided when using large atomic basis sets as is done here (See also the discussion in Chapter 3). Differences in gross populations of centers, described with the same basis set and in a similar environment are, however, an indication of a different electron distribution around the centers. In the present case the MP are calculated to be quite similar for both TM centers in CaFeO₃ and in YNiO₃, independently of the method used. Although there is no direct connection with atomic charges, it is clear that UHF results for CaFeO₃ give smaller Mulliken gross population (MP) at the TM ions than B3LYP and therewith a more ionic picture of the bonding. The differences are smaller for the YNiO₃ crystal.

The gross unpaired spin population ($\mu$) in the UHF description does not show large differences between the two TM ions. The spin populations are calculated to be a bit lower in TM(1) sites, which have smaller octahedral coordination. This is different for the B3LYP method for which a larger difference in spin population between the two TM centers is calculated. The increase in population in going from UHF to B3LYP reflects the delocalization of the spin density. The low value of the B3LYP spin population in the
Temperature phase (15 K) Figure 6.2: Total and projected density of states (DOS) on the Fe(1), Fe(2) and O basis sets for CaFeO₃ crystal in the low.
Figure 6.3: Total and projected density of states (DOS) on the Ni(1), Ni(2) and O basis sets for YNiO$_3$ crystals in the low temperature phase (513 K).
small octahedra, TM(1), can be attributed to a strong overlap between Fe(d) and O(p) basis functions, i.e. an artifact of the Mulliken analysis. This is not seen in the UHF results because the O(p) basis functions play a minor role since the spin density is more localized. The stronger covalency in the small octahedron could easily lead to a misinterpretation of the number of unpaired 3d electrons. The total populations (MP) and the d populations (d) on both TM ions are calculated to be similar leading to the conclusion that B3LYP solution is expressed with crystal orbitals that have different mixed TM-3d and oxygen character for the two different TM ions.

### 6.3.2 Embedded cluster approach

We consider in the following the CaFeO$_3$ and YNiO$_3$ crystals in their distorted low-temperature phase using the embedded cluster approach. We first consider one-center clusters to investigate local charge transfer effects. Secondly, we investigate the charge distribution using a four-center cluster. The results are compared to the periodic calculations discussed above.

#### One-center clusters

Embedded ML$_n$ clusters are used to identify the character of the ground state in a first exploratory set of calculations in which we assume that the number of electrons assigned to the clusters can be taken to be the same as in the high temperature phase. Note that
6.3. Results

this assumption implies that no charge ordering exists. We consider four different [TMO$_6$] clusters that represent the Fe and Ni ions in their large and small octahedral oxygen shells as reported by X-ray experiments [4, 5]. Using these clusters we investigate the local electronic configurations of lowest energy using the *ab initio* CASSCF method. The cluster embedding as described in Section 6.2.2 is used to reproduce the effect of the rest of the crystal.

Calculations on [FeO$_6$]$^{8-}$ clusters representing the TM in a small octahedron of CaFeO$_3$ in the 15 K lattice structure show that the $^5$E$_g$ state becomes almost degenerate with the $^3$T$_{1g}$ state at (0.09 eV) (see Table 6.2) but $^5$E$_g$ remains the ground state. On the contrary for the large octahedron the difference in energy between $^5$E$_g$ and $^3$T$_{1g}$ increases to 0.42 eV compared to 0.24 eV in the high temperature phase (see Table 4.2).

Calculations on [NiO$_6$]$^{9-}$ clusters representing the YNiO$_3$ crystal at 513 K are done in an analogous way. In both crystallographic sites, the ground state is calculated to be $^2$E$_g$ with a low spin $t_{2g}^{6}$ e$_g^{1}$ configuration for the Ni ions. The first excited state, $^4$T$_{1g}$, corresponding mainly to the high spin configuration $t_{2g}^{5}$ e$_g^{2}$, is almost degenerate at the CASSCF level in the small octahedron but the inclusion of the dynamical electron correlation increases the low-spin–high-spin energy difference to approximatively 0.5 eV. At the CASPT2 level of approximation, the energy difference is calculated to be larger showing that there is no doubt that $^2$E$_g$ is the ground state. We note that excitation in the two compounds have quite different character. In CaFeO$_3$ the transition is from high spin to low spin and the crystal field splitting has to be brought up. For Ni ions in YNiO$_3$ it is the inverse. The transition is from low spin to high spin and the crystal field splitting is gained.

The Mulliken population analysis of the active orbitals for the $^5$E$_g$ and $^2$E$_g$ ground states of CaFeO$_3$ and YNiO$_3$ are reported in Table 6.3. The populations reflect a higher mixing with O-2p ligands in the [FeO$_6$]$^{8-}$ compared to [NiO$_6$]$^{9-}$, which suggest a higher covalent character in the Fe compounds. This is to be expected, due to the higher formal charge of Fe$^{4+}$ in CaFeO$_3$ as compared to Ni$^{3+}$ in YNiO$_3$. We see small differences in occupation number and orbital mixing for small en large octahedron.

The ground state wave function, expressed with localized orbitals (see Table 6.4) shows
Table 6.2: Relative energies for the four $[\text{TMO}_6]^{n-}$ clusters using CAS(8,12)SCF as reference wave function representing CaFeO$_3$ at 15 K and YNiO$_3$ at 513 K using CAS(11,12)SCF as reference wave function. $\Delta E$ represents the difference in energy (eV) between the $^5E_g$ (ground state) and $^3T_{2g}$ for CaFeO$_3$ and the difference between the $^2E_g$ (ground state) and $^4T_{1g}$ for YNiO$_3$

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Cluster</th>
<th>Average TM-O Bond length in Å</th>
<th>$\Delta E$ in eV $^1$</th>
<th>CASSCF</th>
<th>CASPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFeO$_3$</td>
<td>$[\text{FeO}_6]^{8-}$</td>
<td>1.872</td>
<td>0.09, 0.13, 0.20</td>
<td>0.10; 0.13; 0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.974</td>
<td>0.50, 0.55, 0.61</td>
<td>0.43; 0.49; 0.55</td>
<td></td>
</tr>
<tr>
<td>YNiO$_3$</td>
<td>$[\text{NiO}_6]^{9-}$</td>
<td>1.916</td>
<td>0.09, 0.15, 0.24</td>
<td>0.43, 0.48, 0.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.009</td>
<td>0.21, 0.25, 0.34</td>
<td>0.53, 0.55, 0.65</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: Mulliken population analysis and occupation number of the natural $e_g$ like active orbitals in the ground state wave function of the TMO$_6$ cluster representing CaFeO$_3$ at 15 K and YNiO$_3$ at 513 K.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Orbital</th>
<th>Occ. Number</th>
<th>TM-3d</th>
<th>O-2p</th>
<th>Occ. Number</th>
<th>TM-3d</th>
<th>O-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFeO$_3$</td>
<td>$e_g$</td>
<td>3.84</td>
<td>0.33</td>
<td>0.67</td>
<td>3.75</td>
<td>0.34</td>
<td>0.66</td>
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<tr>
<td></td>
<td>$t^*_{2g}$</td>
<td>2.99</td>
<td>0.96</td>
<td>0.04</td>
<td>2.99</td>
<td>0.97</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>$e^*_{g}$</td>
<td>1.16</td>
<td>0.68</td>
<td>0.32</td>
<td>1.24</td>
<td>0.66</td>
<td>0.34</td>
</tr>
<tr>
<td>YNiO$_3$</td>
<td>$e_g$</td>
<td>3.91</td>
<td>0.23</td>
<td>0.77</td>
<td>3.87</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>$t^*_{2g}$</td>
<td>5.93</td>
<td>0.99</td>
<td>0.01</td>
<td>5.95</td>
<td>0.99</td>
<td>0.01</td>
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<tr>
<td></td>
<td>$e^*_{g}$</td>
<td>1.11</td>
<td>0.75</td>
<td>0.25</td>
<td>1.15</td>
<td>0.73</td>
<td>0.27</td>
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</table>

that charge transfer configurations are dominant for CaFeO$_3$ and important for YNiO$_3$. The d-count, an approximation for number of electrons in the d-shell of the Fe ions (see Chapter 3, is equal to 5.11 and 5.14 for the large and small environment respectively. This is almost the same number of Fe-3d electrons as calculated for the high temperature phase as discussed in Chapter 3. The d-count obtained from the analysis in terms of optimized atomic orbitals assumes the number of d electrons in the $t^*_{2g}$ orbitals to be three, this is slight overestimation. The same analysis on the two-nickel clusters reveals that the Ni ions have also almost the same number of electrons in their 3d shell. It differs by only 0.16 electrons. We report also the 3d Mulliken population analysis calculated by summing the product of the occupation numbers and the TM-3d weight of the orbitals listed in Table 6.3.
For YNiO$_3$ and CaFeO$_3$ the d-count is somewhat larger than the Mulliken 3d population. The difference between CaFeO$_3$ and YNiO$_3$ is seen in the population analysis reported in Table 6.4 together with d-count analysis of the wave function expressed with localized orbitals. In the two crystallographic environments a difference in the contributions of ligand to metal charge transfer configurations is observed, which turn out to be larger in the large octahedron. This suggests a slightly larger covalency in the large octahedra, as expected.

### Table 6.4: Decomposition of the CASSCF wave function (in %) in terms of the valence bond determinants, calculated TM-3d population from localized orbital analysis (d-count) and Mulliken population analysis

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Average TM-O Bond length in Å</th>
<th>NCT</th>
<th>CT</th>
<th>DCT</th>
<th>d-count</th>
<th>Mulliken 3d population</th>
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</thead>
<tbody>
<tr>
<td>CaFeO$_3$</td>
<td>1.872</td>
<td>13.2</td>
<td>60.9</td>
<td>23.7</td>
<td>5.11</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td>1.974</td>
<td>9.4</td>
<td>65.3</td>
<td>23.3</td>
<td>5.14</td>
<td>5.02</td>
</tr>
<tr>
<td>YNiO$_3$</td>
<td>1.916</td>
<td>61.2</td>
<td>34.5</td>
<td>2.8</td>
<td>7.29</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>2.009</td>
<td>48.1</td>
<td>46.8</td>
<td>3.7</td>
<td>7.45</td>
<td>7.71</td>
</tr>
</tbody>
</table>

### Four-center cluster

In order to get a better description of the electron distribution around the TM ions without putting a fixed number of electrons in a small cluster, we increased the cluster size to four TM ions in the ab plane and the eighteen nearest oxygen ligands. This was feasible only for the YNiO$_3$ crystal. The reason is that the Ni ions possess fully occupied t$_{2g}$ orbitals, which enable us to consider these orbitals as inactive orbitals. The resulting [Ni$_4$O$_{18}$]$^{24-}$ cluster has C$_i$ symmetry and is shown in Fig. 6.1.

The relative energies of the lowest states were calculated with a CAS(4,4)SCF wave function. There are six nearly degenerate low-lying states with different spin couplings between the four Ni centers: one spin quintet, three spin triplets and two spin singlets. The $^1A_g$ state is the lowest state of the cluster. The $^5A_g$ state, which corresponds to ferromagnetic spin coupling in the ab plane is calculated to be 43 meV above the ground
state. The first triplet state (3A_g) is at 19 meV above the ground state. The complete energy spectrum of the six nearly degenerate states would allow to determine all first and second neighbor magnetic interactions. Neglecting all second neighbor and four-body terms [39], the magnetic coupling constant J in the Heisenberg hamiltonian can be obtained from the energy difference between the quintet and the lowest triplet: E(3A_g) - E(5A_g) = 2J, leading to J_{CAS} \approx -12 \text{ meV}, which seems reasonable in comparison to NiO (J_{CAS} \approx -5 \text{ meV}) and La_2NiO_4 (J_{CAS} \approx -8 \text{ meV}). YNiO_3 is more covalent than NiO or La_2NiO_4 and hence a larger J is expected. Experience shows that the CASPT2 significantly enhances J in comparison to CASSCF.

Table 6.5: Mulliken population analysis and occupation number $n$ of the natural active orbitals of the $^1A_g$ (ground state) representing YNiO_3 of a [Ni_4O_{18}]^{24-} cluster.

<table>
<thead>
<tr>
<th>Orbital Occ. Number</th>
<th>Ni(1)-3d</th>
<th>Ni(2)-3d</th>
<th>O-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 a_g</td>
<td>1.00</td>
<td>0.70</td>
<td>0.23</td>
</tr>
<tr>
<td>76 a_g</td>
<td>1.00</td>
<td>0.21</td>
<td>0.67</td>
</tr>
<tr>
<td>75 a_u</td>
<td>1.00</td>
<td>0.60</td>
<td>0.31</td>
</tr>
<tr>
<td>76 a_u</td>
<td>1.00</td>
<td>0.31</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Table 6.6: Mulliken population analysis of the projected orbitals $^1A_g$ (ground state) of a [Ni_4O_{18}]^{24-} cluster representing YNiO_3.

<table>
<thead>
<tr>
<th>Orbital Occ. Number</th>
<th>Ni(1)-3d</th>
<th>Ni(2)-3d</th>
<th>O-2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 a_g</td>
<td>0.96</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>76 a_g</td>
<td>0.00</td>
<td>0.96</td>
<td>0.02</td>
</tr>
<tr>
<td>75 a_u</td>
<td>0.96</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>76 a_u</td>
<td>0.00</td>
<td>0.96</td>
<td>0.01</td>
</tr>
</tbody>
</table>

For a next set of calculations we increased the active space with the eight bonding O-2p(e_g) orbitals. The aim of these CAS(20,12)SCF calculations is the determination of the relative importance of orbital mixing in the large and small octahedron using one cluster instead of the two separate clusters discussed before. The corresponding Mulliken population analysis for the orbitals of mainly TM-3d is reported in Table 6.5. It gives an
indication of the mixed character of the TM-3d and O-2p contributions. The TM-3d and O-2p mixing is lower compared to the one-center clusters discussed before. This effect is expected to originate from the different active space, which for the four-center cluster does not include the TM-3d’ orbitals, which enable ligand to metal charge transfer processes. Moreover the TM-3d(t_{2g}) are also not considered in the active space. Inclusion of these orbitals is also expected to slightly enhance the ligand to metal charge transfer.

To analyze the N-electron wave function and quantify the role of the charge transfer configurations, we performed a projection of the natural orbitals (see Figure 6.4) onto the 3d-TM basis functions. This projection is followed by an orthogonalization procedure that recovers an orthogonal set of active orbitals with localized Ni-3d orbitals (see Figure 6.5). The resulting molecular orbitals that are shown in Figure 6.5 yield the Mulliken population analysis reported in Table 6.6. This unitary transformation is in the same line as the two-by-two rotation presented from the beginning of this dissertation. It leads to the same wave function, i.e. the same total energy but expressed in terms of an increased number of configuration state functions. The wave function expressed in terms of these localized orbitals enables simpler interpretations in terms of atomic contribution to the wave function. The leading configuration (weight = 54 %) corresponds to antiferromagnetic arrangements of the electrons between the TM(1) and TM(2) ions. Unfortunately, we were not able to tune the projection to obtain active orbitals with a TM-3d weight above 96 %. This is not enough to estimate the number of electrons in the 3d-TM shell via the procedure described in Chapter 3.

In order to check that the electron distribution really represents the lowest states, we performed further calculations on the quintet state of [Ni_{4}O_{18}]^{24-} considering all Ni-3d(e_{g}) orbitals using a small CAS(4,8)SCF. The quintet state is simpler from a computational point of view and the electron distributions around the Ni ions are practically the same as in the lowest singlet state. The second set of Ni-3d(e_{g}) orbitals is only weakly occupied in the ground state. However, optimizing the orbitals for an average of states allows us to obtain a set of active orbitals with the desired character.

When considering the extended cluster, the calculated Mulliken charges show effectively
Figure 6.4: Natural active orbitals of a CAS(20,12)SCF for a \([M_4L_{18}]^{24-}\) cluster representing YNiO$_3$. 
6.3. Results

Figure 6.5: Localized Ni-3d(e_g) orbitals from a projection of the natural orbitals of a CAS(20,12)SCF calculation for a [M_4L_{18}]^{21-} cluster representing YNiO_3.

a small variation of charges. The Mulliken gross population is calculated to be respectively 27.4 and 27.5 for the Ni(1) and Ni(2) ions. The difference of only 0.1 electron confirms the conclusions from the periodic and one-center cluster studies discussed before. The number of electrons present in a sphere of 3.0 bohr is calculated to be 26.31 for the Ni(1) and 26.49 for Ni(2) ions. This also suggests that no significant charge disproportionation has
occurred between Ni(1) and Ni(2). We conclude that the transition to the low temperature crystal structure is not accompanied by significant metal to metal charge transfer.

6.4 Discussion and outlook

We start the discussion by considering the results of the calculations in the cluster approach and then compare to periodic calculations to firmly establish the interpretation of the electronic structure derived from the cluster calculations. The first remarkable point of the one-center cluster is the difference in the covalent character of the TM-O bond in the small and large octahedron. For both [FeO$_6$]$^{8-}$-clusters, we find a high spin $^5$E$_g$ ground state corresponding to a weak field $t_{2g}^3 e_g^1$ configuration for the Fe site. The energy difference with the first excited state, which is $^3T_{1g}$, i.e. low spin, strong field, is only 0.1 eV. However, as we argued in Chapter 4, this energy difference is probably slightly underestimated. The two [NiO$_6$]$^{9-}$ clusters both have a low spin, strong field $^2$E$_g$ ground state corresponding to $t_{2g}^6 e_g^1$. The high spin weak field first excited state, $^4T_{1g}$, is at about 0.5 eV. These results show that it is unlikely that the transition to the low temperature structure is accompanied by spin-flip transitions at the TM sites, neither for CaFeO$_3$ nor for YNiO$_3$. The bonding in the large octahedra, TM(2), is somewhat more covalent than the bonding in the small octahedra TM(1). This is evidenced in terms of localized orbitals by larger weights of CT configurations, or, alternatively, by somewhat larger d-population. Furthermore, the results also suggest an almost equivalent charge of the TM ions at the different crystallographic sites. This seems to be in contradiction with the Mössbauer spectrum of the low-temperature phase of CaFeO$_3$. This spectrum shows two distinct signals, which has been interpreted as the signature of two differently charged Fe sites in the crystal. Based on the findings described in Chapter 3, we calculated the isomer shift of the Fe ions in the large and small octahedron from the density at the Fe nucleus. The embedded cluster calculations give $\rho(0) = 11824.194$ and 11825.009 for the large and small octahedron, respectively. With the relation given in Fig. 3.1, we obtain IS=-0.01 and -0.23 mm·s$^{-1}$ in reasonable agreement with the experimental values of 0.31
and -0.03 mm s\(^{-1}\). More important is the fact that we are able to reproduce the difference between the two isomer shifts. This shows that Fe sites with the same effective charge can have different isomer shifts. Recalling the fact that \(\rho(0)\) is largely affected by the weight of the CT configurations in the wave function (see Table 3.4), it is clear that the two different isomer shifts observed in the LT phase of CaFeO\(_3\) can be ascribed to the difference in CT weight in the two octahedra.

To get a description of the electronic distribution without assigning a fixed number of electrons to the TMO\(_6\) octahedra, we performed calculations on a four-center cluster representing YNiO\(_3\) in the distorted phase (582 K). These calculations confirm the information obtained from the one-center clusters that the two types of TM ions in YNiO\(_3\) have similar 3d populations. The distortion observed in this crystal is not accompanied by a change of charge but, instead, with a change of the TM–O bonding with a slightly more covalent character for TM(2) i.e. for the larger octahedra. Comparison with the periodic approach confirms these conclusions. Both the UHF and the B3LYP results give similar d populations as well as total populations for the two different TM sites. This is true for YNiO\(_3\) and CaFeO\(_3\). The B3LYP densities at the iron nucleus \(\rho(0)\) are 11583.890 and 11581.510. Since there is a linear correlation between \(\rho(0)\) and the isomer shift, these different calculated densities are in line with the observation of two different isomer shifts for the low-temperature phase of CaFeO\(_3\). They confirm also the embedded cluster results. The computed populations reveal a good description of the electronic charge distribution using B3LYP formalism. In summary, all periodic and embedded cluster calculations confirm the different importance of charge transfer in the two different octahedral environments. This implies a change of covalent character at the transition metal sites without any significant change in the Ni-3d populations.

A start has been made with calculations on the four-center cluster to find the relative energy of a state with approximately two electrons in the Ni(2)-3d(e\(_g\)) orbitals and close to zero electrons in the Ni(1)-3d(e\(_g\)) orbitals. We expect the alternation to be reflected in the spin populations rather than in the total charge of the two metal sites. It is to be expected that the dynamical correlation effects are important for the relative energy. These will be
estimated using one-center clusters. A second objective is a more conclusive analysis of the charge transfer character in the ground state of the four-center cluster. Attention will be focused on the difference in charge transfer contributions in the large and the small octahedron.

6.5 Conclusions

In many studies, the structural changes in CaFeO$_3$ and YNiO$_3$ with decreasing temperature have been interpreted as being accompanied by an ordering of the charges on the TM ions [4, 5]. Charge disproportionation at the TM site was suggested as the origin of an alternative type of distortion with respect to JT type distortions, which maintains the same charges on all TM centers. This study clearly establishes that the Fe and Ni centers keep the same number of electrons in their 3d-shell in the whole temperature range and only a small change in covalent character of the ground state electron distribution is enough to lead to two non-equivalent centers.

The analysis of periodic solutions using UHF and hybrid functional DFT demonstrates that there is no reason to consider different charges for the TM ions. The relative difference of Mulliken charges is calculated to be almost negligible. However the difference in the total spin population suggests effectively a difference in the importance of the ligand to metal charge transfer.

Embedded cluster calculations agree with an almost equal d-count on the two types of Fe ions for CaFeO$_3$ and the two types of Ni ions for YNiO$_3$ in the low-temperature phase. The electronic configuration on both Fe sites is dominated by d$^5$L$^{-1}$ configurations, but the Fe site at the center of the large octahedron shows a significantly larger contribution of both the CT (d$^5$L$^{-1}$) and DCT (d$^6$L$^{-2}$) configurations indicating stronger covalency. In YNiO$_3$ the d$^8$L$^{-1}$ configuration is less important. This can be understood from the smaller valency of the Ni in the NCT (d$^7$) configuration. This more pronounced character in the large octahedron is in the line with the simple one-electron reasoning that the e$_g^*$ orbitals (which get populated in the ligand-to-metal charge transfer process) have lower
orbital energy in the large octahedron and hence lower the energy of the CT and DCT configurations. Finally, the two different calculated densities at the Fe nucleus agree with the two different IS value observed in the Mössbauer spectrum in the low temperature phase. Using modern quantum mechanics tools to treat more accurately electron correlation demonstrates that the ligand to metal charge transfer can explain the differences observed in both nonequivalent crystallographic sites.