

Charge transfer effects and photoemission in transition metal oxides

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Abstract

The role of charge transfer effects in the X-ray photoelectron spectra of oxides has been studied using a newly developed *ab initio* model Hamiltonian description for MnO and NiO. The reason that these effects are a minor perturbation for MnO while they are extremely important for NiO is identified as an atomic property of the transition metal cations. This property is the energetic advantage of adding a d electron to the cations which increases rapidly for heavier metal atoms.

A knowledge of the character of states which have a core hole on the metal cation is essential for the interpretation of the X-ray photoelectron spectra, XPS, of these levels in transition metal, TM, ionic crystals [1–7]. The particular case of 3s holes on the TM is considered in this Letter. There is agreement that three physical mechanisms make the primary contributions to the electronic structure of these core hole states [5]; two of them are atomic and one is a solid state effect. However, there is not agreement about the relative importance of these mechanisms, especially concerning the role of the solid state effect [2–5] which involves charge transfer, CT, from the ligands to the ionized metal cation in order to screen the core hole. The disagreements relate to the extent to which this CT contributes to the XPS spectra. At one extreme, Hermsmeyer et al. [3] have argued that CT effects make a minor contribution to the 3s XPS

spectra of ionic Mn compounds and that this spectra can be described in terms of atomic effects. At the other extreme, Veal and Paulikas [2] have argued that states which are dominated by CT are observed in the 3s XPS spectra of all first row TM fluorides, including Mn, and that this solid state mechanism is essential to describe the XPS spectra. Recent cluster model theoretical studies [5,8] of the 3s XPS spectra of MnO through NiO indicate that while CT effects lead to only weak satellites for MnO, they make an important contribution for NiO. Our purpose in this paper is to identify the reason for the different importance of the CT effects between Mn and Ni ionic compounds. The reason is related to an atomic property which allows us to predict that CT effects will be less important for the XPS spectra of ionic compounds with lighter TMs and more important for those with heavier TMs.

For TM ionic compounds, CT involves configurations [9] denoted $3s^1 3d^{n+1} \underline{L}$ while the configurations where the ligand to 3d CT has not taken place are denoted $3s^1 3d^n$. For MnO and NiO, the initial, $3s^2 3d^n$, state before ionization is coupled to a maximal spin multiplicity. In the 3s XPS spectra, transitions are allowed to states where the open 3s shell is coupled spin parallel or anti-parallel to the d shell leading to high and low spin ionic states [1,2]. The high spin ionic states are well described by mixtures of the $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ configurations and only the charge transfer effects contribute; this is in contrast to the low spin states where atomic correlation effects are important [1,5–7]. Therefore, we report results for high spin ionic states of cluster models of MnO and NiO. Our major objective is to examine the extent to which the CT and the unscreened configurations mix. This mixing can be directly related to an observable property, namely the intensity of the XPS peaks. The initial states of TM ionic compounds are dominantly $3s^2 3d^n$ and the $3s^1 3d^n$ ionic configuration carries most of the intensity [5]. Hence if the mixing of the allowed configuration, $3s^1 3d^n$, with the CT configuration is small, the XPS intensity of the state which is dominantly $3s^1 3d^{n+1} \underline{L}$ will be weak. On the other hand, when the mixing is large, all final states will be intense.

The present results obtained with ab initio model Hamiltonians provide, for the first time, an interpretation of why the mixing may be large or small depending on the compound. This is possible since the matrix elements, ME, of the model Hamiltonian are not assumed or estimated, as has been done previously [2–4,7,9], but are determined using the full many electron Hamiltonian and ab initio wavefunctions for the $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ configurations. For both MnO and NiO, it is found that $3s^1 3d^n$ is lower in energy; however, the excitation energy to $3s^1 3d^{n+1} \underline{L}$, decreases for the heavier Ni. Further, it is found that the mixing of $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ is only modest for MnO while for it is quite large for NiO. This different mixing is fully consistent with XPS spectra [3,5] for MnO and NiO and with theoretical studies made using a parametrized model Hamiltonian [7] and using accurate ab initio wavefunctions [5,8]. We show that the change in this mixing occurs because the diagonal ME of $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ are much closer for NiO than for

MnO. The atomic property responsible for the change of the cluster ME is the fact that each d electron does not fully shield the nucleus and the effective nuclear charge seen by the d electrons becomes larger as one moves to the right in the TM row.

We use MnO_6 and NiO_6 clusters surrounded by point charges, PCs, to model MnO and NiO; the PCs are fit to reproduce the crystal Madelung potential [5,8,10]. The cluster geometry and bond distances are taken from the bulk crystals and the cluster symmetry is O_h . Consistent with their ionic character (see e.g. Refs. [10,11]), the charges before the 3s ionization are chosen as +2 for the metal cation and –12 for the O_6 unit with a total cluster charge of –10. Orbitals for the metal cation and the O_6 unit were expanded in a large set of Gaussian basis functions [5,8] which allowed accurate representations of the orbitals. For the metal cation, we used Hartree–Fock self-consistent field, SCF, orbitals for the $M^{3+}(3s^1 3p^6 3d^n)$ ion in the field of PCs representing the rest of the ionic crystal. The d electrons are crystal field split into t_{2g} and e_g levels and the open shell s and d electrons are coupled high spin. For the O_6 unit, we used SCF orbitals for an O_6^{12-} cluster in a $^1A_{1g}$ state with a filled p band. The O_6 cluster is in a PC environment which represents the remainder of the ionic crystal and in the center of the O_6 octahedron, there is a frozen M^{3+} cation. This embedding has the effect of keeping the O_6^{12-} orbitals orthogonal to the M^{3+} orbitals; thus, the number of d electrons is rigorously defined for configurations formed with these orbitals.

With this orbital basis, N -electron wavefunctions for $3s^1 3d^n$ or $3s^1 3d^{n+1} \underline{L}$ are formed. For the $3s^1 3d^n$ configurations, the orbital sets for M^{3+} and the closed shell O_6^{12-} are superimposed; the MnO_6 configuration is $3s^1 t_{2g}^3(d) e_g^2(d)$ and the NiO_6 configuration is $3s^1 t_{2g}^6(d) e_g^2(d)$. Recall that we restrict ourselves to high spin coupling. For the $3s^1 3d^n \underline{L}$ configurations, one electron is transferred from an O_6^{12-} orbital of 2p character into either the $t_{2g}(d)$ or $e_g(d)$ metal orbital. The choice of O_6^{12-} orbital from which the electron is removed is unique since there is only one 2p orbital of t_{2g} and one of e_g symmetry and since only t_{2g} to $t_{2g}(d)$ or e_g to $e_g(d)$ is possible. For MnO_6 , there are two CT configurations; the configurations are denoted $3s^1 t_{2g}^4(d) e_g^2(d) \underline{L}$ and $3s^1 t_{2g}^3(d) e_g^3(d) \underline{L}$. For NiO_6 , there is only one CT configuration,

Table 1

Diagonal, H_{ii} , and off-diagonal, H_{ij} , ab initio model Hamiltonian matrix elements, in eV

Cluster	Configuration	H_{ii}	H_{ij}		
MnO ₆	1. $3s^1 t_{2g}^3(d) e_g^2(d)$	H_{11}	0.0	–	
	2. $3s^1 t_{2g}^4(d) e_g^1(d)\underline{L}$	H_{22}	10.8	H_{12}	–2.5
	3. $3s^1 t_{2g}^5(d) e_g^0(d)\underline{L}$	H_{33}	9.2	H_{13}	+3.5
NiO ₆	1. $3s^1 t_{2g}^6(d) e_g^0(d)$	H_{11}	0.0	–	
	2. $3s^1 t_{2g}^5(d) e_g^1(d)\underline{L}$	H_{22}	5.5	H_{12}	+4.2

$3s^1 t_{2g}^6(d) e_g^0(d)\underline{L}$. With the choice of orthogonalization of the M and O₆ orbitals, the number of d electrons in these configurations is rigorously either n or $n + 1$. For these configurations, the diagonal and off-diagonal matrix elements, ME, are calculated exactly; they provide a definitive guide for identification of the important physical properties which influence the values of the ME.

The diagonal ME, H_{ii} , with H_{11} for $3s^1 3d^n$ set to 0 and the off-diagonal ME, H_{ij} , coupling $3s^1 3d^n$ and $3s^1 3d^{n+1}\underline{L}$ are given in Table 1. We consider first the results for MnO. In this case, the diagonal energies of the $3s^1 3d^6\underline{L}$ configurations are large and positive; they are ≈ 10 eV above the $3s^1 3d^5$ configuration. Our calculations, which do not use adjustable parameters, clearly show that $3s^1 3d^5$ is lower in energy than the $3s^1 3d^6\underline{L}$ configurations; thus, the assumption [2] that the configurations have the opposite energetic order is incorrect. Finally, the off-diagonal ME for MnO₆ are modest in magnitude and will not lead to a large mixing of the $3s^1 3d^5$ and $3s^1 3d^6\underline{L}$ configurations. The lowest state for MnO will be dominantly formed from $3s^1 3d^5$ with relatively small weights for $3s^1 3d^6\underline{L}$! On the other hand, the excited states will have only small admixtures of $3s^1 3d^5$, hence a low XPS intensity. The MnO 3s XPS spectra calculated using accurate cluster wavefunctions [8] show that there is a high spin CT satellite at ≈ 10 eV with a small intensity relative to the first, or main, peak, $I_{rel} = 0.04$. The ab initio model Hamiltonian results are consistent with these accurate results in that both predict only weak CT satellites at ≈ 10 eV above the main, dominantly $3s^1 3d^5$, peak. This is important agreement since the intensities, especially for weak satellites, are sensitive to the details of the initial and final, ionized, state wave-

functions. The consistency between the two sets of results shows that the ab initio model Hamiltonian correctly describes the large positive diagonal energy for the CT configurations and the modest off-diagonal ME.

The situation is very different for NiO. The $3s^1 3d^9\underline{L}$ CT configuration is still above the $3s^1 3d^8$ configuration but by only ≈ 5 eV or only one-half the excitation energy found for MnO; this is the major difference in the ab initio Hamiltonian matrices for these two systems. The off-diagonal ME, which is only slightly larger than for MnO, is comparable in magnitude to the energy difference between $3s^1 3d^8$ and $3s^1 3d^9\underline{L}$. Thus, these configurations will be strongly mixed in the two eigenfunctions for NiO and both states will have large XPS intensities. This is consistent with accurate theoretical results for NiO₅ where a high spin satellite with a large $I_{rel} = 0.25$ is found at ≈ 8 eV above the main state. Thus for NiO as well, the ab initio model Hamiltonian properly describes the main features of the interaction between the $3s^1 3d^n$ and $3s^1 3d^{n+1}\underline{L}$ configurations. Clearly, the change in the excitation energy,

$$\Delta E_i = H_{ii}(3s^1 3d^{n+1}\underline{L}) \cdot H_{11}(3s^1 3d^n), \quad (1)$$

is responsible for the different role of CT in MnO and NiO.

The major contributions to ΔE_i are: (1) The Madelung potential which favors high ionicity for both the anions and the cations. (2) The cost of removing an electron from free O²⁻ or the ionization potential, IP, from O²⁻(2p⁶) to O²⁻(2p⁵). And (3) the benefit of adding an electron to the d shell of the free metal cation or the electron affinity, EA, from 3dⁿ to 3dⁿ⁺¹. The Madelung potential favors the combination of M³⁺(3s¹3dⁿ) and O²⁻(2p⁶) over M²⁺(3s¹3dⁿ⁺¹) and O⁻(2p⁵) by twice the potential at the lattice sites. Because their lattice constant differ slightly, this contribution [12] to ΔE_i is +45.3 eV for MnO while it is +48.3 eV for NiO. Thus, the Madelung potential contributions to ΔE_i lead to an excitation energy for NiO which is larger by 3 eV than it is in MnO; this is the opposite direction to that found with the ab initio model Hamiltonian. Clearly, the other contributions to ΔE_i must offset the change caused by the Madelung potential. How-

Table 2

Energy ordering, ΔE in eV, of the $3d^n$ and $3d^{n+1}$ configurations of Mn and Ni cations for both $3s^1$ and $3s^2$ occupations. For $\Delta E < 0$, the energy of $3d^{n+1}$ is lower, see Eq. (2)

	Mn	Ni	Change
$\Delta E(3s^2)$	-11.2	-15.3	-4.0
$\Delta E(3s^1)$	-26.3	-32.4	-6.0

ever while the O^{2-} IP makes a significant contribution to the absolute value of ΔE_i , it cannot lead to changes in ΔE_i between MnO and NiO because its contribution is the same for all ionic oxides.

For the cation EA, we consider the cases where there is a $3s$ hole, $3s^1 3d^n$ to $3s^1 3d^{n+1}$, and where the $3s$ shell is filled, $3s^2 3d^n$ to $3s^2 3d^{n+1}$. The SCF energy has been computed for the highest spin multiplicity of each configuration as is appropriate for comparison with the high spin multiplets of the clusters. The atomic energy differences analogous to the excitation energies for the oxide clusters, ΔE_i ,

$$\Delta E(3s^2) = E(3s^2 3d^{n+1}) - E(3s^2 3d^n),$$

$$\Delta E(3s^1) = E(3s^1 3d^{n+1}) - E(3s^1 3d^n), \quad (2)$$

are given in Table 2. The negative values of ΔE indicate that the $3d^{n+1}$ configuration is lower in energy. The magnitude of the $\Delta E(3s^1)$ are larger than the $\Delta E(3s^2)$ because when there is only one $3s$ electron, the $3d$ electrons see a larger effective nuclear charge and the EA of $3s^1 3d^n$ is larger than the EA of $3s^2 3d^n$. The order of the cation energies, $\Delta E < 0$, is the opposite of the order for the diagonal energies of the ab initio model Hamiltonians. However, the oxide ΔE_i values also have contributions from the O^{2-} IP and the Madelung potential. It is the large, ≈ 45 eV, contribution from this latter effect which changes the sign of the ΔE in the oxides and leads to $3s^1 3d^{n+1} \underline{L}$ being higher in energy. The most important fact shown in Table 2 is that the ΔE are larger in magnitude, more negative, for Ni which has a larger nuclear charge, Z , than for Mn; the $3d^{n+1}$ configuration of Ni is lower in energy relative to the $3d^n$ configuration than is the case for Mn. The change in ΔE from Mn to Ni is -4 eV for $\Delta E(3s^2)$ and -6 eV for $\Delta E(3s^1)$, similar to the change in ΔE_i between MnO and NiO. Thus, the decrease in the excitation energy from $3s^1 3d^n$ to

$3s^1 3d^{n+1} \underline{L}$ is dominantly caused by the large increase in the EA of the $3d^n$ cation, a purely atomic effect.

Slater [13] showed that the effective nuclear charge seen by the $3d$ electrons, $Z_{\text{eff}}(3d)$, increases as one moves toward the heavier TMs. He argued that the contribution to the reduction of $Z_{\text{eff}}(3d)$ from a d shell with k electrons was $0.35(k-1)$. This reduction and other reductions due to the core, $1s$ to $3p$, electrons offset the bare nuclear charge. Thus for equivalent ionic configurations, $Z_{\text{eff}}(3d)$ for Ni is larger than that for Mn by $1.95 = 3 - 3(0.35)$. The smaller $Z_{\text{eff}}(3d)$ for Mn means that its EA will be smaller and, hence, the excitation energy to the CT configurations, $3s^1 3d^{n+1} \underline{L}$, will be larger. This explains why, for MnO, they are only a small perturbation on the atomic effects [1,3,8]. On the other hand, the larger $Z_{\text{eff}}(3d)$ for Ni means that its EA will be larger and this explains why the CT and $3s^1 3d^n$ configurations are very strongly mixed for NiO [5,8].

We have used the same $3d$ orbitals, optimized for the $3s^1 3d^n$ metal cation, to form both the $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ cluster wavefunctions. This choice was made so that a single set of orthogonal orbitals could be used to compute the ME of the ab initio model Hamiltonian; in this way, their calculation is simplified. Further, and even more important, the cluster configurations, $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$, formed with this orbital set are also orthogonal; the use of an orthogonal configuration space greatly simplifies the interpretation of the model Hamiltonian results.

However, an important measure of the value of model Hamiltonians, including the model Hamiltonian used in this work, is their ability to reproduce key features of the results obtained with the exact, many-electron, Schrödinger equation. But in order to obtain accurate cluster wavefunctions for this exact Hamiltonian, it is necessary to take into account, either explicitly or implicitly, orbital relaxation effects [14,15] for the different orbitals which may be needed to describe the $3s^1 3d^n$ and $3s^1 3d^{n+1} \underline{L}$ configurations. Indeed, in related work involving accurate configuration interaction, CI, wavefunctions for NiO [5,8,16] and for MnO [16], careful treatments of the orbital relaxation were made. These treatments included optimization of the metal $3d$ orbitals and, in addition, the work of de Graaf et al. [16] also included explicit localization of the O $2p$ hole for the

CT configuration in NiO. The results with the present *ab initio* model Hamiltonian treatment are quantitatively similar to those obtained with these accurate CI treatments [5,8,16], especially as concerns the mixing of the CT configurations into the various metal 3s hole final states of the clusters. The agreement of our *ab initio* model Hamiltonian results with the accurate CI results provides strong indication that this model Hamiltonian contains the essential physics to explain the trends in the importance of the CT configurations.

In summary, the importance and role of CT configurations in the XPS spectra, in particular for 3s core levels, of 3d TM oxides has been established. The fact that the CT configurations are a perturbation in the XPS spectra for the lighter TM oxide MnO while they are extremely important for the heavier TM oxide NiO is due largely to an atomic effect. The EA of the 3dⁿ TM cations increases as the nuclear charge of the TM increases because a 3d electron only incompletely shields the nuclear charge seen by the other d electrons. For crystals with similar lattice structures, we expect that this atomic effect will cause a trend with the CT configurations having minor importance in the XPS spectra on the left side of the TM row and major importance on the right side. Indeed for the cubic oxides, MnO, FeO, CoO, and NiO, such a trend has been found in recent studies [7,8].

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