Origin of the Chemical Shift in X-Ray Absorption Near-Edge Spectroscopy at the Mn K-Edge in Manganese Oxide Compounds

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ABSTRACT: The absorption edge in Mn K-edge X-ray absorption spectra of manganese oxide compounds shows a shift of several electronvolts in going from MnO through LaMnO₃ to CaMnO₃. On the other hand, in X-ray photoelectron spectra much smaller shifts are observed. To identify the mechanisms that cause the observed chemical shifts, 1s ionization as well as 1s → "4p" transition energies have been determined by electronic structure calculations on embedded Mn ions and embedded MnO₆ clusters. Systematic variation of the cluster geometry and the cluster embedding showed that the chemical shifts are predominantly determined by two effects: the changes in the Mn 3d occupation and the changes in the Madelung potential. The large chemical shift in the 1s → 4p transition energies between different materials occurs because the two effects do not compensate each other. The chemical shifts obtained for the embedded MnO₆ clusters agree reasonably with the experimental shifts. The small sensitivity to the material observed for the Mn 1s ionization energies is explained by the near cancellation of the effects of the Madelung potential and the 3d occupation of the Mn ion. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 91: 57–61, 2003

Key words: Mn oxide compounds; K-edge X-ray absorption spectra; Madelung potential; 3d occupation; 1s → 4p transition energies
study of the local electronic structure can provide important insight into the mechanisms responsible for the properties. Powerful experimental techniques for probing the local electronic structure are X-ray absorption and emission spectroscopies. Recently, a number of theoretical and experimental studies on the CMR systems have provoked a lively discussion of their local electronic structure [1–11].

In X-ray absorption near-edge structure (XANES) spectra of manganese oxides, distinct energy regions can be distinguished. The first ∼10 eV is related to the electronic structure of the absorbing atom, whereas the higher-energy part of the spectrum gives information about the local geometry of the absorbing atom through multiple scattering effects of the excited electron. The XANES spectra at the Mn K-edge of these materials contain a low-intensity region below the band edge. The lowest peaks in this pre-edge region are commonly attributed to empty transition metal 3d levels [5, 6, 9–11], whereas peaks in the higher pre-edge region are usually associated with localized Mn “4p-like” levels [5,6,11]. The edge is thought to be dominated by a 4p band. In the XANES spectra, an appreciable shift in the energy of the band edge can be observed in going from MnO through LaMnO3 to CaMnO3 [1]. On the other hand, the Mn 1s ionization energies [12–14] and Kβ emission energies from the 3p level [15] in these systems are much less sensitive to the material.

The inflection point of the absorption edge is at about 6542 eV in MnO [1, 16], whereas in the series La1−x,CaMnO3 this point shifts from 6551 to 6555 eV with increasing Ca content [1]. A comparable shift occurs for the pre-edge peak associated with localized 4p-like levels, whereas first prepeaks, associated with Mn 3d levels, do not show an appreciable shift. An explanation would be that the 1s → 4p transition energy in the series La1−x,CaMnO3 is 9–13 eV higher than in MnO. At first sight, this is surprising because one would expect 4p levels to be more strongly bound for a larger formal charge on the Mn ion (2+ in MnO, 3+ in LaMnO3, and 4+ in CaMnO3).

In this article, we study Mn 4p-like states by performing ab initio electronic structure calculations on embedded Mn ions and embedded octahedral MnO6 clusters. We use the results to explain the chemical shifts in the Mn K-edge threshold energies. We identify two different physical mechanisms, both related to the formal charge on Mn, that influence the chemical shift of core ionization and excitation processes. The first is the change in local valence electron distribution on going from MnO (formal occupation Mn d3) through LaMnO3 (Mn d4) to CaMnO3 (Mn d5); the second is the change in the Madelung potential.

Method

All-electron LCAO-MO restricted open-shell SCF calculations were performed with the MOLCAS-4 program package [17]. The basis sets used for Mn and O were the standard ANO-L basis sets of the MOLCAS library. For Mn [18], (21s15p10d) primitives were contracted to a [6s5p4d] set. For O [19], (14s9p) primitives were contracted to [4s3p]. Two different cluster models were used: embedded MnO6 clusters and, for comparison, single Mn ions embedded in a finite set of point charges at lattice positions representing the Madelung potential of the rest of the crystal. In calculations on the embedded MnO6 clusters, the nearest neighbors of the cluster O ions were represented by appropriate effective core potentials (ECPs) fitted [20] to represent closed-shell La (Y3+) for La3+ [21], Ca [22], or Mn ions (Mg2+ for Mn2+ [22], Al3+ for Mn3+ [22], and Si4+ for Mn4+ [23]). On these nearest-neighbor atoms, no valence basis functions were present. Depending on the material, the number and formal charge of the nearest-neighbor Mn ions varied. The next shells of ions surrounding the cluster were approximated by a finite number of point charges at lattice positions. The charges were taken from Ref. [20] for the rocksalt structure of MnO and constructed via a fitting procedure for the perovskite structures of LaMnO3 and CaMnO3. The first few shells of point charges around the cluster or the Mn ion were always taken to have the formal charges in a fully ionic model of the material. The charges at outermost shell point charges were fitted to get the best representation of the Madelung potential on a fine grid in the central part of the cluster.

For MnO, we used the rocksalt crystal structure, with Mn—O distances of 4.2 and 3.8 Bohr, respectively. The experimental Mn—O distances in MnO are 4.2 Bohr [24]. In addition, we used Mn—O distances of 3.8 Bohr for MnO because these are close to the Mn—O distances used for LaMnO3. LaMnO3 has a distorted perovskite structure [25], with three different Mn—O distances, and tilting of MnO6 octahedra. In this study, an idealized structure was used with uniform Mn—O distances of 3.81 Bohr and no tilting distortions. CaMnO3 also
TABLE I

1s ionization energies, 4p addition energies, and 1s → 4p excitation energies (eV) for free and embedded Mn ions.

<table>
<thead>
<tr>
<th>Mn ion</th>
<th>Embedding</th>
<th>R(Mn−O) (bohr)</th>
<th>1s ionization</th>
<th>4p addition</th>
<th>1s → 4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{2+}), 3d(^{6})</td>
<td>None</td>
<td></td>
<td>6537.7</td>
<td>−19.7</td>
<td>6518.0</td>
</tr>
<tr>
<td></td>
<td>MnO</td>
<td>4.2</td>
<td>6515.1</td>
<td>+1.8</td>
<td>6516.9</td>
</tr>
<tr>
<td></td>
<td>MnO</td>
<td>3.8</td>
<td>6512.9</td>
<td>+3.1</td>
<td>6516.0</td>
</tr>
<tr>
<td></td>
<td>LaMnO(_3)</td>
<td>3.81</td>
<td>6500.9</td>
<td>+14.8</td>
<td>6515.7</td>
</tr>
<tr>
<td></td>
<td>CaMnO(_3)</td>
<td>3.65</td>
<td>6492.0</td>
<td>+23.2</td>
<td>6515.2</td>
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<tr>
<td>Mn(^{3+}), 3d(^{4})</td>
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<td></td>
<td>6560.1</td>
<td>−30.6</td>
<td>6529.5</td>
</tr>
<tr>
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<td>MnO</td>
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<td>6537.5</td>
<td>−8.4</td>
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<tr>
<td></td>
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<td>6535.1</td>
<td>−7.1</td>
<td>6528.0</td>
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<tr>
<td></td>
<td>LaMnO(_3)</td>
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<td>6523.3</td>
<td>+4.6</td>
<td>6527.9</td>
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<tr>
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<td>CaMnO(_3)</td>
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<td>6513.4</td>
<td>+13.0</td>
<td>6526.4</td>
</tr>
<tr>
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<td></td>
<td>6585.4</td>
<td>−40.2</td>
<td>6545.2</td>
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<tr>
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<td>MnO</td>
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<td>6562.7</td>
<td>−18.6</td>
<td>6544.1</td>
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<td>6560.8</td>
<td>−17.3</td>
<td>6543.5</td>
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<td>LaMnO(_3)</td>
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<td>6549.0</td>
<td>−5.6</td>
<td>6543.4</td>
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<td>3.65</td>
<td>6539.3</td>
<td>+2.9</td>
<td>6542.2</td>
</tr>
</tbody>
</table>

Rows in bold: the ion charge, the Mn−O distance, as well as the Madelung embedding correspond to the same compound.

has a perovskite structure with tilted octahedra [26]. Also for this material, an idealized cubic embedding was employed. The Mn−O distances used for CaMnO\(_3\) were 3.65 bohr. The Mn−O distances used for the idealized structures were averaged values of the distances found in the experimental structures. The 1s-to-4p excited states were always taken to be maximum spin states. To ensure a well-defined 4p level in all material models studied here, an atomic 4p orbital was taken as a starting orbital in all calculations for the excited states. The atomic orbital was obtained from an SCF calculation on the lowest 1s-to-4p excited state of a free Mn\(^{2+}\), Mn\(^{3+}\), or Mn\(^{4+}\) ion. This orbital was orthogonalized to all occupied orbitals of the cluster ground state and subsequently kept frozen in the orbital optimization step for the 1s-to-4p excited state. The reason to freeze the 4p orbital is that its optimization in the small clusters used here may give rise to artificially large delocalization. Larger cluster models enable the study of excited states using optimized 4p-like orbitals. Such larger clusters were used in a separate study, undertaken to assign the fine structure of XANES experiments [11, 27].

Results and Discussion

The 1s ionization and 1s → 4p excitation energies of the free and embedded Mn ions are shown in Table I for various embeddings and 3d occupations. From Table I, it is clear that both the 1s ionization and the 4p addition energies of the ion are sensitive to the 3d occupation and to the embedding Madelung potential. The variations in the Madelung potential at Mn are almost completely reflected in the variations in the ionization energies of the localized 1s electron. The embedding potential has only a small influence on the 1s → 4p excitation energy (at most 3 eV), as one would expect for such excitations involving localized orbitals: The Madelung potential facilitates the removal of the 1s electron but hinders the addition of the 4p electron by approximately the same amount. The small variations are due to the more diffuse character of the 4p orbital.

The 3d occupation number also has a stronger influence on the 1s ionization than on the 4p addition energy. The cost involved in removing the 1s electron increases by more than 20 eV on increasing the charge on Mn, whereas the energy gain of 4p addition increases by ~10 eV for each increase of charge on the Mn ion. The reason for this difference is that the 4p orbital is more diffuse than the 1s orbital and therefore interacts more weakly with the other orbitals. The differential effect between 1s ionization and 4p addition of the 3d occupation is much stronger than that of the Madelung potential. Thus, for isolated Mn ions embedded in point charges the variation in 1s → 4p excitation energies along the series Mn\(_2\), LaMnO\(_3\), and CaMnO\(_3\) is predominantly due to the 3d occupa-
tion of the Mn ion. It shows an increase of \( \sim 10 \) eV per 3d electron removed from the Mn ion.

These results for single Mn ions in a Madelung potential overestimate largely the trends found in the true compounds. The increase in the 1s ionization is 8 eV in going from MnO to LaMnO\(_3\) and another 16 eV in going to CaMnO\(_3\), whereas observed core binding energies show shifts of only a few eV [12–14]. The reason for this is that in the real material the positive charges on the transition metal ions are screened by polarization of electrons from the ligands to the metal. Periodic Hartree–Fock calculations have shown that the changes around Mn are indeed considerably below the formal charge in LaMnO\(_3\) as well as CaMnO\(_3\) [29]. Consequently, the difference in charge around Mn between MnO and CaMnO\(_3\) is less than one electron. Part of this screening effect shows up already in the MnO\(_6\) cluster, where the first layer of O ions around the metal center is included in the cluster model. The results of the calculations for MnO\(_6\) are collected in Table II. As before, the 4p orbital is obtained from free ion calculations, orthogonalized to the occupied orbitals of the cluster ground state and subsequently kept frozen in the 1s-to-4p excited states.

It can be seen from Tables I and II that the chemical shift of the 1s \( \rightarrow \) 4p excitation energies with increasing charge is smaller for the embedded MnO\(_6\) clusters than for the embedded Mn ions. For example, the difference between Mn\(^{3+}\) and Mn\(^{2+}\) in an MnO embedding with Mn–O distances of 3.8 bohr is 12 eV (rows 8 and 2 in Table I). The corresponding difference between [MnO\(_6\)]\(^{3-}\) and [MnO\(_6\)]\(^{10-}\) in an MnO embedding with Mn–O distances of 3.8 bohr is only 6.4 eV (rows 3 and 2 in Table II). Further, in going from the MnO\(_6\) cluster models of MnO to LaMnO\(_3\), the change is \( \sim 8 \) eV rather than 11 eV obtained for the single ion models, and in going from LaMnO\(_3\) to CaMnO\(_3\) it is \( \sim 5 \) eV for the MnO\(_6\) clusters rather than the 14 eV for the single ions. Finally, we note that the shifts found for the MnO\(_6\) clusters are in reasonable agreement with the observed shifts in the threshold energies [1]. All changes are reduced in the MnO\(_6\) cluster, but the effect of the valence charge is more strongly reduced than the effect of the Madelung potential. This causes the 1s ionization energies to be much closer to each other. On the other hand, with the inclusion of the nearest O ligands in the models the Pauli repulsion of the 4p electron with the ligands enters the calculation as an extra effect, pushing the 1s \( \rightarrow \) 4p excitation energy up with decreasing Mn–O distance.

It is clear from Table II that the formal 3d occupation has the strongest influence on the excitation energy (+6 eV in the MnO\(_6\) cluster vs. +2 eV due to the potential) in the step from MnO to LaMnO\(_3\). The inclusion of the Pauli repulsion with the O ligands turns the slight overall decrease in the contribution of the Madelung potential (~1 eV) in the Mn ion model into an extra increase (+2 eV) in the MnO\(_6\) cluster model. In the step from LaMnO\(_3\) to CaMnO\(_3\), the effect of the d occupation is smaller (+2 eV), mainly because the actual 3d occupation is far from the formal occupation in the MnO\(_6\) cluster. Again, the inclusion of the Pauli repulsion with the O ligands turns the slight overall decrease found in the Madelung contribution (~1 eV) in the Mn ion model into an extra increase (+2 eV) in the MnO\(_6\) cluster model.

The absolute energies of the threshold calculated here are not directly comparable to the experimental values, mainly because of the use of a nonrelativistic Hamiltonian. This is a large effect because a 1s electron has a much larger kinetic energy than a

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**TABLE II**

1s ionization energies, 4p addition energies, and 1s \( \rightarrow \) 4p excitation energies (eV) for embedded MnO\(_6\) clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Formal 3d occupation</th>
<th>Embedding</th>
<th>R(Mn–O) (bohr)</th>
<th>1s ionization</th>
<th>4p addition</th>
<th>1s ( \rightarrow ) 4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnO(_6)](^{10-})</td>
<td>3d(^5)</td>
<td>MnO</td>
<td>4.2</td>
<td>6509.8</td>
<td>+8.1</td>
<td>6517.9</td>
</tr>
<tr>
<td>[MnO(_6)](^{9-})</td>
<td>3d(^4)</td>
<td>MnO</td>
<td>3.8</td>
<td>6506.3</td>
<td>+13.6</td>
<td>6519.9</td>
</tr>
<tr>
<td>[MnO(_6)](^{8-})</td>
<td>3d(^3)</td>
<td>LaMnO(_3)</td>
<td>3.81</td>
<td>6512.0</td>
<td>+14.0</td>
<td>6526.0</td>
</tr>
</tbody>
</table>

Rows in bold: the cluster charge, the Mn–O distance, as well as the Madelung embedding correspond to one and the same compound.
the same is true for the effects of the 3\textit{M}\textit{a}\textit{d}\textit{e}\textit{l}\textit{u}\textit{ng} potential.

From our results, this is only seen in the MnO\textsubscript{6} compensated, resulting in a small chemical shift. Changes due to the two mechanisms are largely compensating charge flow from the ligands to the increase of the formal charge on Mn due to a compensation charge around Mn, but the increase is less than the formal charge on Mn causes an increase of the local correlation effects are not included. Again, no large differential effects are expected because the nature of the orbitals involved is similar in all compounds.

Finally, we note that the first prepeaks associated with 1\textit{s}–3\textit{d} transitions are found at about the same positions for MnO, LaMnO\textsubscript{3}, and CaMnO\textsubscript{3} [5, 6, 11]. In our model, this is due to the localized character of the 3\textit{d} orbitals: The effects of the Madelung potential for 1\textit{s} ionization and 3\textit{d} addition cancel and the same is true for the effects of the 3\textit{d} occupation.

In summary, we identified two different physical mechanisms, both related to the formal charge on the Mn ions, that influence the chemical shift of Mn 1\textit{s} ionization and excitation processes. The first is the change in the valence electron distribution around the Mn ions in going from MnO through LaMnO\textsubscript{3} to CaMnO\textsubscript{3}; the second is the change in the Madelung potential.

For Mn core ionization, as in Mn 1\textit{s} XPS, the changes due to the two mechanisms are largely compensated, resulting in a small chemical shift. From our results, this is only seen in the MnO\textsubscript{6} cluster and not in the single Mn ion: Increasing the formal charge on Mn causes an increase of the local charge around Mn, but the increase is less than the increase of the formal charge on Mn due to a compensating charge flow from the ligands to the metal. The Madelung potential has only a small influence on the excitation energy because the excitation is still local. The effect of the valence charge is appreciable, however, despite the compensating charge flow from the ligands. This explains why the threshold energy in the XANES spectra increases along the series studied here, whereas the Mn XPS spectra only show a minor chemical shift.

References