X-ray spectroscopy at the Mn K edge in LaMnO₃: An ab initio study

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We present ab initio quantum chemical embedded cluster calculations of Mn core-valence and d-d transitions in LaMnO₃. The results are also important for the analysis of recent x-ray absorption and x-ray scattering experiments at the Mn K edge in LaMnO₃. We find that the first two peaks of the pre-edge region correspond to majority-spin and minority-spin $e_g(3d)$ states on adjacent Mn ions. For on-site 1s to 4p transitions we find that the ordering of the $p$ components is due to the Jahn-Teller distortion. We also show that the 1s $\rightarrow$ 4p transitions are split due to 3d-4p exchange interactions.

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LaMnO₃ is being intensively studied as parent compound of colossal magnetoresistance (CMR) perovskite-type manganites. Recently, Murakami et al.¹ reported to have found direct evidence of orbital ordering in LaMnO₃ by using dipole resonant x-ray diffraction at the Mn K edge. They argued that azimuthal-angle dependence and polarization plane flipping of the scattering at certain forbidden reflections probe 3d($e_g$) orbital ordering. A simple theory of the resonant scattering mechanism was also provided,¹ relating the peculiar angle dependence of the scattered intensity with the size of the splitting of the $x$, $y$, and $z$ components of the Mn-4p states. Two competing main mechanisms could cause the splitting: the Coulomb repulsion between the occupied 3d($e_g$) orbital and the 4p orbitals and, secondly, the Jahn-Teller (JT) distortion of the MnO₆ octahedra.

Ishihara et al.² have investigated the sensitivity of the Mn-4p levels to the on-site 3d electron orbital occupation by model Hamiltonian calculations on a [MnO₆] cluster. Their results indicate that the orbital dependence of the local 3d-4p Coulomb interaction is the dominant mechanism leading to anomalous x-ray scattering. In contrast, Benfatto et al.³ and Takahashi et al.⁴ have used model calculations to show that the JT distortion of the MnO₆ octahedra has the stronger effect on the 4p splitting and is the source of non-zero scattered intensity at forbidden reflections.

X-ray absorption near edge structure (XANES) measurements for LaMnO₃ samples⁵-⁷ have shown that three energy regions can be distinguished on the Mn K-edge spectrum. First, a low-intensity pre-edge region extending roughly from 6535 to 6550 eV. In this region, the lowest peaks (6537–6542 eV), labeled $A_1$ and $A_2$ in Ref. 5, are generally assumed to be caused by 1s to 3d transitions, while the higher energy feature labeled the $B$ peak (6543–6548 eV) is associated with Mn-4p states.⁵,⁶ Most of the spectral strength lies in the second energy region (6550–6560 eV), which is usually associated with the 4p band. Another resonance extends from 6560 to 6575 eV and was assigned to multiple-scattering events of the photoexcited electron.⁷ Very recently Qian et al.⁸ obtained spin-dependent features for pure and Ca-doped LaMnO₃.

Elfimov et al.⁹ have performed LSDA+U band structure calculations and studied the Mn-4p density of states corresponding to $p_x$, $p_y$, and $p_z$ components. They concluded that the pre-edge 3d features on the absorption spectra correspond to empty 3d states on adjacent Mn ions which hybridize with the 4p states on the parent Mn. Using these calculations as a guide, Bridges et al.⁵ interpret the lower pre-edge peaks observed in their high-resolution XANES measurements as transitions into majority-spin $e_g$ states and minority $e_g$ and $t_{2g}$ states on adjacent metal atoms. Takahashi et al.¹⁰ have studied by LDA band structure calculations the pre-K-edge region of the anomalous x-ray scattering and found a two-peak structure which reproduces well the so-called $A_1$ and $A_2$ peaks of Ref. 5. The two features are again explained in terms of mixing between 4p and neighboring 3d states, but the details are different: they correspond respectively to majority and minority-spin $e_g$ states.

In spite of the large number of studies devoted to LaMnO₃ no detailed information is available on the crystal field (CF) spectrum, and the magnitude of the CF and JT splittings have not been unambiguously established. Previous studies on related compounds¹¹,¹² have shown that advanced ab initio quantum chemical studies on embedded clusters give a very accurate prediction of the CF spectra. Here we present such a study of d-d excitations for LaMnO₃. To interpret the lower pre-edge region of the XANES Mn K-edge spectrum, we further analyze core-valence excitations. We explicitly calculate on-site 1s to 3d transitions as well as transitions to the 3d shell of an adjacent Mn ion. Major physical mechanisms which could lead to the observed peak structure are the CF splitting, the JT splittings and the exchange interaction within the d shell. The relative importance of these mechanisms is investigated. It is shown that the $A$ peaks originate from majority and minority-spin adjacent Mn $e_g(3d)$ states. We also study atomic-like transitions from 1s to 4p, with emphasis on the ordering of the $p_x$, $p_y$, and $p_z$ components. In addition to the JT splitting, which is larger than the effect of the 3d-4p Coulomb repulsion, a considerable splitting arising from the 3d-4p exchange interaction is found.

Our material model is based on embedded clusters containing one or two Mn ions: [MnO₃]⁻⁹ and [Mn₂O₁₁]¹⁶⁻. All-electron calculations were performed at CASSCF (complete active space self consistent field,¹³ a method based on multiconfigurational wave functions) and CASPT2 (complete active space second order perturbation theory¹⁴) levels...
with the MOLCAS 4.1 program package. The crystalline environment is modeled by an array of point charges which reproduce the Madelung potential in the cluster region. The short-range interaction between the cluster and the next coordination shell is accounted for by representing the nearest Mn$^{3+}$ and La$^{3+}$ ions with ab initio model potentials (AIMPs).

Atomic natural orbital (ANO) Gaussian-type basis sets were applied: Mn-$\{21s\,15p\,10d\}/\{6s\,5p\,4d\}$ and O-$\{14s\,9p\}/\{4s\,3p\}$ for the CASSCF calculations, and Mn-$\{21s\,15p\,10d\,6f\}/\{7s\,6p\,4d\,2f\}$ and O-$\{14s\,9p\,4d\}/\{6s\,5p\,1d\}$ for the CASSCF/CASPT2 calculations.

Our study is structured into two sections. We first performed calculations on a [MnO$_6$] cluster, analyzing the $d$-$d$ excited states of the Mn$^{3+}$ ion. Secondly, calculations were carried out on [Mn$_2$O$_{11}$] and [MnO$_6$] to determine the origin of various features of the near Mn $K$-edge absorption spectrum. Our assignments are based on the excitation energies calculated for transitions into local and neighboring orbitals and analysis of the final state splitting mechanisms.

The formal electronic configuration of a Mn$^{3+}$ ion in LaMnO$_3$ is $3d^4$. In (nearly) $O_h$ site symmetry it has a high-spin ground state arising from the weak-field configuration $t_{2g}^3e_g^1$. The orbital degeneracy is broken by JT distortions of the MnO$_6$ octahedra and by the ordering of the occupied $e_g$ orbitals on neighboring ions. In addition to the JT distortion, the MnO$_6$ octahedra are tilted, so that the Mn-O-Mn angles become less than 180°, but this last effect is not considered here.

The lowest $d$-$d$ excitation energies in [MnO$_6$], calculated with the CASSCF/CASPT2 method, are shown in Fig. 1. CASSCF wave functions were constructed with an active space that contains ten orbitals of mainly $d$ character, the five Mn-3$d$ orbitals and five correlating virtuals of the same symmetry, the so-called $d'$ orbitals. All $d$ orbitals are quite localized, although the $e_g$ orbitals turn out to have some O-2$p$ character mixed in. The subsequent CASPT2 step accounts for the electron correlation effects of the Mn-3$s$, $3p$, $3d$ and O-2$s$, 2$p$ electrons. We first performed the calculations in an idealized cubic configuration, with Mn-O distances of 1.95 Å. Secondly, a JT distortion is taken into account and the Mn-O bond lengths become Mn-O$_x$ = 2.14 Å, Mn-O$_y$ = 1.90 Å, and Mn-O$_z$ = 1.95 Å (the $z$ direction is along the $c$ axis of the $Pbnm$ reference system). The distortion of the MnO$_6$ octahedra is repeated within the point charge array surrounding the cluster. The relative energies obtained in cubic symmetry follow the Tanabe-Sugano diagrams, with a CF splitting $\Delta_{JT}$ of 2.4 eV. The first excitation is to a minority $t_{2g}$ level. When distortions are included all levels split up. The $e_g$-JT splitting $\Delta_{JT}$ is 1.2 eV (see Fig. 1). In the ground state, the $d_{3x^2−r^2}$ orbital is occupied.

We estimated possible effects of charge transfer (CT) configurations, i.e., configurations in which an electron is transferred from a ligand orbital to the Mn-3$d$ shell, at CASSCF level, by using an active space with five Mn-3$d$ and five O-2$p$ orbitals. The weight of CT configurations in the ground state wave function is minor, less than 15%. We found no states with predominant CT character below 3 eV above the ground state. It is clear that the lower part of the valence excitation spectrum is dominated by CF excitations, not CT excitations.

In Table I we compare 1$s$ to 3$d$ and 1$s$ to 4$p$ excitation energies for distorted [Mn$_2$O$_{11}$] and [MnO$_6$]. An active space comprising Mn-1$s$, 3$d$, 4$s$, and 4$p$ active orbitals, allowing 1$s$→3$d$ and 1$s$→4$p$ excitations, is sufficient for the present purpose. Transitions energies of the 1$s$ electron to both local and neighboring 3$d$ levels are shown. In [Mn$_2$O$_{11}$] the two Mn ions are at the $x$ axis, ferromagnetically coupled. In the ground state, we find $3x^2−r^2/3y^2−r^2$ orbital ordering. Again the 3$d$ orbitals are rather localized, for both Mn atoms, with some O-2$p$ character mixed into the $e_g$ components. The 1$s$ core hole localizes also the 4$p$ orbitals of the photoionized atom. However, when the core hole is not present, these are diffuse and mix strongly with the O-2$p$ orbitals. We study only on-site 1$s$ to 4$p$ excitations. An accurate treatment of the 1$s$ core excitations to neighboring 4$p$ would require larger clusters, since these 4$p$ states are more delocalized. The energies calculated for each type of excitation correspond to the lowest of the final states to which transitions are spin allowed. In these states the ex-

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>[Mn$<em>2$O$</em>{11}$]</td>
</tr>
<tr>
<td>1$s$→local 3$d$</td>
<td>0</td>
</tr>
<tr>
<td>1$s$→neighboring 3$d$</td>
<td>9.0</td>
</tr>
<tr>
<td>1$s$→local 4$p$</td>
<td>17.5</td>
</tr>
</tbody>
</table>

$^a$The 1$s$ ionized state is calculated at 5.5 eV higher energy.

$^b$Increase in Mn 3$d^{4}→3d^{5}$ electron affinity due to the 1$s$ hole (12.4 eV in [MnO$_6$]) minus the Coulomb repulsion between two unit charges at neighboring Mn sites.
cited electron is high-spin coupled to the total 3d spin. Because relativistic effects are not included in our computational approach, the excitation energies are systematically too low. For this reason we give relative energies only.

We find that transitions into the neighboring 3d shell start at 9 eV above the lowest 1s to local 3d transition and 8.5 eV below the lowest 1s to local 4p transition. The large energy difference calculated between on-site 1s-3d and 1s-4p excitations (≈17.5 eV) cannot explain the A1–B peak splitting. The interpretation that the A feature arises from transitions into 3d states on the neighboring Mn ion is more plausible. The calculated ≈8.5 eV energy difference between these 3d and local 4p excited states is in agreement with the observed A1–B splitting. The energy differences discussed above were also estimated using the smaller [MnO6] cluster, and the energies agree well with those obtained for [Mn2O11] (see Table I).

A similar interpretation of the A features was proposed by Efimov et al. They argued that these transitions get intensity due to hybridization of the 4p states with 3d states on adjacent Mn ions. We found very little mixing between the 4p-like orbitals at the photoionized Mn atom and the 3d(e g) orbitals on neighboring Mn ions. However, both have significant O-2p character, and this gives rise to nonzero intensity. In fact, we find the ratio of the squared transition dipole element between transitions into majority-spin neighboring 3d(e g) and local 4p orbitals to be 1/50.

We also investigated 1s excited states with CT character. The lowest of these have a hole in the 2p shell of the oxygen ion between two Mn 3d5 ions. Their energies are above those of local 1s-3d excited states and below those of 1s to neighboring Mn-3d excited states. Since such CT states correspond to a two-electron excitation, they could affect the spectrum only if they mixed with states that correspond to an one-electron excitation. However, we found negligible mixing.

The key of the A1–A2 splitting can be found by studying the 3d5 configuration of a Mn2+ ion in an embedded [MnO6] cluster. The lowest d-d excitation energies, calculated with the CASSCF/CASPT2 method, are given in Table II, for cubic and JT distorted geometries. The CASSCF active space contains again five Mn-3d orbitals and five d 4 virtual orbitals. Transition dipole matrix elements calculated in [Mn2O11] indicate that excitations into the 1t2g orbitals (states 2 in Table II) carry negligible small intensity. We therefore conclude that the A1 peak corresponds to transitions into e g majority-spin orbitals (state 1) and A2 to transitions into the e g minority-spin orbitals (states 3). Previous studies on related compounds have shown that CASSCF/CASPT2 calculations as reported here usually give a very reasonable prediction of the valence electronic structure, within 0.2 eV of the experimental results. However, the calculated high-spin–low-spin splitting of the 1t2g3e 2 configuration (3.0–3.8 eV) is larger than the A1–A2 splitting (≈2.2 eV) observed experimentally by Bridges et al. Possible sources of this difference are the shift of the spectrum when the 1s electron is promoted to different neighboring Mn ions, located at the x, y, or z axis, and the tilting of the oxygen octahedra. A rigorous study of these effects will be provided in a forthcoming paper.

Atomlike transitions from 1s into 4p orbitals, associated with the B shoulder, were studied in more detail also on a [MnO6] cluster. The calculated CASSCF relative energies of the 1s–4p transitions which get intensity are illustrated in Table III. An active space including five 3d and three 4p orbitals was used. The zero of energy is the lowest spin-allowed excited state. Within the JT distorted structure, with the longest Mn-O distance along the x axis, the lowest 1s–4p excited state is given by a s1t2g 3py, 3pz = 0 configuration, in spite of the p y, p z orbitals being parallel. Transitions into p y and p z occur at 1 eV higher energy, showing that the effect of the JT distortion is stronger than that of the 3d–4p Coulomb interaction. This result agrees with the findings of Ref. 3 and contradicts with the conclusion of Ref. 2.

We analyzed the different spin-couplings between the 1s electron and the valence (3d, 4p) electrons and found, as expected, small energy differences (≈0.1 eV) between them. More important is the coupling of the 4p electron to the local S = 2 3d spin, leading to exchange splitting of the 1s–4p transitions. In Table III, the h and the l states indicate high and low-spin coupling schemes, respectively, between the 4p electron and the 3d shell. In a first approximation, neglecting the small 1s-valence exchange interaction, the two final state couplings obtain equal intensity. We find

<table>
<thead>
<tr>
<th>State</th>
<th>Relative energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>1. 6A1g (t2g3e 2g)</td>
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</tr>
<tr>
<td>2. 4T 2g (t2g3e 2g)</td>
<td>1.60</td>
</tr>
<tr>
<td>3. 4A2g (t2g3e 2g)</td>
<td>3.10</td>
</tr>
<tr>
<td>4. 4B2u (t2g3e 2g)</td>
<td>5.20</td>
</tr>
</tbody>
</table>

\*Notations corresponding to D2h symmetry are used.

In parentheses, 1s to neighboring 3d squared transition dipole moments in [Mn2O11]; CASSCF results.

### Table II. Relative energies for states arising from the Mn 2 O 11 −like orbitals at the photoionized Mn atom and the 3 d 5 electronic configuration. CASSCF/CASPT2 results for embedded [MnO6] clusters.

<table>
<thead>
<tr>
<th>State</th>
<th>Occupied 4 p</th>
<th>Relative energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h5B3u</td>
<td>4 p z</td>
<td>0.00</td>
</tr>
<tr>
<td>h5B3u</td>
<td>4 p y</td>
<td>0.90</td>
</tr>
<tr>
<td>h5B1u</td>
<td>4 p y, 4 p z</td>
<td>1.00</td>
</tr>
<tr>
<td>h5B1u</td>
<td>4 p z</td>
<td>1.20</td>
</tr>
</tbody>
</table>

\*Notations corresponding to D2h symmetry are used; h and l indicate high and low-spin coupling schemes, respectively, between the 4p electron and the 3d shell.
exchange splitting of 0.9 eV for transitions into the $p_x$ component and 0.2 eV for transitions into $p_y$ and $p_z$. These results indicate that the final 4$p$ states on the parent atom with the core hole are more sensitive to the JT distortion of the MnO$_6$ octahedron (which lowers the $p_z$ level lying parallel to the occupied $d_{3z^2-2}$), and to the exchange interaction between the occupied 3$d$ orbitals and the 4$p$ electron (which is larger for the $p_z$ states) than to the 3$d$-4$p$ Coulomb repulsion.

It is instructive to compare our values for 3$d$-4$p$ exchange splittings with observed splittings for free ions, where unambiguous data are available. The observed $6F\rightarrow4F$ splitting in free Mn$^{2+}$ (1$s^23d^44p^1$) is 0.7 eV. Our value is 0.8 eV. We find 1.0 eV in the presence of a 1$s$ core hole. No experiments are available for Mn$^{3+}$ (1$s^13d^44p^1$), but for Fe$^{2+}$ (1$s^23d^44p^1$), which has a similar valence electron distribution, a $6F\rightarrow4F$ splitting of 0.9 eV is reported. These numbers confirm that, apart from a slight overestimation, our results give reasonable term splittings within a particular 3$d$-4$p$ configuration. In summary, we studied $d$-$d$ and core-valence transitions in LaMnO$_3$ by first principles electronic structure calculations on embedded clusters, in order to analyze the pre-edge x-ray absorption spectrum in LaMnO$_3$. The lower part of the valence excitation spectrum is dominated by CF excitations. In an idealized structure with $O_h$ site symmetry we find a CF splitting of 2.4 eV; for the $e_g$-JT splitting we find 1.2 eV. We showed that the energy separation between on-site 1$s$ to 3$d$ and 1$s$ to 4$p$ excitations is much too large to account for the $A$-$B$ peak separation. We confirm the conclusion of Refs. 5,9,10, that the lowest two peaks of the pre-edge region correspond to transitions to the $d$ shell of neighboring Mn ions. However, unlike the interpretation of Bridges et al., we found no transition probability for excitations into the $t_2g$ orbitals. We also investigated on-site transitions from Mn 1$s$ to empty 4$p$-like states in detail and found an ordering of the $p_x$, $p_y$, and $p_z$ components, which is due to the JT distortion of the MnO$_6$ octahedron. In addition, the energies associated with 1$s$ to 4$p$ transitions we find for on-site 1$s$ to 4$p$ excitations can explain a similar $\approx1$ eV exchange splitting that was found for the main peak at the edge by very recent spin-dependent measurements of Qian et al.

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