

BRIEF COMMUNICATION

Electronic Structures of Perovskite Oxides of Transition Metals of the Type LaMO_3 ($M = \text{Ti–Ni}$) as Revealed by $\text{MSX}\alpha$ Investigations¹

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Systematic investigations of the electronic structures of MO_6^{9-} ($M = \text{Ti–Ni}$) clusters, as in the LaMO_3 type perovskite oxides, have been carried out by employing the multiple-scattering $\text{X}\alpha$ ($\text{MSX}\alpha$) method. The crystal-field splitting of the metal d level is found to increase, while the oxygen-to-metal charge-transfer energy decreases across the transition metal series. Systematic trends are also seen in the mixing (covalency) between the metal d and the oxygen $2p$ orbitals in the series. © 1994 Academic Press, Inc.

INTRODUCTION

Understanding the electronic structure of transition metal oxides is of vital importance because of the variety of fascinating phenomena exhibited by these materials (1). It is, however, difficult to fully describe their electronic structure in a manner that would account for the wide range of properties such as metal–insulator transitions and high-temperature superconductivity. It is therefore worthwhile to study the electronic structures of a related series of isostructural transition metal oxides. Such a systematic study for the monoxides of $3d$ transition metals (Ti–Ni) in the rock salt structure has been carried out in terms of band structure calculations (2). On the other hand, no such investigation has been carried out on the electronic structure of transition metal perovskites, LaMO_3 ($M = \text{Ti–Ni}$). These oxides show fascinating optical, magnetic, and electronic properties (1, 3). For example, LaNiO_3 is metallic, while LaCoO_3 is an insulator at ordinary temperatures, becoming metallic around 1200 K. LaCrO_3 and LaFeO_3 are antiferromagnetic insulators. An understanding of the electronic structures of these compounds would provide the basis to understand the behavior of the other complex oxides containing the perovskite motif, such as the layered superconducting cuprates. An ab initio band structure study of these oxides is compli-

cated by the deviation of the real crystals from the idealized cubic structure, leading to as many as 20 atoms per unit cell. On the other hand, the electronic and magnetic properties in these systems are dominated by local interactions within the transition metals MO_6 octahedra. The ensuing molecular orbitals then interact with the different octahedra, resulting in band formation. We have employed spin-restricted $\text{MSX}\alpha$ calculations (4, 5) on the MO_6^{9-} ($M = \text{Ti–Ni}$) clusters to study the electronic structures of the perovskite oxides. To our knowledge, there has been no systematic $\text{MSX}\alpha$ investigation of these clusters hitherto. It is noteworthy that the $\text{MSX}\alpha$ method has been successfully used in calculating the electronic structures of solids, including quasi-crystals (6).

MSX α PARAMETERS AND COMPUTATIONAL DETAILS

We have carried out nonrelativistic spin-restricted $\text{MSX}\alpha$ calculations on isolated MO_6^{9-} ($M = \text{Ti–Ni}$) clusters. Details of the $\text{MSX}\alpha$ method can be found in the literature (4, 5). In the present calculations, the muffin-tin radius around the atomic spheres, M and O were taken to be equal to the corresponding ionic radii (Table I). The outer sphere radius was so chosen as to be approximately tangent to the outer oxygen spheres. The exchange parameters, α , were taken from Schwarz's tabulation (7) for the atomic spheres. The values of α for the outer sphere as well as the intersphere region were set equal to the average of the atomic α 's in the cluster. The radius and the α value for the oxygen muffin-tin sphere were 2.6465 a.u. and 0.74447, respectively. All the parameters employed are given in Table 1. A Watson sphere (8) of radius equal to that of the outer sphere and with a charge of 12+ was used to stabilize the electronic levels. It was verified that a smaller charge on the Watson sphere leads only to rigid shifts of the energy levels with negligible effect on the energy separations.

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TABLE I
MSX α Parameters

	Electronic configuration	d_{M-O} (a.u.)	r_M (a.u.)	r_{out} (a.u.)	α_M	$\alpha_{in/out}$
LaTiO ₃	$t_{2g}^1 e_g^0$	3.7051	1.2665	6.2516	0.71695	0.74171
LaVO ₃	$t_{2g}^2 e_g^0$	3.6957	1.2098	6.2422	0.71556	0.74094
LaCrO ₃	$t_{2g}^3 e_g^0$	3.6862	1.1626	6.2327	0.71352	0.74005
LaMnO ₃	$t_{2g}^3 e_g^1$	3.6862	1.2287	6.2138	0.71279	0.73931
LaFeO ₃	$t_{2g}^4 e_g^2$	3.6673	1.2193	6.2516	0.71151	0.73848
LaCoO ₃	$t_{2g}^4 e_g^2$	3.7051	1.1531	6.1571	0.71018	0.73761
LaNiO ₃	$t_{2g}^5 e_g^2$	3.6484	1.1342	6.1949	0.70896	0.73675

Note. Parameters used: the distance between metal and oxygen (d_{M-O}), muffin-tin radius of the metal (r_M) and outer sphere (r_{out}), the exchange parameter for metal (α_M), and inter- or outer sphere ($\alpha_{in/out}$).

RESULTS AND DISCUSSION

In order to compare the orbital energies of the MO_6^{9-} clusters with different transition metal ions, we have made use of the fact that the O 2s binding energy in transition metal oxides appears around 21 eV, somewhat independent of the metal ion (9). We have therefore shifted the energy scale of each of the clusters in order to adjust the centroid of the O 2s related state energies to 21 eV and compared the energies of the various valence levels of the different clusters in Fig. 1. The $1a_{1g}$ orbital in each case corresponds to the metal 3s level, while the $1t_{1u}$ orbitals correspond to the metal 3p orbitals. The orbitals ($2a_{1g}$, $2t_{1u}$, and $1e_g$) around 21 eV are essentially O 2s derived states. The bunch of seven orbitals labeled $1t_{2g}$, $3t_{1u}$, $3a_{1g}$, $2e_g$, $1t_{2u}$, $4t_{1u}$, and $1t_{1g}$ is primarily derived from the oxygen 2p atomic orbitals, only the $1t_{2g}$ and $2e_g$ orbitals among these having significant covalent mixing with the metal 3d

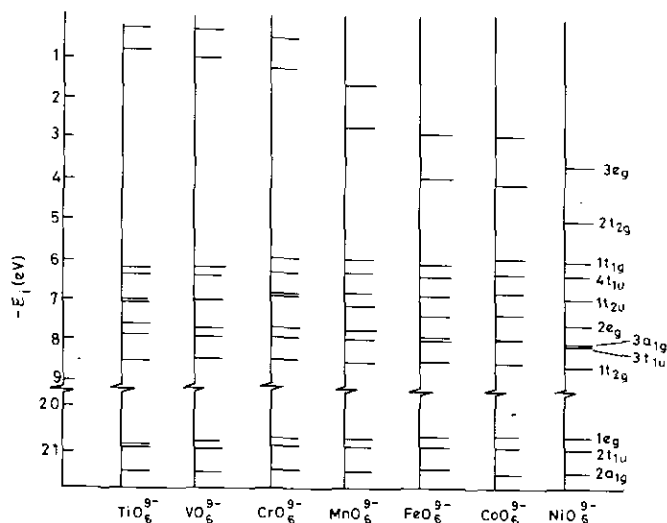


FIG. 1. Eigen values (E) of the outer orbitals of the MO_6^{9-} ($M = \text{Ti-Ni}$) clusters.

states. The two highest lying orbitals, $2t_{2g}$ and $3e_g$, are the corresponding metal 3d-O 2p antibonding levels. We find from the figure that the adopted procedure of aligning the centroid of the O 2s orbitals at 21 eV also brings the O 2p related orbitals to a common energy range in all the clusters. In fact, the centroid of the O 2p related orbitals (E_{2p}^c) appears at about 7.22 ± 0.04 eV for all the clusters. This is in good agreement with the experimental observation that the O 2p related spectral features always appear as a broad peak at about 6–7 eV, binding energy in nearly all these oxides (9, 10). The total energy spread of the seven O 2p related levels is about 2.3 eV for the TiO_6^{9-} cluster and slightly increases across the series to become 2.6 eV for the NiO_6^{9-} cluster. The cluster chosen by us necessarily truncates half of the coordination shell for the oxygen atom in the solid, with each oxygen having only one transition metal and four oxygens as neighbors. This implies that the spread of the O 2p derived levels in the solid should be double (around 5 eV) compared to what is found for the MO_6^{9-} clusters here. This estimate of the width of the O 2p band in the oxides is in fair agreement with the experimentally observed width of the O 2p related spectral features in the photoemission spectra of these oxides (10).

Figure 1 shows that the energy difference (charge-transfer energy), Δ_{CT} , between the O 2p derived $1t_{1g}$ level and primarily metal 3d derived $2t_{2g}$ level monotonically decreases across the series from Ti to Ni. Thus, the energy difference is 6.4 eV for the TiO_6^{9-} cluster and 1.05 eV for the NiO_6^{9-} cluster. Since the O 2p derived levels have a wider energy spread due to the larger coordination in the solid compared to that in the cluster, as already discussed, the charge-transfer energy is expected to be smaller by at least 1 eV in the solid than that calculated here. This indicates that the primarily 3d derived $2t_{2g}$ levels will be close to the oxygen band edge in the NiO_6^{9-} cluster. The $2t_{2g}$ levels of the MO_6^{9-}

cluster will themselves broaden into a band in the solid, the band width depending on the $M-O-M$ transfer integral through pd π -interaction. Thus, it appears almost certain that the metal $2t_{2g}$ band will overlap the essentially O $2p$ derived band in the NiO_6^{2-} cluster, since the charge-transfer gap is the smallest for this cluster. The pd π -interaction responsible for the metal t_{2g} derived bandwidth is, however, considerably weaker than the pd σ -interaction (2). It is therefore reasonable to expect the t_{2g} bandwidth not to be sufficient to overcome the large gap between the oxygen band edge and the metal derived $2t_{2g}$ levels in the early transition metal oxides (Fig. 1). Thus, for the beginning members of the $LaMO_3$ series, there will exist a clear gap between the oxygen derived and the metal derived bands.

Band formation from the metal derived levels in the $LaMO_3$ perovskites structure is driven by the metal-oxygen-metal hopping interaction. The $2t_{2g}$ orbital is formed from π -overlap between the metal $3d$ and the O $2p$ derived t_{2g} orbitals, whereas the $3e_g$ molecular orbital is formed from the corresponding σ -interaction. A measure of the extent of covalent mixing of the O $2p$ levels in the $2t_{2g}$ and the $3e_g$ levels is provided by the fraction of the charge from these orbitals lying inside the oxygen muffin-tin spheres. In Fig. 2, we plot these fractions of the orbital charges (q_t and q_e) from the $2t_{2g}$ and the $3e_g$ orbitals against the atomic number of the transition metal. From this plot we find that q_e arising from a σ -interaction is always larger than q_t , for all the clusters; q_t remains essentially unaltered, indicating that the mixing due to the π -overlap does not substantially change in this series. This covalent mixing is dependent on the bare charge-

transfer energy and the transfer integral. Since the charge-transfer energy decreases across the series (Fig. 1), the M $3d-O$ $2p$ π -transfer integral should also decrease across the series in order to give rise to a relatively constant covalent mixing. A similar trend of a decreasing transfer integral with an increasing atomic number is also seen in the monoxide series (2) and is related to $3d$ orbital contraction. The mixing of the O $2p$ characteristics in the $3e_g$ orbital due to the σ -overlap, however, increases substantially across the series. This indicates that the e_g bandwidth increases across the series, while the t_{2g} bandwidth remains essentially the same.

The energy difference, Δ_{CF} , between the $2t_{2g}$ and the $3e_g$ orbitals is related to the crystal-field splitting of the metal $3d$ orbital modified to different extents by the transfer integrals of the metal t_{2g} and e_g levels with the O $2p$ orbitals. We find a systematic increase of Δ_{CF} with the atomic number of the transition metal in the MO_6^{2-} cluster (Fig. 1). To some extent, this effect must be related to the decreasing trend of the charge-transfer energy, Δ_{CT} , across the series (Fig. 1) and the consequent increasing trend of the covalent mixing of the O $2p$ orbitals with the metal $3d$ orbitals (Fig. 2). Considering the small energy separation, Δ_{CF} , between the $2t_{2g}$ and the $3e_g$ orbitals and the typical hopping interaction strengths in the first row transition metal oxides (2), it appears reasonable to expect the bands in the solid formed from the $2t_{2g}$ and the $3e_g$ levels to overlap energetically. Metal d orbitals with substantial O $2p$ admixture are therefore expected to form one band with predominantly t_{2g} characteristics at the bottom of the band and the e_g characteristics at the top, rather than forming two separate bands, at least for the late transition elements. This is all the more true for the seven orbital ($1t_{2g}$, $3t_{1u}$, $3a_{1g}$, $2e_g$, $1t_{2u}$, $4t_{1u}$, and $1t_{1g}$) with predominantly O $2p$ character. Thus, these are expected to form one continuous density of states with no energy gap. This electronic structure scheme will be valid for the $LaMO_3$ series of oxides, as the ordering of energy levels is crucially dependent on symmetry of the representative clusters. This scenario would suggest a metallic ground state in all the $LaMO_3$ compounds, with Fermi energy lying within the metal derived band. This is a well-known difficulty of the independent particle approximation employed for the calculations, excluding effects of electron correlations. While the overall electronic structures of $LaMO_3$ oxides are governed primarily by the energetics of charge-transfer energy, crystal-field splitting, and transfer integrals, as discussed in this work, the insulating/metallic property is controlled by a competition between the bandwidths and the Coulomb correlation energy, which is outside the scope of the present work.

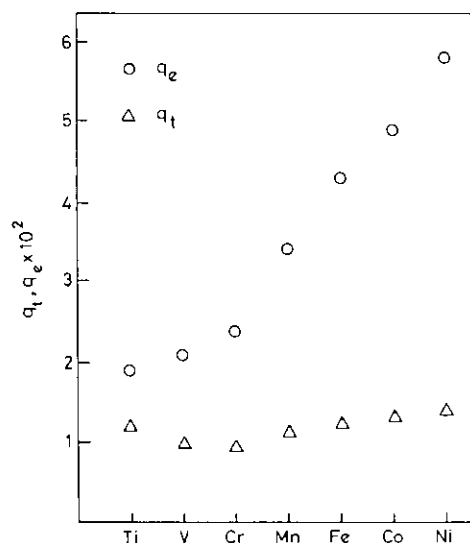


FIG. 2. Variation in the contributions of O $2p$ states in the orbital charges for the $2t_{2g}$ and $3e_g$ states (q_t and q_e) with the transition metal ion, M in $LaMO_3$ ($M = Ti-Ni$).

In conclusion, we have shown that there are well-defined trends in the calculated electronic structures of the perovskites of the type LaMO_3 ($M = \text{Ti-Ni}$). Thus, the metal derived $t_{2g}-e_g$ separation increases while the energy difference between the oxygen- p derived states and metal- d derived states decreases across the series ($M = \text{Ti-Ni}$). We have suggested that this decreasing energy separation is responsible for the metallic properties of LaNiO_3 , while the Coulomb correlation interaction causes all the other perovskites to be insulating.

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