Density-functional studies of the electronic structure of the perovskite oxides: $La_{1-x}Ca_xMnO_3$

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Using density-functional methods, we study the electronic structures of the lanthanum-based "double-exchange" perovskite magnets. Antiferromagnetic insulating solutions are obtained for both the end members, $LaMnO_3$ and $CaMnO_3$, within the local density approximation (LDA), with the Jahn-Teller (JT) distortion of the oxygen octrahedron taken into account. The JT distortion splits off the Mn$(3d)e_g$ bands producing an energy gap within the LDA, with the bands derived from the (z^2-1) orbital, pointed along the long basal-plane Mn—O bond, occupied and the (x^2-y^2) bands empty. The on-site Coulomb repulsion and the intra-site exchange terms are found to be, respectively, $U\simeq 8-10$ eV and $J\simeq 0.9$ eV, from the "constrained" density-functional theory. The large value of U as compared to the bandwidth indicates that the manganese perovskite oxides are strongly correlated systems. © *1996 American Institute of Physics.* [S0021-8979(96)49208-8]

The hole-doped manganese perovskite oxides, such as $La_{1-x}Ca_xMnO_3$, are prime examples of solids with a ferromagnetic conducting state caused by the "double exchange" mechanism, where the magnetic coupling between localized spins on neighboring atoms is mediated via conduction electrons.[1–4] Both the end-members, $LaMnO_3$ and $CaMnO_3$, are antiferromagnetic (AF) insulators with, respectively, Mn^{3+} $(t_{2g}^3e_g^1)$ and Mn^{4+} $(t_{2g}^3e_g^0)$ configurations of the Mn ions. The localized spins of the t_{2g} electrons are coupled ferromagnetically by the doped holes in the partially filled e_g band introduced by the Ca atoms. Thus, the partially filled e_g band is responsible simultaneously for ferromagnetism and conduction in the solid. This is precisely what is experimentally observed, viz., that the mixed valence compound $La_{1-x}Ca_xMnO_3$ shows the highest electrical conductivity for $0.2\leqslant x\leqslant 0.4$, exactly in the concentration range where the material is ferromagnetic.[5] New interest on these systems has been revived by the recent discovery of colossal magnetoresistance (CMR) in the La-Ca-Mn-O films.[6,7]

In this paper, we examine the electronic structure of the two end members, $LaMnO_3$ and $CaMnO_3$, from density-functional band calculations using the local spin-density approximation (LDA), as well as the "constrained" density-functional and the "LDA+U" theories.[8]

Both $LaMnO_3$ and $CaMnO_3$ form in the orthorhombic crystal structure[9] which is a distorted form of the cubic perovskite structure. While in the Ca compound, the distortion of the O octahedra surrounding the manganese atoms is largely absent, in the La compound, the octahedra are distorted significantly with three distinct Mn—O bond lengths. The Jahn-Teller (JT) distortion of the O octahedron is understandable in view of the $t_{2g}^3e_g^1$ configuration of the Mn ion. In addition to the JT distortion, there is a slight rotation of the octahedra, which is neglected in the calculations reported here. All our calculations reported here were performed using the linear muffin-tin orbitals (LMTO-ASA) method[10] and the ideal tetragonal crystal structure for the two perovskites with inclusion of the JT distortions. Thus, the magnetic unit cell in our calculation has four formula units for $LaMnO_3$ and two for $CaMnO_3$.

The antiferromagnetic band structures of $LaMnO_3$ and $CaMnO_3$ are shown in Fig. 1. The observed AF order, type A for the former and type G for the later compound,[11] is reproduced from the local-density calculations. The key features of the AF band structures agree with the independent LAPW calculations of Pickett and Singh.[12] As seen from Fig. 1, the key orbitals near E_f are the O$(2p)$ and Mn$(3d)$ orbitals with the energy gap occurring in the middle of the Mn$(3d)$ bands. The outer electrons from the La, Ca, and Mn atoms are transferred to complete the $2p$ shell of the oxygen atoms, resulting in the nominal chemical formulas of $La^{3+}Mn^{3+}O_3^{2-}$ and $Ca^{2+}Mn^{4+}O_3^{2-}$, respectively.

We have studied the effect of the Jahn-Teller distortion of the cubic octahedra on the band structure by performing a series of calculations for $LaMnO_3$ with various amounts of the distortion. There are three types of distortions[13] affecting the Mn—O bond lengths: (i) The breathing mode (Q_1), (ii) the basal-plane distortion mode (Q_2) with one diagonally opposite O pair displaced outwards and the other pair displaced inwards, and (iii) the octahedral stretching mode (Q_3) where the four in-plane O atoms are displaced inwards and the two apical O atoms are displaced outwards. The amplitudes of these three modes in $LaMnO_3$ are, respectively, 0.08, 0.20, and 0.11 Å, resulting in the three distinct Mn—O bond lengths: 1.91, 2.19, and 1.96 Å. We find that the basal-plane distortion mode Q_2 is the most effective in splitting up the e_g bands in $LaMnO_3$ thereby producing an energy gap, and that the Q_1 or the Q_3 distortions are relatively ineffective in opening up the gap. We find that a JT distortion of the Q_2 type, with the oxygen atoms displaced by at least the amount ≈ 0.1 Å from their ideal positions, is necessary to produce a band gap in $LaMnO_3$. In the crystal, the measured value of this distortion is about 0.15 Å, which is therefore enough for the insulating solution. The t_{2g} bands in contrast remain more-or-less unaffected by the distortions.

The splitting of the Mn$(3d)$ bands in $LaMnO_3$ due to the

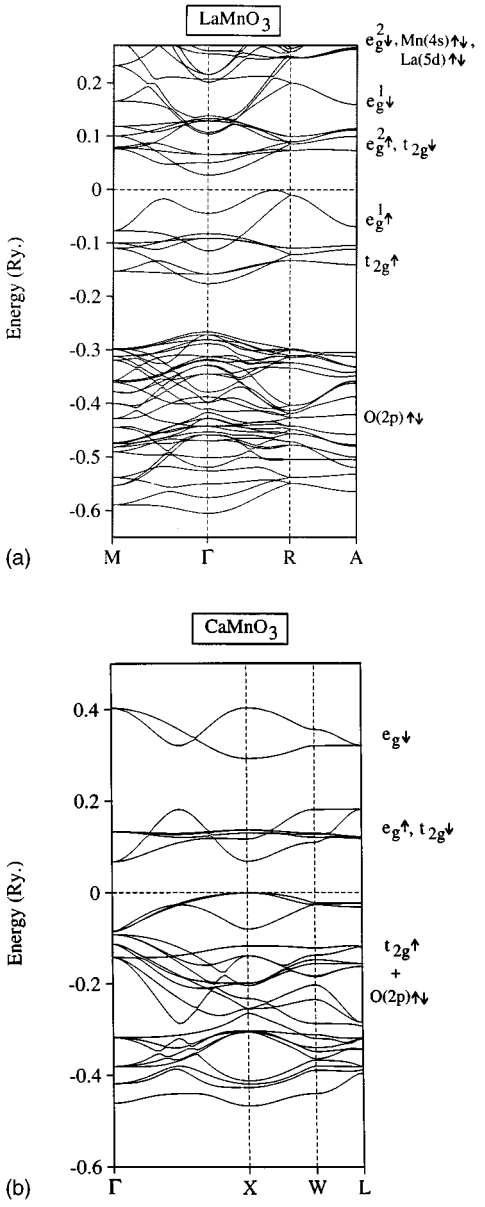

FIG. 1. Electronic band structures of antiferromagnetic $LaMnO_3$ and $CaMnO_3$ in the ideal tetragonal structure with, respectively, type A and type G magnetic configurations. The Jahn-Teller distortion of the oxygen octahedra was included for $LaMnO_3$. The symmetry components e_g and t_{2g} correspond to the Mn($3d$) orbital, and spin components ($\uparrow$ or $\downarrow$) are local to individual atoms. Energies are with respect to E_f.

combined effects of the cubic crystal field, exchange, and the Jahn-Teller distortion as obtained from our calculations has been shown in Fig. 2. The exchange splitting is about 3.0 eV which removes the minority-spin bands up above E_f. The cubic crystal-field splitting between the t_{2g} and the e_g orbitals is about $\Delta_{cf} \simeq 2.0$ eV, while the Q_2 distortion of the oxygen octahedron splits the e_g bands by $\Delta_{JT} \simeq 1.5$ eV. The total band width of the occupied Mn($3d$) bands is about 2.4 eV. Of this, the t_{2g} bands are 1.3 eV wide, while the Jahn-Teller split e_g^1 band just below E_f has a width of about 1.6 eV.

We find that the occupied Mn(e_g) band is derived from the z^2-1 orbital, while the unoccupied band is derived from the x^2-y^2 orbital, in a Mn-atom-based *local* coordinate system with the z axis along the long, basal-plane Mn—O bond. This is illustrated in Fig. 3, where we have shown the dominant orbital contribution[14] to the band structure. Occupation of the z^2-1 band gives rise to the $t_{2g}^3 e_g^1$ configuration of the Mn atom for $LaMnO_3$. In the mixed compound, the e_g^1 band is progressively depleted with Ca concentration x, with complete depletion for the end-member $CaMnO_3$ ($x=1$).

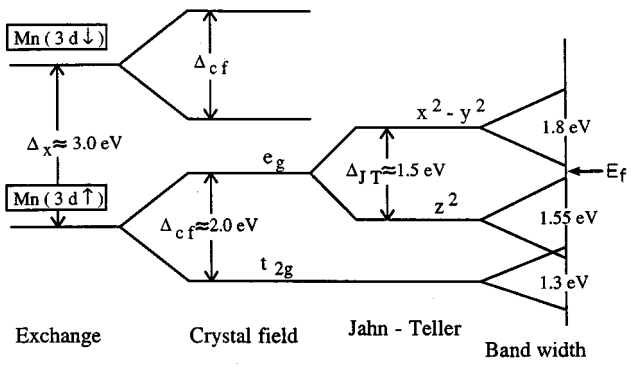

FIG. 2. Multiplet splitting of the Mn($3d$) orbital for $LaMnO_3$ as obtained from the density-functional calculation.

Electron bands[12,16] for $LaMnO_3$ in the experimentally observed crystal structure are not very different from the band structure shown in Fig. 1(a). Two differences may be noticed: (i) the O($2p$) bands are separated from the Mn($3d$) bands here, a feature that disappears for the experimental structure, and (ii) the e_g^1 and the t_{2g} bands just below the E_f overlap, while for the experimental crystal structure, additional interaction results in a small separation between the e_g^1 and the t_{2g} bands. In spite of this separation, however, the

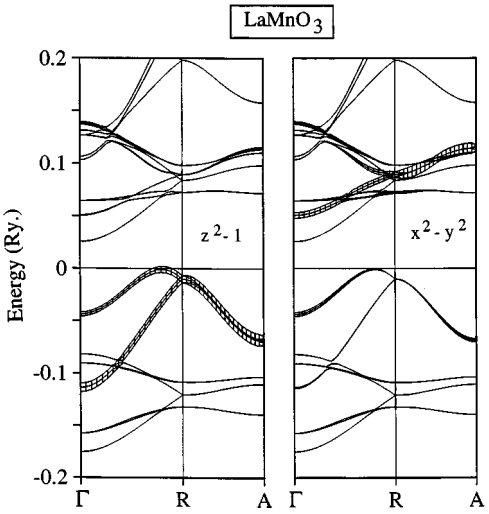

FIG. 3. Contribution of the Mn($3d$)z^2-1 and x^2-y^2 orbitals, to the band structure. The orbitals are with respect to a Mn-atom-based *local* coordinate system with the z axis pointing towards a long Mn—O bond on the basal plane. The width of each band in the figure shown by cross hatching, is proportional to the contribution of the $3d$ orbital (z^2-1 or x^2-y^2) on a specific Mn atom.

TABLE I. Energy $\bar{\epsilon}_d$ of the central site Mn($3d$) level (in Rydberg) for two different values of the "constrained" occupancy n_d for the case of $LaMnO_3$. The occupancies of the s and p electrons on the Mn site and the total valence charges on the neighboring in-plane (n_{O1}) and out-of-plane (n_{O2}) oxygen atoms are also shown.

n_d	$\bar{\epsilon}_d$	n_s	n_p	n_{O1}	n_{O2}
4.5	−0.44	0.39	0.51	6.05	6.16
5.5	0.33	0.26	0.38	5.96	6.17

excursion of the z^2-1 character into the t_{2g} group of bands, as seen from the left panel of Fig. 3 near the Γ point, is nevertheless retained in the electron bands for thef experimental crystal structure [see inset of Fig. 2(a) in Ref. 16].

To assess the importance of the correlation effects, we have estimated the magnitudes for the on-site Coulomb (U) and the intra-atomic exchange (J) parameters for the Mn atom from constrained density-functional calculations.[15] The Coulomb parameter U was calculated from the dependence of the on-site energy $\bar{\epsilon}_d$ of the Mn(d) orbital on the number occupancy n_d of a central Mn site,

$$\bar{\epsilon}_d = \epsilon_d + U \times (n_d - 1), \tag{1}$$

with the interaction of the central Mn(d) orbitals with the rest of the system switched off. This procedure is somewhat different from the one we reported earlier,[16] where we employed a Slater's transition rule for the calculation of U, but we get very similar results in both cases. By constraining all d electrons on a central Mn site in a 4-atom supercell calculation, we obtain a value of about 10.4 eV for U.[17]

In Table I, we show the screening charges on the central Mn atom and the neighboring O atoms, for two different constrained values of n_d. The change in the number of $3d$ electrons is screened by only about 13% each by the Mn s and p electrons. The four in-plane oxygen atoms together contribute about 36% while the two out-of-plane oxygen atoms contribute a negligible 2% to the screening charge. The rest of the screening charge resides on more distant neighbors. Such relatively poor screening results in the high value for the Coulomb parameter U.

However, since the screening charges reside on the sphere centers in the LMTO calculation, while in reality such charges on neighboring atoms are displaced towards the central atom, the Coulomb interaction may be somewhat overestimated.[18] A lower bound for U is obtained by supposing that the screened charges on the neighboring oxygen atoms are located at the surface of the central Mn sphere, which then yields the maximum value for the error to be about 2.1 eV, with the resultant lower bound of $U \simeq 8.3$ eV. Thus, our calculations indicate a value of $U \simeq 8—10$ eV, which is consistent with the estimate of $U \simeq 7.5$ eV from an analysis of the photoemission data.[19] Such large values for U indicate significant electronic correlation. The calculated magnitude of the on-site parameter is $J \simeq 0.86$ eV, which is typical of binary transition-metal oxides, where it varies between 0.78 to 0.98 eV.[8]

With the calculated Coulomb and exchange parameters, we have minimized the LDA+U functional,[8] which takes into account the effects of the large Hubbard U term in a meanfield sense. The results discussed in detail elsewhere[16] show that there is a significant spectral redistribution. In particular, while in the LDA calculations, the Mn($3d$) bands occur above O($2p$) bands, in the LDA+U calculations in the Mn($3d$) bands have shifted down in energy with respect to the O($2p$) states and occur in the lower part of a joint band of about 7-eV wide, which is consistent with the valence-band photoemission data.[22] Even though the relative positions of the Mn($3d$) and the O($2p$) bands are reversed in the LDA+U results as compared to the LDA results, both results are consistent with the 7-eV-wide joint Mn($3d$)—O($2p$) double-peak structure seen in the valence-band photoemission.[20–22] A clearer experimental evidence for a large Coulomb U is indicated by the Mn($2p$) core-level photoemission spectra, where a satellite peak is seen at the binding energy of ≈ 10 eV.[19,20,23]

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