Effect of oxygen stoichiometry on spin, charge, and orbital ordering in manganites

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(Received 8 September 2003; published 18 March 2004)

Using full-potential density-functional calculations we show that oxygen stoichiometry plays an important role on spin, charge, and orbital ordering in manganites. The electronic structure and magnetic properties of LaBaMn$_2$O$_{5+\delta}$ have been studied for $\delta=0$, 0.5, and 1; for $\delta=0$ and 0.5 the system exhibits charge, orbital, and antiferromagnetic spin ordering, whereas at $\delta=1$ the charge and orbital orderings disappear but the spin ordering remains. We also bring out an insulator-to-metal transition upon going from $\delta=0$ to 1. The study suggests that one can manipulate the charge and orbital orderings in certain perovskite-like oxides by merely varying the oxygen stoichiometry and hence design oxides with desired electrical and magnetic properties.

DOI: 10.1103/PhysRevB.69.092405

PACS numbers: 71.15.Nc, 71.20.--b, 81.05.Je, 81.40.Rs

There has been an upsurge of interest in perovskite-like manganese-based oxides since the discovery of colossal magnetoresistance (CMR). The CMR manganites display a fascinating diversity of behaviors including several forms of spin, charge, and orbital orderings (hereafter SO, CO, and OO). The electronic, magnetic, and CMR features of a given material are largely determined by the chemical composition and crystal structure and these properties may be quite sensitive to even tiny changes in the atomic architecture. Hence an improved understanding of how composition and structure affect transport and magnetism and this may guide the search for new CMR materials.

The interplay between the crystal symmetry and the atomic orbitals plays a crucial role in the conductivity of the $e_g$ electrons in manganites. The transfer integral ($t$) of the $e_g$ electrons between neighboring Mn sites is mediated by the O-2$p$ orbitals and hence depends on the degree of hybridization between Mn-3$d$ and O-2$p$ orbitals. The substitution of divalent cations on the A site of REMnO$_3$ (RE stands for rare earth) perovskites (e.g., the parent CMR material LaMnO$_3$) induces holes in the $e_g$ band. Many studies have addressed the effect of A-site-substituted cations on SO, CO, and OO. Although it is well known that the long-range CO and the transfer efficiency of CMR materials are very sensitive to even tiny changes in the atomic architecture, hence the basis included are the chemical composition and crystal structure and these properties may be quite sensitive to even tiny changes in the atomic architecture. Hence an improved understanding of how composition and structure affect transport and magnetism and this may guide the search for new CMR materials.

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functions of each LAPW were calculated up to \( t \), quantities were expanded in a Fourier series. The radial basis in the atomic spheres were represented by spherical harmonics up to \( t \), treated using the GGA. For all three compositions the AF state is found to have the lowest energy. Table II shows that AF \( \text{LaBaMn}_2\text{O}_5 \) has a finite total moment of \( 0.97 \mu_B \), implying that it is in fact ferrimagnetic (Ferri). The Ferri ground state and the calculated magnetic moment are in good agreement with the experimental findings. From the difference in the ionic size and magnetic moment, it is experimentally established that \( \text{Mn}(1) \) corresponds to \( \text{Mn}^{3+} \) and \( \text{Mn}(2) \) to \( \text{Mn}^{2+} \) both in high spin (HS) states. This picture for \( \text{LaBaMn}_2\text{O}_5 \) agrees fully with the outcome of the present calculations. In order to analyze changes in the electronic structure with respect to the oxygen stoichiometry, the density of states (DOS) in the ground-state configurations of \( \text{LaBaMn}_2\text{O}_{5+\delta} \) is given in Fig. 2. An energy gap \( (E_g) \) of ca. 0.84 eV opens up between the valence and conduction bands in \( \text{LaBaMn}_2\text{O}_5 \) [Fig. 2(a)], giving an insulating state in accordance with the experiments. The Ferri ordering leads to significant topological differences in the up- and down-spin DOS.

In general, local-density approximation including Coulomb correlations effects \( (\text{LDA}+\text{U}) \) calculations\(^1\) are thought to be necessary to study the electronic and magnetic properties of transition-metal oxides. However, our calculations show that the insulating behavior and magnetic properties are correctly reproduced by the usual density-functional calculations for the manganites considered in the present study.

As mentioned, \( t \) depends on the degree of the hybridization between the \( \text{Mn}-3d \) and \( \text{O}-2p \) orbitals, which in turn makes this parameter sensitive to the oxygen stoichiometry. The Jahn-Teller (JT) distortion (associated with HS \( \text{Mn}^{3+} \)) induces an anisotropy in the interaction between \( \text{Mn}-d \) and \( \text{O}-p \) orbitals. Moreover, owing to the size difference between \( \text{La}^{3+} \) and \( \text{Ba}^{2+} \) and the oxygen vacancies in the \( \text{La}^{3+} \) layer, the degree of hybridization between the \( \text{Mn}-d \) and \( \text{O}-p \) orbitals is reduced. Hence \( t \) and consequently \( W \) also decrease. Moreover, the differences in \( \text{Mn}-\text{O}-\text{Mn} \) bond angles and \( \text{Mn}-\text{O} \) bond lengths promote significant distinctions between \( t \) within and perpendicular to the basal plane of \( \text{LaBaMn}_2\text{O}_5 \). The decreases in \( t \) and \( W \) reduce the double-exchange (DE) interaction, and hence the superexchange interaction overcomes the DE, thus favoring the insulating AF/Ferri CO and/or OO state. Therefore, in addition to Ferri SO, CO occurs with the equal amounts of \( \text{Mn}^{3+} \) and \( \text{Mn}^{2+} \) in \( \text{LaBaMn}_2\text{O}_5 \). In order to elucidate the effect of oxygen stoichiometry on CO and OO, we show the spatial \( 3d \)-electron distribution at each Mn site for the majority and minority spins in Figs. 1(a) and 1(b). The appreciable difference in the distribution of majority and minority \( d \) electrons between \( \text{Mn}^{3+} \) and \( \text{Mn}^{2+} \) in \( \text{LaBaMn}_2\text{O}_5 \), implies the presence of CO.

![FIG. 1. (Color online) The majority- and minority-spin \( \text{Mn}-3d \)-electron distribution in (a,b) \( \text{LaBaMn}_2\text{O}_5 \), (c,d) \( \text{LaBaMn}_2\text{O}_{5.5} \), and (e,f) \( \text{LaBaMn}_2\text{O}_6 \). Atoms inside cyan-colored square pyramids correspond to \( \text{Mn}(1) \) (Mn in e,f) and those inside pink-colored square pyramids/octahedra correspond to \( \text{Mn}(2) \).](image)
It is well established that OO plays a crucial role in the magnetic and electronic properties of manganites. As electrons closer to the Fermi level \( (E_F) \) participate more in hopping interaction and determine the electronic properties, we show the orbital distribution of such electrons for LaBaMn\(_2\)O\(_5\) in Fig. 3(a). Owing to the Mn-O-Mn bond angle of 161° for Mn(1), the transfer of the 3d electrons is not complete and these electrons therefore tend to localize in a certain pattern over the Mn sites of LaBaMn\(_2\)O\(_5\). According to the orbital-projected DOS, the \( d_{xy} \), \( d_{yz} \), and \( d_{xz} \) orbitals of Mn\(^{3+}\) and the \( d_{x^2-y^2} \) orbital of Mn\(^{2+}\) are found in the energy range \(-1\) eV to \( E_F \), leading to the ordering of these orbitals as shown in Fig. 3(a).

For LaBaMn\(_2\)O\(_{5.5}\), the ground-state SO is found to be AF, in perfect agreement with the experimental findings.\(^5\) Further, the Mn atoms in the square pyramidal and octahedral coordinations take a HS Mn\(^{3+}\) state. The system remains insulating on going to LaBaMn\(_2\)O\(_{5.5}\), but \( E_F \) is reduced to 0.26 eV [Fig. 2(b)]. As half of the square pyramids at \( \delta=0 \) has been converted into octahedra at \( \delta=0.5 \), half of the O vacancies in the La layers is filled, and the overlap interaction between Mn-\( d \) and O-\( p \) orbitals is thereby increased. The bandwidth in turn increases, reducing the band gap. The difference in the crystal fields of square pyramids and octahedra and the accompanied JT distortion increase the carrier-to-lattice coupling and result in localization of electrons between the \( d \) orbitals of Mn\(^{2+}\) and the octahedral Mn have only \( d_{x^2-y^2} \) in the vicinity of \( E_F \). Therefore these orbitals localize to form an OO pattern as shown in Fig. 3(b).

Experimentally, F ordering is found\(^5\) for LaBaMn\(_2\)O\(_6\), whereas our (FPLMTO and FPLAPW) calculations give AF as the ground state. However, recent experimental studies conclude that both F and CE-type AF ordering coexist in LaBaMn\(_2\)O\(_6\) below 150 K.\(^{12}\) Moreover, as the calculated energy difference between the F and AF states of LaBaMn\(_2\)O\(_6\) is very small, a little perturbation may flip the spin arrangement either to F or AF. Hence the coexistence of F and AF states must be considered as a viable outcome. LaBaMn\(_2\)O\(_6\) contains only one crystallographic type of Mn with an average valence state between 3+ and 4+. The Mn-\( d \) exchange splitting is found to be around 3.3, 3.0, and 2.5 eV for LaBaMn\(_2\)O\(_5\), LaBaMn\(_2\)O\(_{5.5}\), and LaBaMn\(_2\)O\(_6\), respectively. The systematic decrease appears to reflect the increasing Mn-\( d \) and O-\( p \) hybridization interaction and the reduction in magnetic moment of Mn due to increase in its valence state, in the said sequence.

As the oxygen vacancies are filled to the \( \delta=1 \) limit, the electron bands are broadened and more overlap between the Mn-\( d \) and O-\( p \) bands is seen. Moreover, the small energy difference between the F and AF states implies that the DE

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TABLE I. Total energy (relative to the lowest-energy state in meV/f.u.) in LaBaMn\(_2\)O\(_{5+\delta}\) for the P, F, and AF phases using FPLMTO with GGA and spin-orbit coupling included.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Energy (meV/f.u.)</th>
<th>P</th>
<th>F</th>
<th>AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaBaMn(_2)O(_5)</td>
<td>3922</td>
<td>438</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>LaBaMn(<em>2)O(</em>{5.5})</td>
<td>3850</td>
<td>593</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>LaBaMn(_2)O(_6)</td>
<td>2625</td>
<td>6</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

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TABLE II. Calculated magnetic moment (in \( \mu_B \) per Mn atom) for LaBaMn\(_2\)O\(_{5+\delta}\) in the AF ground state. Total refers to the total magnetic moment per formula unit.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mn(1)</th>
<th>Mn(2)</th>
<th>Total</th>
<th>Mn(1)</th>
<th>Mn(2)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaBaMn(_2)O(_5)</td>
<td>3.13</td>
<td>3.99</td>
<td>0.97</td>
<td>2.71(^a)</td>
<td>3.21</td>
<td>0.70</td>
</tr>
<tr>
<td>LaBaMn(<em>2)O(</em>{5.5})</td>
<td>3.30</td>
<td>3.34</td>
<td>0.0</td>
<td>3.03(^b)</td>
<td>3.43</td>
<td></td>
</tr>
<tr>
<td>LaBaMn(_2)O(_6)</td>
<td>2.98</td>
<td></td>
<td>0.0</td>
<td>3.50(^a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a\)Low-temperature neutron-diffraction data, Ref. 3.

\( ^b\)Low-temperature neutron-diffraction data, Ref. 5.
The HMF state of LaBaMn$_2$O$_6$ gains more importance owing to disappearance of CO and/or OO due to increased W can be achieved by application of external field or pressure. Since the band characteristics $t$ and $W$, as well as the valence state of Mn change more drastically with the oxygen contents than by A-site cation substitution in (RE,AE)MnO$_3$, one can tune an insulator-to-metal transition from the AF or Ferri CO and/or OO state to a metallic F state by merely varying the oxygen stoichiometry. Practice has shown that such a conversion may be accompanied by resistivity changes of several orders of magnitude (the CMR effect).

In conclusion, variations in the spin, charge, and orbital orderings by changes in the oxygen content have been illustrated with LaBaMn$_{2.5}$O$_6$ as an example. The changes in the oxygen stoichiometry controls the valence state of Mn and the hybridization interaction between Mn and O. Hence, a reduction in oxygen stoichiometry narrows the bandwidth and consequently decreases the double-exchange interactions at the expense of the competing superexchange interactions. Consequently the ferromagnetic state becomes destabilized relative to the antiferromagnetic state with localized spin, charge, and orbital order as well as Jahn-Teller-type electron-lattice coupling. Therefore by adjusting the oxygen stoichiometry in manganites one can convert the insulating antiferromagnetic charge- and/or orbital-ordered state into a metallic ferromagnetic state.

The authors are grateful to the Research Council of Norway for financial support. Part of these calculations were carried out on the Norwegian supercomputer facilities.

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12 T. Nakajima (private communication).