Double-exchange ferromagnetism in La(Mn$_{1-x}$Co$_x$)O$_3$

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We have investigated the appearance of ferromagnetism in a mixture of nonferromagnets LaMnO$_3$ and LaCoO$_3$, without heterovalent ion substitution in La sites. LaMn$_{0.85}$Co$_{0.15}$O$_3$ and La$_{0.7}$Sr$_{0.3}$Mn$_{0.8}$Co$_{0.2}$O$_3$ are studied by using x-ray-absorption and resonant photoemission spectroscopies. The results show that the dopant Co in LaMn$_{1-x}$Co$_x$O$_3$ becomes divalent rather than expected trivalent and induces Mn^{3+}-Mn^{4+} mixed valence states. Therefore, at variance with the earlier proposal of a structure-induced Mn^{3+}-Mn^{3+} ferromagnetic coupling, the ferromagnetic state in LaMn$_{1-x}$Co$_x$O$_3$ is consistent with the Mn^{3+}-Mn^{4+} double-exchange mechanism. [S0163-1829(97)07917-4]

Transition-metal perovskites have been known to exhibit varieties of electrical properties, from a large-gap insulator to a metal, and of magnetic properties such as paramagnetism, ferromagnetism, antiferromagnetism, and diamagnetism.[1] The perovskite has a typical formula BMO$_3$ in which B is either a rare earth such as La, Pr, etc., or an alkali metal such as Ca, Sr, etc. and M is $3d$ transition metal. The valence of the transition metal becomes either trivalent, M^{3+}, or tetravalent, M^{4+} depending on the B ion being trivalent rare earth or divalent alkali metal, respectively. With partial substitution of rare earth with alkali metal, the system becomes M^{3+}-M^{4+} mixed valent, and their relative content can also be controlled by the substitution amount.

Recently, doped manganese perovskites have attracted much renewed attention due to the recent discovery of colossal magnetoresistance (CMR).[2] The doped manganese perovskite, which is mixed-valent system with Mn^{3+}-Mn^{4+}, exhibits a paramagnetic to ferromagnetic transition accompanied by a large decrease of resistivity upon cooling.[3] This large change in the resistivity has been found to be associated with a metal-insulator transition in recent photoemission studies.[4] The ferromagnetic ground state has been understood by the Mn^{3+}-O^{2-}-Mn^{4+} double-exchange mechanism,[5] in which mobile Mn $3d$ electrons hop easily in the circumstance of ferromagnetic alignment of the manganese spins where the hopping avoids the strong Hund's-rule exchange energy.

A mixed-perovskite system LaMn$_{1-x}$Co$_x$O$_3$ has been the subject of crystallographic and magnetic studies.[6,7] LaCoO$_3$ is a diamagnetic insulator with low-spin-state Co^{3+} ($3d^6$, $S=0$) and displays a gradual low-spin to high-spin transition in a wide temperature range,[8] while LaMnO$_3$, which has an orthorhombic crystal structure, is an antiferromagnetic insulator with high-spin Mn^{3+} ($3d^4$, spin $S=2$) state and exhibits a severe Jahn-Teller lattice distortion which disappears around 700 K. Upon Co doping, the crystal structure becomes a rhombohedral structure, with a severe change in the structural distortion, and the ground state becomes a ferromagnetic state. The saturated ferromagnetic moment rapidly increases with the increase of Co concentration until it

reaches the maximum moment, $\sim 3.5\mu_B$, at $x\approx 0.15$, and then the moment decreases almost linearly with x for further Co concentration up to $x\sim 0.8$ in which the moment starts disappearing.[6,7] This behavior of the saturated magnetic moment has been attributed to a ferromagnetic Mn^{3+}-Mn^{3+} interaction, which was suggested to be driven by the crystal structure change from the orthorhombic to the rhombohedral structure, and Co^{3+} ions are considered to stay in the diamagnetic state, which contributes no magnetic moment.[6] However, the room-temperature resistivity of LaMn$_{1-x}$Co$_x$O$_3$ for $0.96 < x < 1.00$ exhibits similar behavior to that of La$_{1-x'}$Th$_{x'}$CoO$_3$, in which the substitution of La^{3+} with Th^{4+} is expected to induce Co^{2+} and the charge redistribution of Mn^{3+}+Co^{3+}$\rightarrow$Mn^{4+}+Co^{2+} has been suggested.[7]

In order to investigate the Co doping effects on manganese perovskites, we have studied the electronic structure of LaMn$_{0.85}$Co$_{0.15}$O$_3$ and La$_{0.7}$Sr$_{0.3}$Mn$_{0.8}$Co$_{0.2}$O$_3$ by utilizing Co $L_{2,3}$-edge and Mn $L_{2,3}$-edge x-ray-absorption spectroscopy (XAS), valence-band photoemission spectroscopy (PES), and Mn L_3-edge resonant photoemission spectroscopy (RPES). The Co $L_{2,3}$ XAS spectrum displays a spectral line shape which resembles that of the standard divalent cobalt oxide, CoO, and furthermore the Mn $L_{2,3}$ XAS spectrum of LaMn$_{0.85}$Co$_{0.15}$O$_3$ is also found to be almost identical to that of the Mn^{3+}-Mn^{4+} mixed-valent system La$_{0.80}$Ca$_{0.20}$MnO$_3$. These results provide strong evidence that the charge redistribution Mn^{3+}+Co^{3+}$\rightarrow$Mn^{4+}+Co^{2+} occurs in Co-doped manganese perovskites and the system becomes Mn^{3+}-Mn^{4+} mixed valent. Thus, at variance with the earlier proposal of the structure-induced Mn^{3+}-Mn^{3+} ferromagnetic interaction, the ferromagnetic states in LaMn$_{1-x}$Co$_x$O$_3$ should be understood in the framework of the double-exchange mechanism, as in La$_{1-x}$(Sr,Ca)$_x$MnO$_3$. Our findings provide a potential way for realizing CMR by Mn-site substitution, rather than the La-site doping in LaMnO$_3$.

The measurements were performed at the Dragon Beamline at the National Synchrotron Light Source (NSLS).[9] Polycrystalline LaCoO$_3$, LaMnO$_3$, La$_{0.8}$Ca$_{0.2}$MnO$_3$,
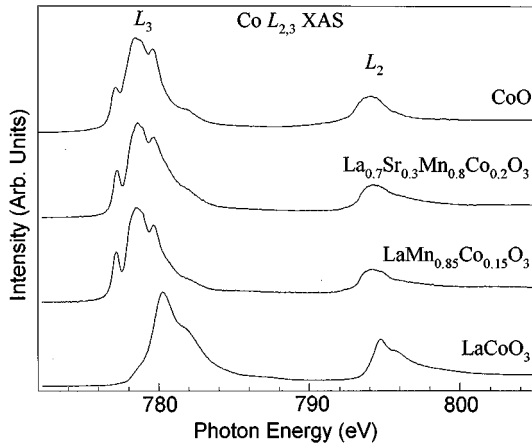
FIG. 1. Co $L_{2,3}$-edge XAS spectra of $LaMn_{0.85}Co_{0.15}O_3$, $La_{0.7}Sr_{0.3}Mn_{0.8}Co_{0.2}O_3$, $LaCoO_3$, and CoO.

$LaMn_{0.85}Co_{0.15}O_3$, and $La_{0.7}Sr_{0.3}Mn_{0.8}Co_{0.2}O_3$ were prepared by standard solid-state reaction in air, and x-ray-powder-diffraction measurements showed single-phase patterns. All spectra were normalized by the incident photon flux. The XAS spectra were collected in the total electron yield mode, and the photon resolutions were set at 250 and 200 meV for Co $L_{2,3}$ and Mn $L_{2,3}$ XAS spectra, respectively. The binding energy in PES spectra are referred to the chemical potential of a clean Pt sample in electrical and thermal contact with the sample, and the overall experimental resolutions were set at 600 and 700 meV for 500 eV PES and Mn L_3-edge RPES, respectively. The samples were cleaved at 80 K in a vacuum better than 1.5×10^{-10} Torr. The surface cleanness was confirmed by the absence of O $1s$ satellite in the PES spectrum taken at 700 eV. This satellite is known to appear with surface contamination.

The $3d$ transition-metal $L_{2,3}$ XAS spectrum has often been utilized to determine the ground-state symmetry since the spectrum displays a characteristic multiplet structure depending on the ground-state $3d$ configuration.[10] We have performed Co $L_{2,3}$ XAS to investigate the valence of the dopant Co in manganese perovskites. Figure 1 shows the XAS spectra of $LaMn_{0.85}Co_{0.15}O_3$ and $La_{0.7}Sr_{0.3}Mn_{0.8}Co_{0.2}O_3$ in comparison with those of CoO with divalent cobalt ions and $LaCoO_3$ with trivalent cobalt ions. The transition-metal sites in these three oxides have octahedral symmetry. All three spectra consist of L_3 and L_2 regions in low- and high-photon-energy regions, respectively. The spectra of CoO and of $LaCoO_3$ display different multiplet structures since the multiplet structures are induced from different ground states, the high-spin Co^{2+} ($3d^7$, spin $S=3/2$) state[10,11] and the low-spin Co^{3+} ($3d^6$, spin $S=0$) state,[12] respectively. Surprisingly, the Co $L_{2,3}$ XAS spectra of both $LaMn_{0.85}Co_{0.15}O_3$ and $La_{0.7}Sr_{0.3}Mn_{0.8}Co_{0.2}O_3$ are almost identical to the spectrum of CoO, but different from the spectrum of $LaCoO_3$, in the spectral line shape as well as in the absorption energies. This result shows that the dopant Co in manganese perovskites is divalent, not the expected trivalent.

There are two possible explanations for the divalent Co. One can be oxygen deficiency which is observed in $La_{1-x}Sr_xCoO_{3-\delta}$. However, the oxygen content in
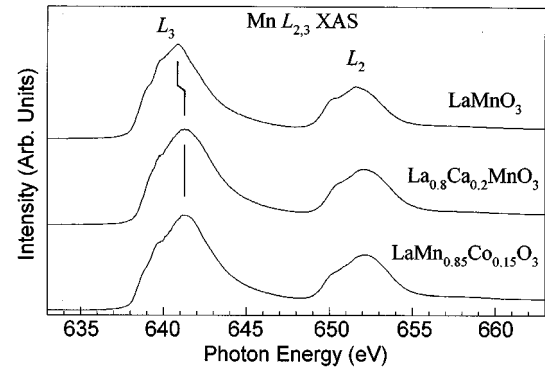

FIG. 2. Mn $L_{2,3}$-edge XAS spectra of $LaMn_{0.85}Co_{0.15}O_3$, $La_{0.8}Ca_{0.2}MnO_3$, and $LaMnO_3$.

Co-doped manganese perovskites has been known to be very close to the stoichiometry.[6,7] The other is a $Mn^{3+}+Co^{3+}\rightarrow Mn^{4+}+Co^{2+}$ type charge redistribution. The former does not affect the manganese state while the latter introduces Mn^{4+} and makes the system Mn^{3+}-Mn^{4+} mixed valent. Therefore, the cause for the divalent Co can be clarified by investigating the Mn states. Figure 2 shows Mn $L_{2,3}$ XAS spectra of $La_{0.8}Ca_{0.2}MnO_3$ and $LaMn_{0.85}Co_{0.15}O_3$. The $LaMnO_3$ has been found to have 1% excess oxygen, i.e., $LaMnO_{3.03}$, resulting in 6% of Mn^{4+}.[4] Although the XAS spectral line shape of $La_{0.8}Ca_{0.2}MnO_3$, which contains 20% of Mn^{4+}, changes only slightly from that of $LaMnO_{3.03}$, and the overall spectral weight shifts to higher photon energy by ~ 0.4 eV due to the higher absorption energy of the Mn^{4+}. Similar spectral changes were also observed in the spectrum of $LaMn_{0.85}Co_{0.15}O_3$, and the spectrum turns out to be almost identical to that of $La_{0.8}Ca_{0.2}MnO_3$, showing a similar Mn^{4+} to Mn^{3+} ratio. This result confirms a $Mn^{3+}+Co^{3+}\rightarrow Mn^{4+}+Co^{2+}$ type charge redistribution and eliminates the possibility of Co^{2+} formation due to the oxygen deficiency.

The Co $3d$ state in the valence band is investigated by comparing the valence-band PES spectrum of $LaMn_{0.85}Co_{0.15}O_3$ with those of $La_{0.8}Sr_{0.2}MnO_3$ and CoO. Figure 3 shows the spectra of $LaMn_{0.85}Co_{0.15}O_3$ and $La_{0.8}Sr_{0.2}MnO_3$ taken with 500 eV photons and that of CoO taken with 1486.6 eV photons as described in Ref. 11. According to the photoionization atomic cross section,[13] the Mn $3d$ spectral weight is comparable to that of the O $2p$ in the spectra of manganese perovskites, while the Co $3d$ spectral weight dominates the spectrum of CoO. $LaMn_{0.85}Co_{0.15}O_3$ contains only 15% of Co^{2+}, which contributes about 10% spectral weight to the valence-band spectrum. It is expected that the spectrum should be quite similar to that of $La_{0.8}Sr_{0.2}MnO_3$ except for the considerable difference observed near 1.5 eV binding energy. This difference can be understood by comparing to the CoO valence-band spectrum. As can be seen in the figure, the CoO spectrum displays a very intense peak, which was known to have a $t_{2g}^4 e_g^2(^5T_2)$ symmetry,[11,14] in the energy region. The Co $3d$ spectrum of $LaMn_{0.85}Co_{0.15}O_3$ is approximately obtained by subtracting 85% of the $La_{0.8}Sr_{0.2}MnO_3$ spectrum. The difference spectrum, which is presented in the figure, exhibits a quite similar line shape as the CoO spectrum. This result
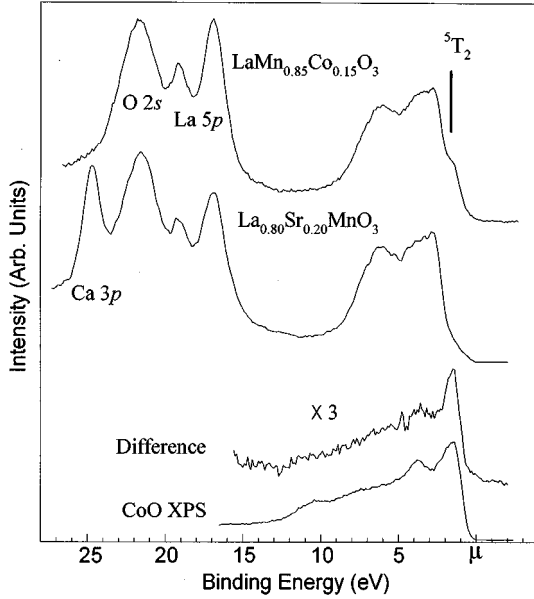
FIG. 3. Valence-band spectra of $LaMn_{0.85}Co_{0.15}O_3$, $La_{0.8}Ca_{0.2}MnO_3$, and CoO, and the difference spectrum as described in the text. The difference spectrum is obtained by subtracting 85% of the $La_{0.8}Ca_{0.2}MnO_3$ spectrum from the $LaMn_{0.85}Co_{0.15}O_3$ spectrum. The CoO spectrum is shifted to be aligned with the difference spectrum.

indicates that the electronic structure of Co $3d$ in $LaMn_{0.85}Co_{0.15}O_3$ is almost identical to that in CoO.

Now we will compare the electronic structure of Co $3d$ states with that of Mn $3d$ states. In previous photoemission studies of $La_{1-x}(Ca,Sr)_xMnO_3$, the spectral weight between 0 and 2 eV binding energies has been identified to be the t_{2g}^3 ($^4A_2$) photoemission state from the Mn^{3+} site.[4] But this state is completely obscured by the Co $3d$ states in the spectrum of $LaMn_{0.85}Co_{0.15}O_3$. In order to highlight the Mn $3d$ states, we have performed Mn L_3-edge RPES. In the RPES, the Mn $3d$ photoemission is enhanced exclusively by the process $3d^n \rightarrow c3d^{n+1} \rightarrow 3d^{n-1}+e^-$, where c denotes a Mn $2p$ hole. The on- and off-resonant spectra, which were taken with 641 and 635 eV photons, respectively, are presented in Fig. 4. The difference spectrum was obtained from subtraction of the off-resonance spectrum from the on-resonance spectrum. Large spectral enhancement is observed in the 0–14 eV valence-band region without any significant change in the O $2s$ and La $5p$ shallow core levels. The difference spectrum consists of a main peak region with two rather sharp features in the 0–4 eV region, a satellite state region with two broad features in the 4–9 eV region, and a long tail in the 9–14 eV region. The long-tail feature is the Mn L_3VV Auger signal with specific kinetic energies as confirmed by our detailed RPES measurements.[15] The main and satellite states can be understood by a many-body approach, which includes configuration interactions. This theoretical approach has successfully reproduced the photoemission spectra of various transition metal compounds.[16] The two peaks in the main state region were interpreted as the $t_{2g}^3(^4A_2)$ symmetry state and the $t_{2g}^2e_g^1(^4T_2)$ symmetry state in previous studies,[4] and their peak positions are estimated as 1.2 and 2.6 eV, respectively. Hence the Co $3d$ $t_{2g}^4e_g^2$
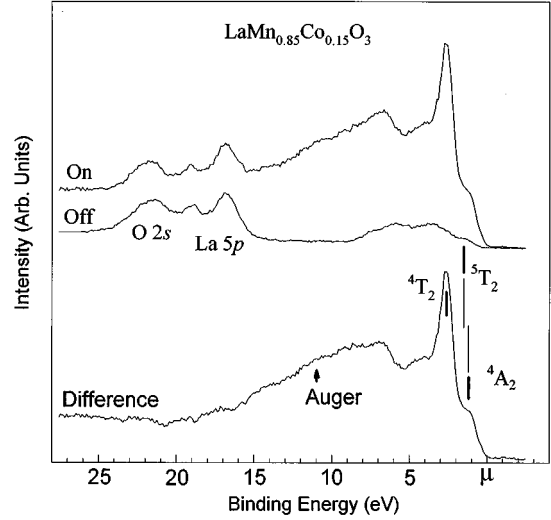

FIG. 4. Mn L_3-edge valence-band spectra of $LaMn_{0.85}Co_{0.15}O_3$ as described in the text. The difference spectrum is obtained by subtracting the off-resonance spectrum from the on-resonance spectrum.

($^5T_2$) state peak is located at ~ 0.3 eV lower binding energy than the Mn $3d$ t_{2g}^3 ($^4A_2$) state one.

In Co-doped manganese perovskite, the charge redistribution $Mn^{3+}+Co^{3+} \rightarrow Mn^{4+}+Co^{2+}$ occurs and reduces the system energy. The reduction energy ΔE corresponds the difference in ionization energies of Co^{2+} and Mn^{3+}:

$$\Delta E \equiv E(Mn^{3+}+Co^{3+}) - E(Mn^{4+}+Co^{2+})$$
$$= E(Co^{2+} \rightarrow Co^{3+}) - E(Mn^{3+} \rightarrow Mn^{4+}).$$

Photoemission spectroscopy yields ionization energies, but one should notice that the photoionization is a "sudden" process, in which the obtainable ionized states are restricted by the dipole selection rules, while, in the charge redistribution, the ionized states are the corresponding lowest-energy states. Thus the lowest-ionized-energy states are possibly not obtainable in the photoionization processes.

Under octahedral site symmetry, the ground states of $LaMnO_3$ (Mn^{3+}) and of CoO (Co^{2+}) are $t_{2g}^3e_g^1(^5E)$ and $t_{2g}^5e_g^2(^4T_1)$ symmetry states, respectively. The ground state at Mn^{4+} sites in the doped manganese perovskite is a $t_{2g}^3(^4A_2)$ symmetry state, which can be reached through the photoionization process from the Mn^{3+} $t_{2g}^3e_g^1$ (^5E) ground state, while the ground state of $LaCoO_3$ (Co^{3+}) is a $t_{2g}^6(^1A_1)$ symmetry state, which is not allowed in the photoionization process from the Co^{2+} $t_{2g}^5e_g^2(^4T_1)$ ground state. However, in $LaCoO_3$, the energy of the $t_{2g}^4e_g^2(^5T_2)$ high-spin state, which can be reached by the photoemission process, turns out to be very slightly higher than that of the $t_{2g}^6(^1A_1)$ low-spin state, and the energy difference, which has been estimated to be 5–80 meV,[8] can be overcome even by thermal activation. Hence, in the first approximation, the ionization energy $E[Co^{2+} \rightarrow Co^{3+}(^1A_1)]$ can be replaced with $E[Co^{2+} \rightarrow Co^{3+}(^5T_2)]$.

A lattice relaxation energy should be also considered, since the lattice is not fully relaxed in the sudden photoion-

ization process. With the relaxation energy corrections, the energy reduction can be presented by

$$\Delta E \approx E_{\mathrm{PI}}[\mathrm{Co}^{2+} \rightarrow \mathrm{Co}^{3+}(^5T_2)]$$
$$- E_{\mathrm{PI}}[\mathrm{Mn}^{3+} \rightarrow \mathrm{Mn}^{4+}(^4A_2)] - \Delta E_L ,$$

where E_{PI}'s denote the corresponding photoionization energy and ΔE_L is the difference in the lattice relaxation energy, $E_L(\mathrm{Co}^{3+}) - E_L(\mathrm{Mn}^{4+})$. The photoionization energies were obtained to be 1.2 eV for $E_{\mathrm{PI}}[\mathrm{Mn}^{3+} \rightarrow \mathrm{Mn}^{4+}(^4A_2)]$ and 1.5 eV for $E_{\mathrm{PI}}[\mathrm{Co}^{2+} \rightarrow \mathrm{Co}^{3+}(^5T_2)]$, and thus the redistribution energy $\Delta E \approx 0.3$ eV $- \Delta E_L$. A theoretical estimation for ΔE_L is not available at this time due to the complicated solid-state reactions. An empirical estimation based on the ionic sizes in oxides[17] shows that the reduction of the manganese ionic size in the valence change, Mn^{3+} to Mn^{4+}, is quite similar to that of cobalt ionic size in the valence change, Co^{2+} to Co^{3+}.[18] Thus the lattice relaxation energy

of the manganese, $E_L(\mathrm{Mn}^{4+})$, is expected to be very similar to that of the cobalt, $E_L(\mathrm{Co}^{3+})$.[19] With the assumption of $\Delta E_L \approx 0$, the energy reduction in the $\mathrm{Mn}^{3+} + \mathrm{Co}^{3+} \rightarrow \mathrm{Mn}^{4+} + \mathrm{Co}^{2+}$ charge redistribution is estimated to be $\Delta E \approx 0.3$ eV.

In conclusion, we report spectroscopic studies of Co-doped manganese perovskites. We have found that the dopant Co is not trivalent as expected in LaCoO_3 but divalent as in CoO. This result shows that, with the partial substitution of Mn by Co, the manganese perovskite becomes mixed valent. Therefore, the ferromagnetic state observed in $\mathrm{LaMn}_{1-x}\mathrm{Co}_x\mathrm{O}_3$ should be understood in the framework of the double-exchange mechanism of Mn^{3+}-Mn^{4+}. The energy reduction in the $\mathrm{Mn}^{3+} + \mathrm{Co}^{3+} \rightarrow \mathrm{Mn}^{4+} + \mathrm{Co}^{2+}$ charge redistribution is also estimated to be a few tenths of eV.

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[18] The reduction is about 20%, which yields about a 6% shorter metal-oxygen distance.

[19] The relaxation energy is the order of 1 eV. The photoionization energy in $\mathrm{Mn}^{3+} \rightarrow \mathrm{Mn}^{4+}$ is compensated by the lattice relaxation energy, and thus Mn^{3+} and Mn^{4+} can coexist in the ground state.