

Electronic state and valence control of LaCoO_3 : Difference between La-deficient and Sr-substituting effects

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The difference between La-deficient and Sr-substituting effects for La in LaCoO_3 has been investigated by using x-ray photoelectron spectroscopy (XPS). On the basis of the relationship between the intensity of the 2T_2 line and the amount of low-spin Co^{3+} ions in these compounds, it is pointed out that $\text{La}_{0.9}\text{CoO}_{3-\delta}$ is in a highly covalent low-spin state and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ is in a mixed spin state. From the Co $2p$ and valence-band XPS results, it is pointed out that the electronic state of $\text{La}_{0.9}\text{CoO}_{3-\delta}$ is quite different from that of Sr-substituting $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. In order to explain the difference between La-deficiency and Sr-substitution effects in valence controlling of LaCoO_3 , it is considered that Sr substitution produces the Co $3d$ holes and La deficiency yields the O $2p$ holes. [S0163-1829(97)03727-2]

LaCoO_3 is one of the $3d$ transition-metal oxides with the simple perovskite structure and exhibits a semiconductor-to-metal transition as well as a spin-state transition; that is, a change in the spin state of Co^{3+} ($3d^6$).^{1,2} As for the spin-state transition, recent theoretical³ and experimental^{4,5} works suggested that the spin-state transition in LaCoO_3 occurs in two steps. That is, the first spin step is basically a conversion from the low-spin state of Co^{3+} ($S=0$) as a ground state to the intermediate-spin state ($S=1$) around 100 K. The second step corresponds to a change from the intermediate-spin state to a mixed state of the intermediate- and high-spin state around 500 K. In addition, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, in which a La site in LaCoO_3 is partially substituted by Sr^{2+} , shows itinerant ferromagnetism in $x>0.1$.⁶ Because the ionic radius of Sr^{2+} is larger than that of La^{3+} , the Sr doping favors the high-spin state and the introduction of Co^{4+} ($3d^5$).

As was mentioned above, the character of doped carriers was not experimentally determined for LaCoO_3 , but only for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. The Sr doping, however, makes the Co-O bond length longer and favors the high-spin state instead of the low-spin one. That is, there is a possibility that the Sr doping results in the change in the ground state. This clearly implies that the character of doped carriers in LaCoO_3 with the low-spin state as the ground state has not been established experimentally. Recently, we found that a phase with La vacancies in LaCoO_3 was stable in air.⁷ It should be remarked that the La deficiency in $\text{La}_{0.9}\text{CoO}_3$ also introduces holes, like the Sr doping does. In order to know the difference between La deficient and Sr substituting effects for La in LaCoO_3 , we have investigated elec-

tronic structures of $\text{La}_{0.9}\text{CoO}_3$ as well as LaCoO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ by x-ray photoelectron spectroscopy. On the basis of experimentally obtained data, we discuss the differences between characters of doped holes in $\text{La}_{0.9}\text{CoO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$.

Sample powders of $\text{LaCoO}_{3-\delta}$, $\text{La}_{0.9}\text{CoO}_{3-\delta}$, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, were prepared from coprecipitation of citrates. After having been calcined at 1373 K for 5 h in air, sample powders were ground and pressed into pellets, and then heated again at 1373 K for 10 h in air. A characterization of crystal structures of sample pellets made in the present work, together with the determination of their lattice constants, was performed by x-ray powder diffraction. All the samples were, as a result, confirmed to consist of a single phase. The details of the crystal structures of the pellets were also examined by electron diffraction by means of a Hitachi HF-2000 transmission electron microscope (TEM). Specimens for the TEM observation, i.e., ceramic flakes, were prepared by crushing the sample pellets. X-ray photoelectron spectra (XPS) were measured at room temperature, by using a commercial x-ray photoelectron spectrometer (PHI ESCA-5600). The base pressure in the chamber was about 10^{-12} atm. The x-ray source is a monochromatized Al $K\alpha$ line (1486.6 eV) with a combined energy resolution of about 0.3 eV. The cleanliness of a sample surface was ensured by *in situ* scraping of the surface with an alumina file, so that the C $1s$ signal due to carbonate impurity in the surface was found to be very weak in all of the samples. Core-level binding energies were assigned with respect to the C $1s$ peak at 285.0 eV as a reference in order to account for the surface

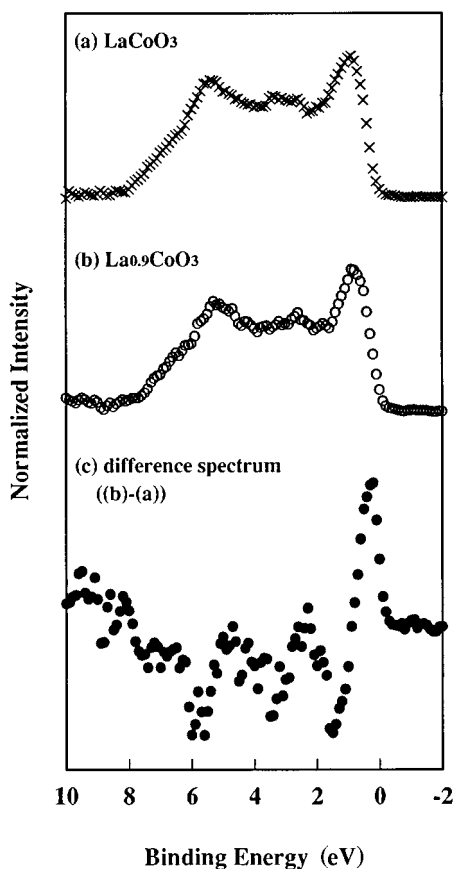


FIG. 1. Difference spectrum for valence-band XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.9}\text{CoO}_{3-\delta}$: (a) $\text{LaCoO}_{3-\delta}$, (b) $\text{La}_{0.9}\text{CoO}_{3-\delta}$, and (c) difference spectrum [(b)-(a)].

charge up. In order to easily see a difference among the measured XPS profiles in $\text{LaCoO}_{3-\delta}$, $\text{La}_{0.9}\text{CoO}_{3-\delta}$, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, with the difference spectra for the valence-band and Co 2*p* XPS data were obtained. Typically both spectra had their peak maximum set to the same value and then normalization was carried out on the basis of height. Valence-band and Co 2*p* XPS spectra were, respectively, normalized with respect to a background intensity at 10 eV below the Fermi level and the height of the Co 2*p* $\frac{3}{2}$ peak.

Figures 1 and 2 show the difference spectra for the valence-band XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.9}\text{CoO}_{3-\delta}$ (Fig. 1), and between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (Fig. 2). These spectra show several features in the first 8 eV below the Fermi level. Among their features, the intensity of the line peak at about 1 eV (2T_2 line) was already analyzed to correspond to the $t_{2g}^6({}^1A_1) + hv \rightarrow t_{2g}^5({}^2T_2) + e$ photoemission channel, and its integrated intensity is proportional to the amount of low-spin Co^{3+} ions.⁸ The most important feature is that intensity of the 2T_2 line of $\text{LaCoO}_{3-\delta}$ is weaker than that of $\text{La}_{0.9}\text{CoO}_{3-\delta}$, but is stronger than that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. That is, the difference between the difference spectra shown in Figs. 1 and 2 is clear evidence that features of the valence band in $\text{La}_{0.9}\text{CoO}_{3-\delta}$ are different from $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. It is worth noticing that the obtained spectra of $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ are identical to those reported in previous works.^{8,9} That is,

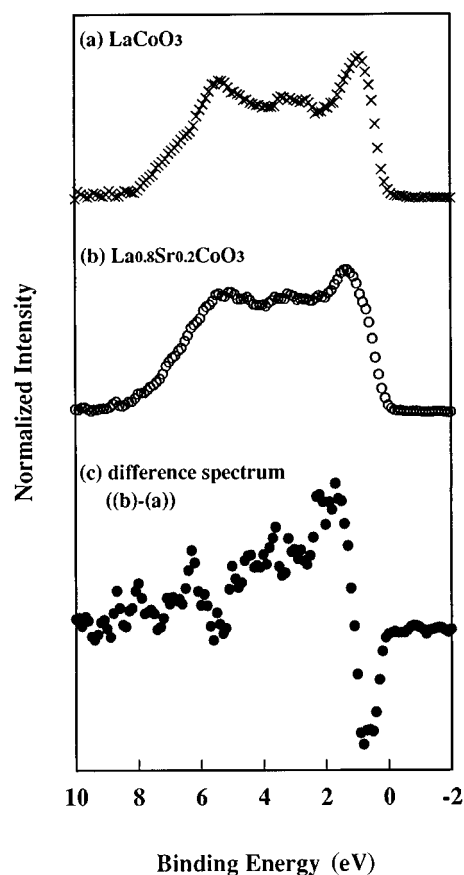


FIG. 2. Difference spectrum for valence-band XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$: (a) $\text{LaCoO}_{3-\delta}$, (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, and (c) difference spectrum [(b)-(a)].

$\text{LaCoO}_{3-\delta}$ at room temperature is characterized by mixed spin states of the low-spin and intermediate-spin state. From these results, La deficiency is understood to inhibit the excitation of the intermediate-spin state and then stabilizes the low-spin state, while the Sr substitution results in the reducing of the stability of the low-spin state. Figures 3 and 4 show the difference spectra for the Co 2*p* XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.9}\text{CoO}_{3-\delta}$ (Fig. 3), and between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (Fig. 4). The most intense peak at 780-eV binding energy is due to the Co 2*p* $\frac{3}{2}$ main peak and the peak at 794.5 eV is due to the Co 2*p* $\frac{1}{2}$ main peak. The weak satellite feature of Co 2*p* XPS data can also be seen at about 790 eV for three compounds. Among these results, the Co 2*p* XPS data for $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ agree well with the previous data obtained by Chainani *et al.*⁹ The difference spectrum in Fig. 3 shows increased intensity below 780 eV (peak A) and decreased intensity above 780 eV (peak B). On the contrary, the difference spectrum in Fig. 4 shows a decreased intensity below 780 eV (peak A) and increased intensity above 780 eV (peak B). From these results, it should be pointed out that the electronic state of La-deficient $\text{La}_{0.9}\text{CoO}_{3-\delta}$ is quite different from that of Sr substituting $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. The lattice constants determined by x-ray diffraction of these compounds are shown in Table I. The lattice constant of $\text{La}_{0.9}\text{CoO}_{3-\delta}$ is almost equal to LaCoO_3 , while the lattice constant of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ is longer than that of LaCoO_3 . Figure 5 shows electron diffraction patterns for

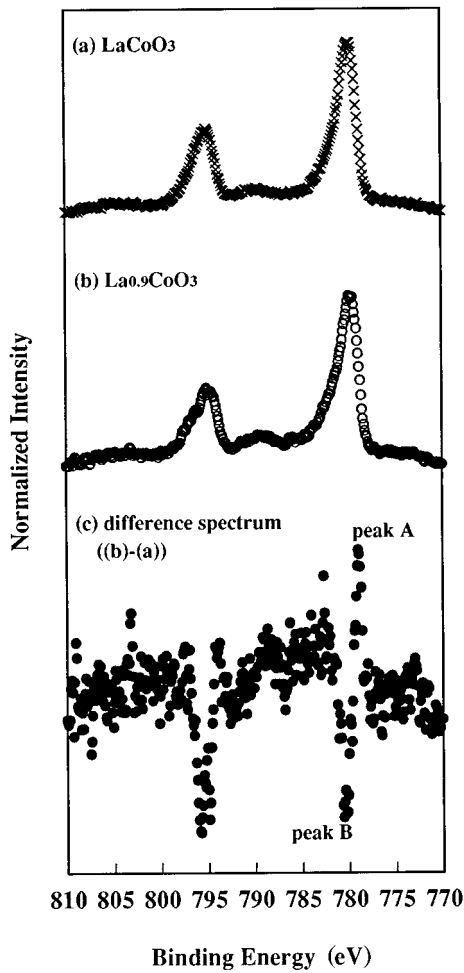


FIG. 3. Difference spectrum for Co 2p XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.9}\text{CoO}_{3-\delta}$: (a) $\text{LaCoO}_{3-\delta}$, (b) $\text{La}_{0.9}\text{CoO}_{3-\delta}$, and (c) difference spectrum [(b)-(a)].

$\text{La}_{0.9}\text{CoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. The electron incidence of these patterns is parallel to the [110] direction where diffraction spots are indexed in terms of the cubic perovskite structure. There exist $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ -type superlattice spots (indicated by A in Fig. 5). This shows that the space group of these compounds is $R\bar{3}c$ or $R\bar{3}$. From the detailed analysis of electron diffraction patterns of $\text{LaCoO}_{3-\delta}$ by Koyama *et al.*,¹⁰ there are no $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ -type superlattice spots along the [111] direction. In other words, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ -type superlattice spots along the [111] direction are due to double diffraction. From its extinction rule, the space group of these compounds is $R\bar{3}c$.

Recently, our work¹¹ based on the theoretical investigation of the electronic structure of LaCoO_3 by *ab initio* molecular-orbital calculations showed that the covalency of LaCoO_3 in the low-spin state was larger than that in

TABLE I. Lattice parameters of LaCoO_3 , $\text{La}_{0.9}\text{CoO}_3$, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$. * denotes the rhombohedral unit cell.

Lattice parameter*	LaCoO_3	$\text{La}_{0.9}\text{CoO}_3$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$
a (Å)	5.377	5.380	5.403
α (°)	60.81	60.80	60.55

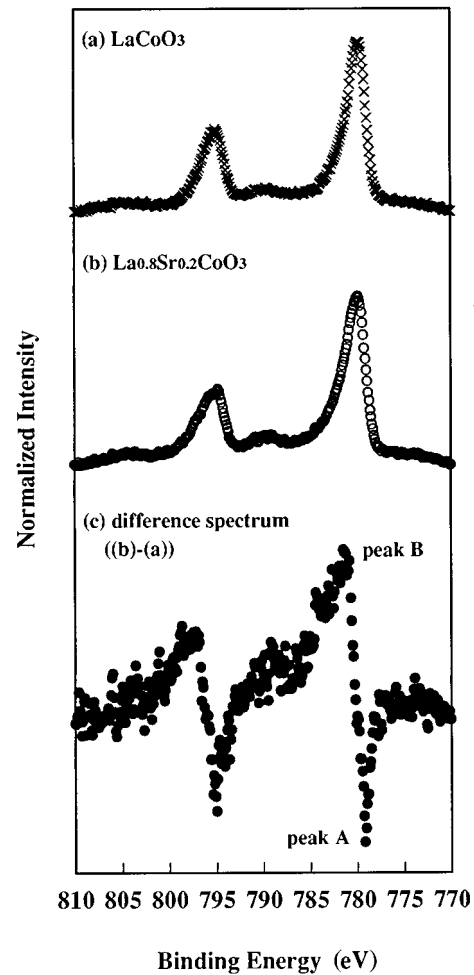


FIG. 4. Difference spectrum for Co 2p XPS data between $\text{LaCoO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$: (a) $\text{LaCoO}_{3-\delta}$, (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$, and (c) difference spectrum [(b)-(a)].

the high-spin state, due to the main contribution of the hybridization between Co and O orbitals, and the spin-state transition of LaCoO_3 occurred mainly due to the variation of Co-O bond length. Also, Abbate *et al.*⁸ pointed out that the Co 3d-O 2p hybridization could play an important role in causing the spin-state transition of LaCoO_3 mainly due to the variation of Co-O bond length with increasing temperature. It was pointed out that the most relevant contribution to the spectra in the case of the low-spin Co^{3+} ions was a single line corresponding to the photoionization of the

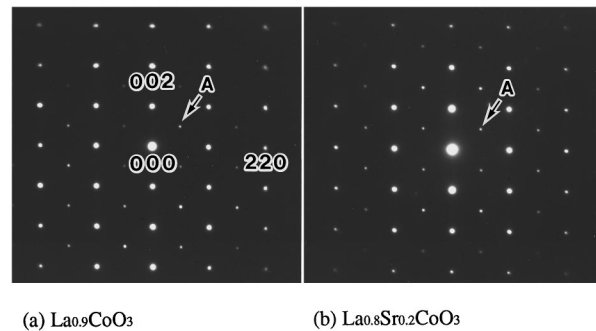


FIG. 5. Electron-diffraction patterns of (a) $\text{La}_{0.9}\text{CoO}_{3-\delta}$ and (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$. (See text.)

$3d^6$ part of the ground state, i.e., the $t_{2g}^6(^1A_1) + hv \rightarrow t_{2g}^5(^2T_2) + e$ photoemission channel, and these spectra were similar to the spectrum of the well-known low-spin Co^{3+} compound LiCoO_2 in Ref. 12.⁸ In a previous report,¹² it was found experimentally that the low-spin Co^{3+} ions in LiCoO_2 were stabilized due to the small Co-O distance. From the cluster calculation of the Co^{3+} low spin of LiCoO_2 in the CoO_6 cluster,¹² it was reported that the ground state was of very mixed character and consisted of d^6, d^7L, d^8L^2 , where L represented an O $2p$ hole, yielding a strongly covalent bonding in this compound. In the oxide, the introduction of crystal and ligand fields can lead to a low-spin ground state depending on the competition between the cubic crystal field ($10Dq$) and the intra-atomic exchange (J). For a d^6 compound, the low-spin state ($t_{2g}^6e_g^0$) is more stable than the high-spin state ($t_{2g}^4e_g^2$) if $10Dq > 2J$ (see Fig. 2 in Ref. 13). In the oxygen band, the states which hybridize with the metal states of e_g symmetry are higher in energy with respect to those that hybridize with the states of t_{2g} symmetry because of oxygen-oxygen interactions. This energy difference in an octahedral oxygen cluster is $2(pp\sigma - pp\pi)$, where $pp\pi$ and $pp\sigma$ are the oxygen-oxygen transfer integrals.¹³ Therefore, O $2p$ hole states with e_g symmetry are stabilized with respect to O $2p$ holes with t_{2g} symmetry. Thus it was suggested that if the Co $3d$ -O $2p$ hybridization results in a ligand field strong enough to stabilize a low-spin state, then holes introduced by doping will be O $2p$ holes. It is worth noticing that the increased intensity of the 2T_2 line in Fig. 1 shows the increase of low-spin Co^{3+} ions and is similar to the spectrum of well-known low-spin Co^{3+} compound LiCoO_2 in Ref. 12. That is, the increased intensity of the 2T_2 line in Fig. 1 indicates that the

valence controlling by La deficiency strongly affects the $d-p$ hybridization. From the above discussion, the valence controlled by La deficiency stabilizes the low-spin Co^{3+} ion, and introduces the O $2p$ hole into LaCoO_3 . The photoelectron spectroscopy study in Ref. 9 showed that the line shape of the 2T_2 line was distinctly broadened by Sr doping, and it indicated that the Sr substituting for La introduced hole states above the Fermi level with substantial Co $3d$ character and gave the metallic behavior. Actually, the valence-band and Co $2p$ XPS data of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ in Figs. 2 and 4 show the similar profile to the spectra of mixed high- and low-spin states in previous data of Ref. 9. Because the intensity of line peak at about 1 eV (2T_2 line) relates the amount of low-spin Co^{3+} ions,⁸ the decreased intensity of the 2T_2 line in Fig. 2 suggests the decrease of low-spin Co^{3+} ions and the increase of the high-spin state. That is, the present results mean that Sr substitution introduces the Co $3d$ holes.

From the results based on the relationship between the intensity of the 2T_2 line and the amount of low-spin Co^{3+} ions, it may be concluded that $\text{La}_{0.9}\text{CoO}_{3-\delta}$ is in a highly covalent low-spin state, while $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ is in mixed spin states. Thus, La deficiency introduces the holes without the change of lattice constants, and Sr substituting increases the lattice constants without the change of space group as shown in Table I. On the basis of these experimental and calculated¹¹ results, in order to understand the electronic states in valence controlled LaCoO_3 , it can be considered that the Co-O bond length is related to the change of electronic state.

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