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Ab initio study of the electronic structures in $LaCoO_3$-$SrCoO_3$ systems

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Electronic structures of $LaCoO_3$ and $SrCoO_3$ cluster models near the Fermi level were investigated from *ab initio* molecular-orbital calculations using the Hartree-Fock approximation, the single-excitation configuration-interaction approximation, and local density approximations in order to reveal the electronic structures of $La_{1-x}Sr_xCoO_3$. The obtained results are summarized as follows: (1) $La_{1-x}Sr_xCoO_3$ is nearly intermediate between Mott-Hubbard-type compounds and charge-transfer-type compounds, with interaction between Co and O ions. (2) The covalency of $La_{1-x}Sr_xCoO_3$ is due to the main contribution of the hybridization between Co and O orbitals. (3) With the decrease of the crystal field, i.e., the increase of Co-O bond length, the low-spin state gradually becomes unstable, while the high-spin state becomes stable. There is the possibility of the existence of an intermediate spin state. (4) The metal-insulator transition occurs due to the interaction between mixed states consisting of electrons for Co ions and holes for O ions. From the above results, the correlation between the spins of Co ions and O holes plays an important role in determining the physical properties of $La_{1-x}Sr_xCoO_3$. [S0163-1829(98)02324-8]

I. INTRODUCTION

To elucidate the properties of strongly correlated electron systems, many works on the electronic structures of $3d$ transition-metal oxides and metal-insulator transition by carrier doping have been made. Giant magnetoresistance phenomena have recently been found in provskite-type Mn oxide compounds with controlled carrier density,[1] the study of which further reveals abundant magnetotransport properties and related functionalities. $La_{1-x}D_xMnO_3$ (D=Ca,Sr,Ba) shows phase transitions such as a metal-insulator transition and a magnetic transition. Recently it has been found that Co oxide compounds such as $La_{1-x}Sr_xCoO_3$ also show a similar fairly large negative magnetroresistance.[2] $La_{1-x}Sr_xCoO_3$ shows interesting phase transitions such as a metal-insulator transition (insulator→metal) with increasing temperature ($T>570$ K at $x=0$),[3] or with an increasing amount of Sr substitution ($x>0.2$).[4] In addition, $La_{1-x}Sr_xCoO_3$ becomes paramagnetic, spin glass, and ferromagnetic at $x<0.05, 0.2> x\geqslant 0.05$ and $x\geqslant 0.2$, respectively.[5] Many physicists have endeavored to reveal the electronic structure of $La_{1-x}Sr_xCoO_3$ according to the Mott[6,7]-Hubbard[8] model.

Mott and Hubbard suggested that the d-d Coulomb interaction energy U and d-band-width w dominated the electronic structure near the Fermi level. If $U>w$, it is an insulator with a gap between the conduction and valence bands determined by the energy required for the fluctuations as $2d^n \rightarrow d^{n+1}+d^{n-1}$. In the case of $U<w$, it is a metal without a gap. From experimental results which show that $LaCoO_3$ is an insulator, the former case has been satisfied, and is called a Mott insulator. The above interpretation of electronic structures has long been considered to be effective.

According to the Mott-Hubbard model, conventionally, the conductivity and magnetism (ferromagnetism) observed in $La_{1-x}Sr_xCoO_3$ could be due to one of three mechanisms: (1) ordering of high- and low-spin cations through ferromagnetic superexchange in between them via the intervening oxygen ion,[9] (2) Zener double exchange,[10] and (3) itinerant-electron ferromagnetism.[4] The first mechanism, based on a localized electron model due to Anderson, was modified by Raccah and Goodenough to account for the ferromagnetic interaction observed in this system.

The itinerant-electron model was proposed by Raccah and Goodenough. Thermal excitation to the high-spin Co^{3+} configuration creates a magnetic ion, but it does not produce a mobile hole. Mobile holes are created by excitation of an electron from the π^* band to an acceptor level. As the amount of Sr substitution is increased, the acceptor orbitals interact to form an impurity band. If the high- and low-spin states have comparable energies, the formation of impurity bands generate a spontaneous ferromagnetism, wherein the σ^* bands of up-spin overlap the π^* band of down-spin. Recently Senaris-Rodriguez and Goodenough proposed a mechanism described by the complicated Co $3d$ band structure of $La_{1-x}Sr_xCoO_3$ on magnetic and transport properties using magnetic susceptibility and thermoelectric measurement (they postulate a complicated interaction between $3d$ electrons).[11,12] Using molecular-orbital theory, they assumed the highest occupied molecular orbital (HOMO) contained Co $3d$ and O $2p$ orbitals. Sarma *et al.*[40] obtained the result that the electronic structures of $LaCoO_3$ were of a Mott-Hubbard type. Wang and Zhang suggested that double-exchange interaction played an important role in the ferromagnetic metallic conductivity of $La_{1-x}Sr_xCoO_3$.[13]

Fujimori and Minami[14] and Sawatzky and co-workers[15–17] pointed out the importance of the charge-transfer energy Δ from the O $2p$ band to the upper $3d$ metal band (conduction band), and O $2p$ bandwidth W, as well as the transfer energy from the lower $3d$ metal band to the upper $3d$ metal band U and the $3d$ metal bandwidth w, in order to understand the electronic structures of charge-transfer-type metal oxides, especially the nature of the band gap. They suggested that Mn and Co oxides should belong to this charge-transfer type. Abbate and co-workers[18,19] and Mizokawa and Fujimori[20] concluded that $LaCoO_3$ was a charge-transfer insulator. Recently, from a theoretical point of view, using methods developed by an *ab initio* molecular orbital method using a supercomputer,[21] we also concluded that $LaCoO_3$ was a charge-transfer insulator. The metal-insulator transition which appears at high temperatures is not a Mott-Hubbard transition but a charge-transfer-type transition. The spin state transition occurs mainly due to the variation of the Co-O bond length with increasing temperature. The transition occurs through the interaction between the O $2p$ orbitals or the Co $3d$ and O $2p$ orbitals. Munakata *et al.* suggested that the top of the valence band could be assigned mainly to the O $2p$ band by analysis of the x-ray photoemission spectrum.[22] Moreover recently, Saitoh *et al.* emphasized that the band gap in $LaCoO_3$ did not have a d-d gap, nor a p-d gap, but a p-p gap.[23]

To date, there are only the above three explanations of the electronic structures of $La_{1-x}Sr_xCoO_3$. One cannot understand the electronic structure. Therefore, we tried to reveal the electronic structures of $La_{1-x}Sr_xCoO_3$ using calculations. We believe that *ab initio* molecular-orbital methods based on the Hartree-Fock approximation are appropriate for revealing the electronic structures. Regarding the electronic correlation by using the configuration interaction (CI) method and the density-functional-theory (DFT) method, we tried to investigate how the calculated electronic structures of the system change, and the role of the correlation in determining the band structures. In the present paper, we report a study of the electronic structures of $La_{1-x}Sr_xCoO_3$ based on the results of the *ab initio* molecular orbitals of $SrCoO_3$ and $LaCoO_3$ as well as the previous results for $LaCoO_3$. We concentrate on the magnitude of the band gap, the ordering of Co $3d$ and O $2p$ bands, and the spin state in the ground state of $SrCoO_3$. The effects caused by the interaction between the Co $3d$ and O $2p$ electrons are explained by the calculated results. In addition, we discuss the relation between the conductivity and magnetism of $La_{1-x}Sr_xCoO_3$ from the ground and excited states.

II. METHOD

A. Model

We calculated the electronic structures of $SrCoO_3$ using an *ab initio* molecular-orbital method. $LaCoO_3$ has a pseudocubic perovskite structure with a rhombohedral distortion along the (111) direction. However, with Sr doping, $La_{1-x}Sr_xCoO_3$ gradually becomes of a pure perovskite type. Finally, $SrCoO_3$ is a pure perovskite crystal. We made the assumption that the electronic structure of a cluster made of finite unit cells could be representative of the structures of $SrCoO_3$, determined mainly due to the localization effect of the Co $3d$ atomic orbitals and the plane-wave-like character of O $2p$ orbitals. In the present analysis, we use the following cluster model. The Co-O bond length ds is taken as 2.0–2.5 Å in order to explain the temperature dependence of the electronic structures and the variation of the bond length with Sr doping.

The $[Co-O_6]^{8-}$, $[Co_2-O_{11}]^{14-}$, and $[Co_4-O_{20}]^{24-}$ clusters have the calculated structures ($+4e$ for a Co ion, $-2e$ for an O ion, and $+2e$ for a Sr ion). In addition, in order to consider the effect of the Madelung potential, the calculated structure is composed of the $n\times n\times n$ ($n=1-7$) unit cells in consideration of the translational symmetry of the crystal by crystallography, as shown in Fig. 1.

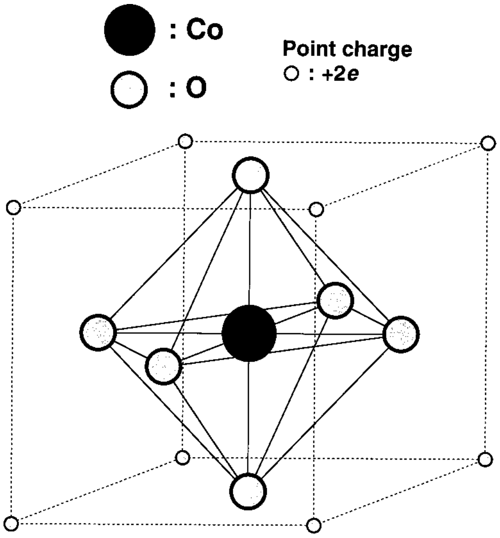

FIG. 1. The structure of the unit cell situated in the center of the finite unit cells used. Small circles represent the point charges corresponding to Sr, Co, and O ions, respectively.

Similarly the $[Co-O_6]^{9-}$ cluster for $LaCoO_3$ is situated in the center of the calculated structure, and the other Co, O, and La ions are replaced by the point charges $+3e$ for a Co ion, $-2e$ for an O ion, and $+3e$ for a La ion.

B. Approximation method

Using the GAUSSIAN 94 program package in the CRAY T94 system,[24] calculations were carried out by the restricted Hartree-Fock method, the unrestricted Hartree-Fock (UHF) method, the fourth-order Moller-Plesset perturbation (MP4) method, the single-excitation configuration-interaction method belonging to the CI method,[25] and the DFT method based on the local-spin-density approximation (LSDA) with the exchange functionals of Hartree-Fock-Slater, Xa, and Beck, and with the correlation functionals proposed in Refs. 26–29, appropriate for the ground states of the systems.

In Hartree-Fock (HF) theory, the energy has the form

$$E_{\mathrm{HF}}=V+\langle hP\rangle+\tfrac{1}{2}\langle P_J(P)\rangle-\tfrac{1}{2}\langle P_K(P)\rangle, \tag{1}$$

where V is the nuclear repulsion energy, P is the density matrix, $\langle hP\rangle$ is the one-electron (kinetic plus potential) energy, $\frac{1}{2}\langle P_J(P)\rangle$ is the classical Coulomb repulsion of the electrons, and $-\frac{1}{2}\langle P_K(P)\rangle$ is the exchange resulting from the quantum nature of electrons; and

$$E=V+\langle h_P\rangle+\tfrac{1}{2}\langle P_{J(P)}\rangle+E_X[P]+E_C[P], \tag{2}$$

where $E_X[P]$ is the exchange functional, and $E_C[P]$ is the correlation functional.

Hartree-Fock theory is really a special case of density-functional theory, with $E_X[P]$ given by the exchange integral $-\frac{1}{2}\langle P_{K(P)}\rangle$ and $E_C=0$.

The excited-state wave function is written as a linear combination of all possible singly excited determinants,

$$\Psi_{\mathrm{CIS}}=\sum_{ia} a_{ia}\Psi_{ia}. \tag{3}$$

The CI coefficient can be deduced as a normalized eigenvector of the Hamiltonian matrix,

$$\langle \psi_{ia}|H|\psi_{jb}\rangle=[E_{\mathrm{HF}}+\varepsilon_a-\varepsilon_i]\delta_{ij}\delta_{ab}-(ja\|ib), \tag{4}$$

where ε_i is the ith molecular-orbital energy, and $(ja\|ib)$ are the two electron integrals.

The total energy for a CI single excited state is an eigenvalue of the matrix given in Eq. (4). It can be written as

$$E_{\mathrm{CIS}}=E_{\mathrm{HF}}+\sum_{ia} a_{ia}^2(\varepsilon_a-\varepsilon_i)+\sum_{ijab} a_{ia}a_{jb}(ja\|ib). \tag{5}$$

In order to take into account the spin multiplicity of the $[\mathrm{Co}-\mathrm{O}_6]^{8-}$ cluster, we calculated the electronic structures in the doublet, quartet, and sextet configurations corresponding to the low-spin state, intermediate-spin state, and high-spin state of SrCoO_3, respectively. In the case of the $[\mathrm{Co}_2-\mathrm{O}_{11}]^{14-}$ and $[\mathrm{Co}_4-\mathrm{O}_{20}]^{24-}$ clusters, a similar consideration for the spin multiplicity was taken into account.

C. Basis sets

We used basis sets for a Co atom proposed in Ref. 30, which gave the results with high accuracy. Although each Co $1s$, $2s$, $3s$, and $4s$ basis function is composed of a linear combination of 12 primitive Gaussian functions with appropriate contraction coefficients, the ten largest contraction coefficients in the basis functions were chosen owing to the limitation of our program package. On the other hand, p and d basis functions were used as uncontracted. We used the basis sets for O atoms (43/3) proposed by Huzinaga *et al.* as uncontracted.[31]

III. COMPUTATIONAL RESULTS AND DISCUSSIONS

A. Computational results

First, we treated the doublet, quartet, and sextet states of the $[\mathrm{Co}-\mathrm{O}_6]^{8-}$ cluster. Next, self-consistent-field iterations were required, with the convergence criterion that the variation of the density matrix was within 10^{-9}. Finally, taking account of the symmetry of the point group, we obtained molecular orbitals, energies, and molecular coefficients that main contributing to each molecular orbital and to the total energy E. Using Mulliken population analysis, we performed a calculation of the average net charge of atoms N_x (x=Co or O) and the spin distribution on each ion. Similarly we treated the electronic states $[\mathrm{Co}_2-\mathrm{O}_{11}]^{14-}$, $[\mathrm{Co}_4-\mathrm{O}_{20}]^{24-}$, and $[\mathrm{Co}-\mathrm{O}_6]^{9-}$. The obtained discrete molecular energy levels are considered to form continuous energy bands. The Fermi energy level is considered to exist between the HOMO and lowest unoccupied molecular orbital. The electronic structures of SrCoO_3 are summarized using the local density of states (LDOS's) for total spins in Fig. 2. We explain these electronic structures in the following.

1. Electronic structures of $[\mathrm{Co}-\mathrm{O}_6]^{8-}$ *clusters*

The LDOS of the $[\mathrm{Co}-\mathrm{O}_6]^{8-}$ cluster, as shown in Fig. 2(a), is derived from the $n=0$ cluster corresponding to the high-spin configuration in the case when $ds=2.0$ Å using the UHF method. The magnitude of the charge transfer between Co and O atoms is inconsistent with that predicted by the ionic model. Since the average net charge of O atoms is $-1.48e$, the electronic structure of the cluster is $d^7\underline{L}^2$, corresponding to the $t_{2g\uparrow}^3t_{2g\downarrow}^2e_{g\uparrow}^2$ configuration. The calculated electronic structure corresponding to a cluster containing a Madelung potential in the case when $ds=2.0$ Å is shown in the following. The average net charge of O atoms is $-1.52e$, and the electronic structures of the cluster are $d^7\underline{L}^2$, corresponding to the $t_{2g\uparrow}^3t_{2g\downarrow}^2e_{g\uparrow}^2$ configuration. Both the results are similar. In addition, we obtained similar electronic structures by performing several calculations with the charge neutrality condition of the cluster used, by choosing the appropriate boundary condition so that the fractional ($\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{8}$) charges proposed by Evjen for NaCl (Ref. 32) were positioned on faces, edges, and corners, respectively, in the outer of the whole cells, in order to satisfy the charge neutrality. Therefore, the Madelung potential merely makes the molecular-orbital energies shift toward lower energies (energy sequences almost do not change). We also obtained similar electronic structures by using basis sets containing a polarization function and split valence.

The obtained LDOS's of $n=0$ clusters in the high-spin state, when $ds=2.0$ Å, based on the LSDA, are shown in Fig. 2(b). The electronic structures of the cluster are $d^7\underline{L}^2$ corresponding to the $t_{2g\uparrow}^3t_{2g\downarrow}^1e_{g\uparrow}^2e_{g\downarrow}^1$ configuration. We obtained similar electronic structures of SrCoO_3 by using the Xa method.

There are two peaks concerning O $2p$ and Co $3d$ bands which are centered around 2 and 10 eV below the top of the filled bands in Fig. 2(a), and those centered around 2 and 6 eV in Fig. 2(b). The band gap in the former appears, while that in the latter does not appear. These LDOS's are qualitatively similar to those of experimental results[33,34] except for the position of peaks (at $x=0.5$,[33] two peaks are at 1.5 and 7.5 eV, and at $x=0.4$,[34] at 1.0 and 5.3 eV). They are also similar to our previously obtained LDOS of LaCoO_3 in the high-spin state ($S=\frac{5}{2}$).

The obtained electronic structures of the clusters in the low- and intermediate-spin states using the HF method are similar to those in the high-spin states, as shown in Fig. 2. The obtained electronic configurations are $t_{2g\uparrow}^3t_{2g\downarrow}^3e_{g\uparrow}^{0.2}e_{g\downarrow}^1$ for the low-spin state and $t_{2g\uparrow}^3t_{2g\downarrow}^3e_{g\uparrow}^1e_{g\downarrow}^{0.3}$ for the intermediate-spin state, respectively. The obtained electronic structures of the clusters in the low- and intermediate-spin states using the LSDA are also similar to those shown in Fig. 2(b). With an increase of the cluster size, the electronic structures obtained using the HF method are similar to those shown in Fig. 2(a).

We tried to judge the main configuration for each excited state by the single-electron CI method. The obtained results for the cluster ($n=3$) satisfying the charge neutrality in the low-, intermediate-, and high-spin states are as follows.

(a) The minimum transition energies between occupied bands containing contributions of O $2p$ and Co $3d$ electrons and the unoccupied bands containing the contribution of

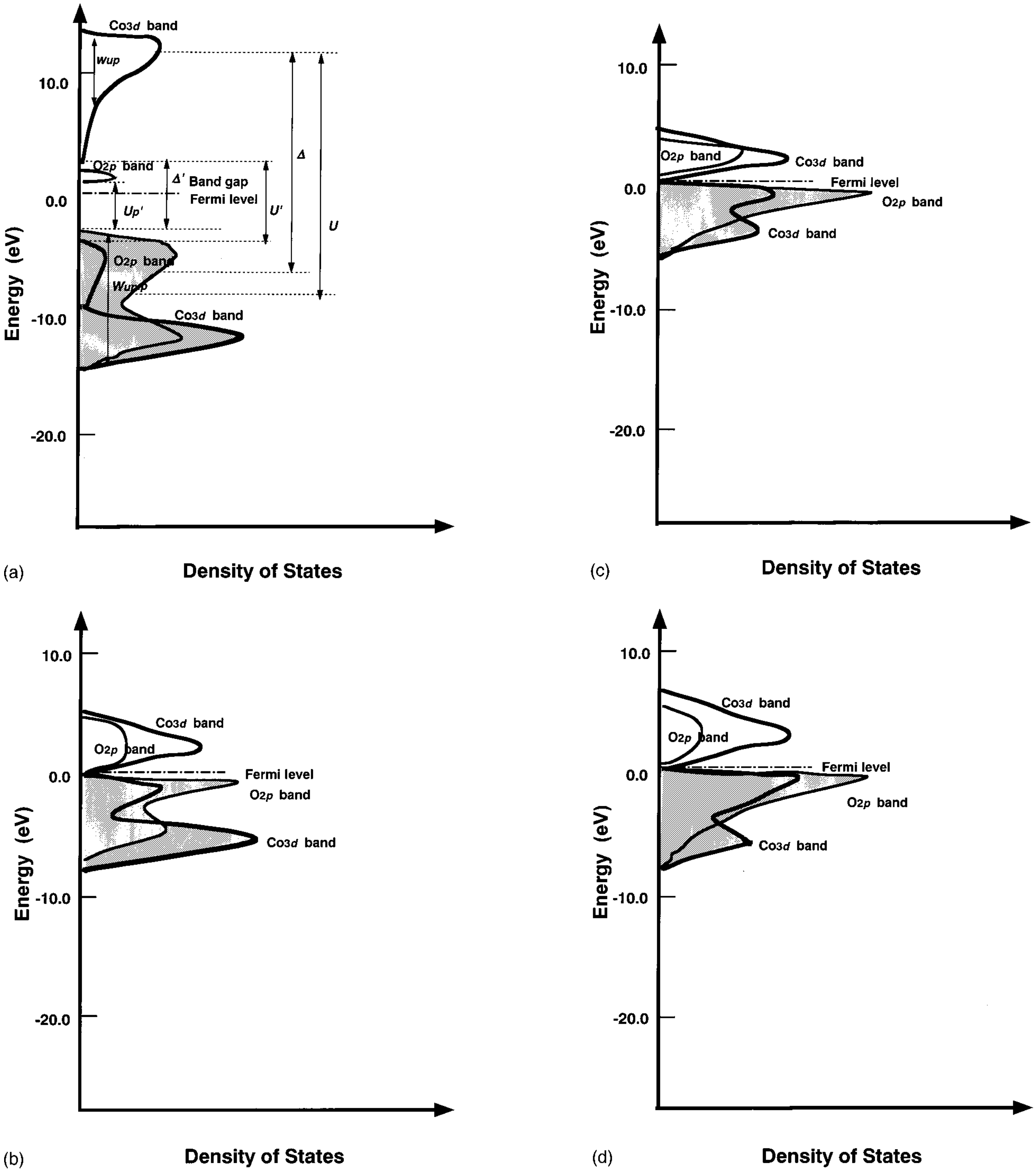

FIG. 2. The comparison of an artist's concept of the obtained LDOS near the Fermi level for total spins. (a) $SrCoO_3$ in the high-spin state using the HF approximation on the $[Co-O_6]^{8-}$ cluster. (b) $SrCoO_3$ in the high-spin state using the LSDA approximation on the $[Co-O_6]^{8-}$ cluster. (c) $SrCoO_3$ in the high-spin state using the CI approximation on the $[Co-O_6]^{8-}$ cluster. (d) $SrCoO_3$ in the high-spin state using the LSDA approximation on the $[Co_2-O_{11}]^{14-}$ cluster. (e) $LaCoO_3$ in the low-spin state using the CI approximation on the $[Co-O_6]^{9-}$ cluster.

O 2p electrons, are negative. That is to say, the system becomes metallic.

(b) The O 2p–Co 3d transition energies are about 0–7 eV.

(c) The minimum Co 3d–Co 3d transition energies are 0.0 eV, and these energies are mainly 6–7 eV.

The obtained LDOS's near the Fermi level in the high-spin state for total spins using the CI approximation on the $[Co-O_6]^{8-}$ cluster are shown in Fig. 2(c). The obtained LDOS's in the low- and intermediate-spin states are similar to those shown in Fig. 2(c).

2. Electronic structures of $[Co_2-O_{11}]^{14-}$ *clusters*

The obtained results for an $n=0$ cluster in a high-spin state when $ds=2.0$ Å, based on the UHF method, are similar to those shown in Fig. 2(a). The electronic structures of the cluster are $d^7\underline{L}^2$, corresponding to the $t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^2$ configura-

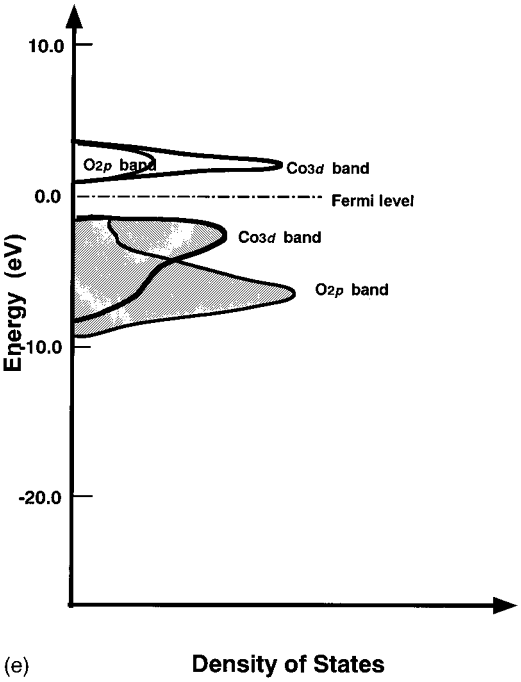

FIG. 2. (*Continued*).

tion. The obtained electronic structures of the clusters in the low- and intermediate-spin states are similar to those of $[\mathrm{Co-O_6}]^{8-}$ clusters.

The obtained LDOS's of an $n=0$ cluster corresponding to $t_{2g\uparrow}^3 t_{2g\downarrow}^2$ when $ds=2.0$ Å, based on the LSDA, are shown in Fig. 2(d). We obtained the electronic structures of $[\mathrm{Co_2-O_{11}}]^{14-}$ clusters in other spin states similar to those in the high-spin state within the same approximation.

3. *Electronic structures of* $[\mathbf{Co_4-O_{20}}]^{24-}$ *clusters*

The obtained electronic structures of $[\mathrm{Co_4-O_{20}}]^{24-}$ clusters using the HF method are similar to those of $[\mathrm{Co_2-O_{11}}]^{14-}$ clusters. The ground state is the $t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^{1.9}$ configuration. We believe the electronic configurations will approach the $t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^{1.0}$ configuration with a further increase of the cluster size (because of the necessity of the tremendous computational time, we could not calculate the electronic structures of clusters of larger size). The net charge of the O atom in the $[\mathrm{Co_4-O_{20}}]^{24-}$ clusters becomes larger than that of $[\mathrm{Co-O_6}]^{8-}$ clusters.

4. *Change of energies with the variation of Co-O bond length for* $[\mathbf{Co-O_6}]^{8-}$ *clusters*

The energy changes corresponding to the low-, intermediate-, and high-spin states in the case of an $n=0$ cluster calculation, using the HF method are, shown in Fig. 3. When ds is short, the low-spin state is stable. With an increase of ds, the high- and intermediate-spin states gradually become stable. As $ds=2.3$ Å, the energies of the three states are almost equal. As $ds>2.3$ Å, the high-spin state is more stable than the others.

The energy changes corresponding to the intermediate- and high-spin states in the case of an $n=3$ cluster are calculated using the HF and the MP4 methods. The obtained results are similar to those shown in Fig. 3.

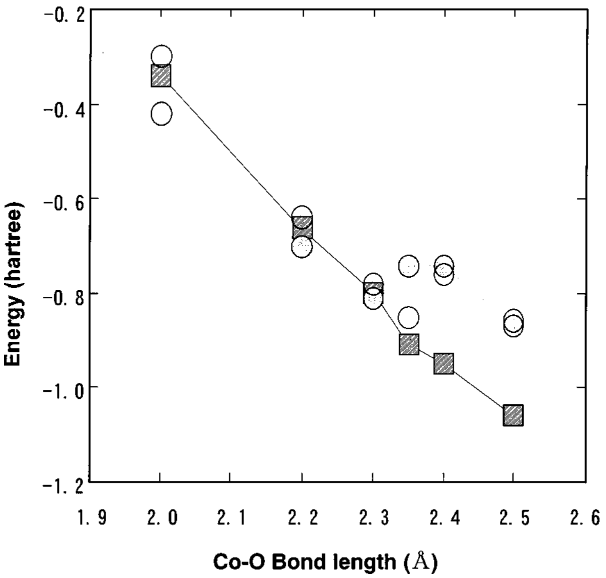

FIG. 3. Comparison of the energy difference between the low-, intermediate-, and high-spin states in the $n=0$ cluster calculation using the HF method. Solid circles, open circles, and squares represent the data on the low-, intermediate-, and high-spin states, respectively.

The tendency of the change in the ground state is similar to that obtained in Ref. 35. That is to say, with the increase of the crystal field, the lower-spin states become stable.

5. *Electronic structures of* $[\mathbf{Co-O_6}]^{9-}$ *clusters*

We obtained the electronic structures of $[\mathrm{Co-O_6}]^{9-}$ clusters similar to those shown in Fig. 2(a) using the HF method.[21] In addition, by using CI calculations, we obtained the LDOS as shown in Fig. 2(e). The obtained band gap is 2.1 eV.

B. Electronic structures of $\mathbf{LaCoO_3}$ and $\mathbf{SrCoO_3}$

According to the above results, we concluded that main features of $\mathrm{LaCoO_3}$ and $\mathrm{SrCoO_3}$ were similar to that of the cluster. The increase of cluster size makes the electronic structures of clusters close to those of the real materials. The obtained electronic structures hardly change with an increase of the cluster size. Therefore, we can qualitatively discuss the electronic structures mainly by using the results derived from the present cluster calculations.

Therefore, we tried to investigate these electronic structures. First, we tried to derive a qualitative understanding of the ground states of a $\mathrm{SrCoO_3}$ system containing n, $n+1$, and $n-1$ electrons, derived from calculating the ground state of $[\mathrm{Co-O_6}]^{8-}$, $[\mathrm{Co-O_6}]^{9-}$ (electron addition), and $[\mathrm{Co-O_6}]^{7-}$ (electron removal) clusters, respectively (the ground states corresponding to the $t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\downarrow}^2$ configuration for the $[\mathrm{Co-O_6}]^{8-}$ cluster, to the $t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\uparrow}^{0.8} e_{g\downarrow}^{0.5}$ configuration for the $[\mathrm{Co-O_6}]^{7-}$ cluster, and to the $t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\downarrow}^1$ configuration for $[\mathrm{Co-O_6}]^{9-}$ cluster, respectively, in the case of the $n=2$ cluster with $ds=2.0$ Å using the MP4 method). The obtained band gap is too large (more than 10 eV, inconsistent with experimental results). Therefore, we tried to ob-

TABLE I. Comparison of transition energies of $SrCoO_3$ in low, intermediate, and high-spin states from the $[Co-O_6]^{8-}$ cluster calculations (the energy is in eV). The p-p transition energies are estimated from the energy difference between the unoccupied O-2p orbital and the highest occupied O-2p orbital. The values in parentheses are evaluated from the $[Co_2-O_{11}]^{14-}$ cluster.

Approximation	Spin state	p-d transition energy		d-d transition energy		p-p transition energy
		Δ	Δ'	U	U'	U'_p
HF	low $s=\frac{1}{2}$	20.8	10.7	21.3	11.6	7.7
CI		4.0	0.0	4.0	0.0	0.0
HF	intermediate $s=\frac{3}{2}$	20.8	13.0	21.3	13.0	5.4
CI		4.0	0.0	4.0	0.0	0.0
HF	high $s=\frac{5}{2}$	19.1	5.6	19.9	7.2	5.3
LSDA		3.6	0.0	7.6	0.0	0.0
		(5.5)		(2.4)		
CI		5.0	0.0	5.0	0.0	0.0

tain the band gaps from tables using Koopmans' theorem. We listed the comparison among the LDOS's of $SrCoO_3$ in the low-, intermediate-, and high-spin states, with respect to the transition energies, as shown in Table I. From the obtained electronic structures using the HF approximation, $SrCoO_3$ is not a Mott-Hubbard-type insulator ($\Delta > U$), but a charge transfer-type insulator $[\frac{1}{2}(w_{up}+W_{up}) < \Delta < U]$ in terms of the Zaanen-Sawatzky-Allen phase diagram,[16] where w_{up} and W_{up} are the bandwidths of the upper Co 3d and upper O 2p bands, respectively. Our results are consistent with those obtained in Ref. 35, where it was suggested, by using a semiempirical method that $SrCoO_3$ is of a charge-transfer type (however our obtained results indicate that the calculation based on one-electron theory could not give the metallic property of $SrCoO_3$). Therefore, the peaks at 0–5 and 5–10 eV, observed in x-ray photoelectron spectroscopy,[33,34] are assigned to O 2p bands which make a small contribution of Co 3d band, and to mixed bands of O 2p and Co 3d, respectively. However, the obtained U and Δ are larger than those obtained by experimental results.

On the other hand, from the electronic structure obtained using the LSDA as shown in Table I, $SrCoO_3$ is a Mott-Hubbard-type metal ($\Delta > U$) as further shown by the calculation of the $[Co_2-O_{11}]^{14-}$ cluster. From the calculation of the $[Co-O_6]^{8-}$ cluster, we obtain that $SrCoO_3$ is a charge-transfer metal ($\Delta < U$). However, the obtained $U'(=\text{zero})$ for $LaCoO_3$ in the low-spin state is inconsistent with the experimental result that the band gap is 1 ± 0.5 eV.[18] In general, band calculations based on the local density approximation (LDA) for the 3d metal oxides give results that the electronic structures of these oxides are of a Mott-Hubbard type, because the calculated U is too small. The LDA is not self-interaction free (the HF method is intrinsically self-interaction free). Near the Fermi level, the electronic structures cannot be described by the LDA, which is inappropriate for a system with large U. However, according to the results obtained by Anisimov and co-workers[36–38] using band calculations (the so-called LDA+U method), the electronic structures of NiO and $LaCoO_3$ are a charge-transfer-type insulator. These authors still used a model Hamiltonian. Our view is that the band calculations are not appropriate for describing a system containing 3d transition metals.

In addition, from CI calculations, we obtained that the band gaps are 2.1 eV for $LaCoO_3$ and 0.0 eV for $SrCoO_3$, as shown in Table I, respectively, which are consistent with the experimental values. The transition energies between bands containing the Co 3d and O 2p bands are smallest and negative for $SrCoO_3$. These results are very consistent with those obtained by Yamaguchi *et al.*[39] We cannot use the conventional Zaanen-Sawatzky-Allen phase diagram. Therefore, $SrCoO_3$ is not of a conventional charge-transfer type. We explain the above results in the following.

Since the polarization effect for the Co 3d electron in the cluster is smaller than that in real materials, the position of the main band of the Co 3d electrons is lower than the observed values. Anderson suggested that this effect on the Co 3d electron is about 4–5 eV, and the effect of the covalency between Co 3d and O 2p is about 4 eV. Our results, based on the HF method, do not contain enough correlation effects. From the CI calculations, the Co 3d band almost goes toward the Fermi level. Therefore, the correlation effect causes the position of the second peak to lift up to about 8 eV below the Fermi level, which is consistent with the observed value, i.e., 8 eV. On the other hand, using the LSDA involving the correlation effect, the U for the $[Co_2-O_{11}]^{14-}$ cluster is 2.4 eV, which is too small (in real material, the magnitude of U is about 8 eV). Therefore, we can suppose that the electronic structures of $SrCoO_3$ are not of a Mott-Hubbard type, but nearly intermediate between Mott-Hubbard-type compounds and charge-transfer-type compounds (it is not a pure charge-transfer type).

An unfilled O 2p band in the upper Hubbard band appears, which indicates the possibility of the existence of holes on O ions (recently, Sarma *et al.* suggested the importance of O 2p bands in the conduction band,[40] but they obtained that the electronic structures of $LaCoO_3$ are of a Mott-Hubbard type[41]).

Therefore, the transition is not the Mott-Hubbard transition which occurs when electrons in the half-filled lower Hubbard band are localized and the Coulomb repulsion energy U is larger than the effectively d-d intraband kinetic energy, but a transition of the intermediate regime between Mott-Hubbard and charge-transfer types.

The net charges of $SrCoO_3$ using the HF and LSDA methods are different in the point of the magnitude. The absolute net charges of Co and O measured, using the HF method are smaller than those measured by the LSDA method. That is to say, the former method indicated that the ground state of $SrCoO_3$ was mainly $d^7\underline{L}^2$, i.e., not fully ionic but covalent due to the large hybridization of the O $2p$ and Co $3d$ orbitals, which is almost consistent with the results suggested in Ref. 35 that the ground states of $SrCoO_3$ are mainly $d^6\underline{L}$ (67% of the contribution) and $d^7\underline{L}^2$ (25% contribution). Harrison indicated that the net charges of O ions in the perovskite are much less than -2, and near -1.0 to -1.5,[42] which are consistent with the obtained net charges.

C. Explanation of the obtained electronic structures

1. *Mechanism of conductivity*

Based on the above results, we discuss the mechanism of the conduction as follows. For a small amount x in $La_{1-x}Sr_xCoO_3$, the interesting state in the band gap, which cannot be obtained by calculation within the HF method based on the single Slater determinant, appears to be one of mixed states mainly corresponding to the Co $3d$ and O $2p$ bands at a CI approximate level. This is strongly supported by the fact that $La_{1-x}Sr_xCoO_3$ becomes metallic near $x=0.20$. Therefore, electrons (holes) move indirectly between Co ions via an O ion rather than directly between Co ions, i.e., the fluctuation of the charges of O ions as well as Co ions causes electrons (holes) to move with a complicated interaction between the generated holes and electrons. Since the upper Hubbard band contains some contributions of the O $2p$ band, and the p-p transition energy U_p' is small, it is possible that electrons (holes) move between O ions.

Veenendaal, Sawatzky, and Groen proposed that, with Sr doping, a transfer of spectral weight from the upper to the lower Hubbard bands occurs in the metal-insulator transition mechanism of the hole-doped compound $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$, i.e., the Fermi level shifts toward the top of the lower Hubbard band, and consequently the system becomes metallic.[43] From the obtained results, the unoccupied O $2p$ band approaches the top of the lower Hubbard band. Therefore, there is a possibility that the mechanism of the metal-insulator transition in $La_{1-x}Sr_xCoO_3$ is similar to that of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$. This is consistent with the mechanism proposed by Saitoh *et al.*, who emphasized the importance of the p-p gap in $La_{1-x}Sr_xCoO_3$.[23] Our proposed mixed states also resemble the Emery-Reiter triplet, which is thought to appear in cuprates.[44–46]

The sign of the Seebeck coefficient changes with increasing temperature and Sr doping. We think that such an abnormal temperature dependence of the Seebeck coefficient is due to the temperature dependence of the overlapping between the unoccupied O $2p$ and Co $3d$ bands. In $La_{1-x}Ca_xMnO_3$, Mahendiran, Tiwary, and Raychaudhuri suggested that the sign of the thermopower in certain circumstances can be used to determine the sign of the carrier, and that there is substantial charge transfer from the the ligand to the cation.[47] This will give an electronlike behavior for metal d bands and holelike behavior for the oxygen p orbital. We think that a similar explanation can be used for $La_{1-x}Sr_xCoO_3$.

2. *Origin of magnetism*

Potze, Sawatzy, and Abbate suggested the importance of a coupling between O $2p$ and Co $3d$ electrons and in the $La_{1-x}Sr_xMnO_3$, recently, Saitoh *et al.* suggested the existence of this ferromagnetic coupling.[48] Yamaguchi *et al.* suggested the existence of spin polarons caused by Co $3d$ states and the O $2p$ hole.[39] Our results (see Fig. 3) also indicate the possibility of the existence of ferromagnetic coupling in $La_{1-x}Sr_xCoO_3$. That is to say, the state of spin coupling between Co $3d$ and O $2p$ electrons in the ground state drastically changes with the increase of Co-O bond length, i.e., Sr doping (this phenomenon was observed in Ref. 22), and the ground state changes from a low-spin state to intermediate- and high-spin states with the increase of the Co-O bond length. According to the experimental results, at $x=0.5$, the magnetic moment per Co ion is $3.0\mu_B$,[49] which is consistent with our result. By the above interpretation, $La_{1-x}Sr_xCoO_3$ becomes metallic near $x=0.2$ because of the ferromagnetic coupling between O $2p$ and Co $3d$ electrons.

IV. CONCLUSIONS

In conclusion, we calculated electronic structures of the cluster surrounded by several point charges in order to mimic the situation in a $La_{1-x}Sr_xCoO_3$ crystal using *ab initio* molecular-orbital method. We showed that the obtained density of states agreed reasonably well with experimental results. The above results led to the conclusion that the main electronic structures of $La_{1-x}Sr_xCoO_3$ were similar to those of the cluster, due to the interaction of Co atoms with surrounding O atoms rather than the interaction between Co-Co atoms. Our adopted cluster calculation provided an important explanation of the main electronic structures of $La_{1-x}Sr_xCoO_3$. The obtained results are summarized as follows: (1) $La_{1-x}Sr_xCoO_3$ is nearly intermediate between Mott-Hubbard-type compounds and charge-transfer-type compounds, with interaction between Co and O ions with valence and conduction bands consisting of strongly mixed O $2p$ and Co $3d$ bands because of the electronic correlation. (2) The covalency of $La_{1-x}Sr_xCoO_3$ is due to the main contribution of the hybridization between Co and O orbitals. (3) With a decrease of the crystal field, i.e., an increase of the Co-O bond length, the low-spin state gradually becomes unstable, while the high-spin state becomes stable. There is the possibility of the existence of an intermediate-spin state, which is consistent with the magnitude of the observed magnetic moment. (4) The metal-insulator transition occurs due to the interaction between mixed states consisting of electrons for Co ions and holes for O ions.

From the above results, the phase changes on both conductivity and magnetism for a system correlate with each other. In particular, the correlation between the spins of Co ions and O holes plays an important role in determining the physical properties of $La_{1-x}Sr_xCoO_3$. From the present analysis, our method is appropriate for a qualitative understanding of physical properties such as the conductivity and magnetism of $3d$ transition-metal compounds.

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