Excitation spectra of LaCoO$_3$

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We study the excitation spectra of LaCoO$_3$ using a multiorbital tight-binding model. Making the self-energy correction due to local three-body scattering to the Hartree-Fock (HF) approximation, we calculate the spectral density for the low-spin phase. It is shown that the band gap is strongly reduced from the HF value, and that the intensity is transferred from the lower part to the upper part of the valence band and to the satellite in the spectral density projected onto the Co 3d states. The results are in good agreement with the spectra of photoemission experiments. We also calculate the spectral densities for the intermediate-spin phase and the high-spin phase in relation to the nonmagnetic-to-paramagnetic transition. The peak intensities around the top of the valence band are smaller than that for the low-spin phase. In La$_{1-x}$Sr$_x$CoO$_3$, the energies for the intermediate-spin and high-spin phases are found to become lower than for the low-spin phase with increasing x, indicating the instability of the low-spin phase. This is consistent with the susceptibility data and the photoemission spectra. [S0163-1829(97)06020-7]

I. INTRODUCTION

Transition-metal perovskites LaMO$_3$ (M denoting transition-metal element) have attracted much interest. Especially LaCoO$_3$ has been studied since the early 1960s due to the anomalous spin-state transition.[1,2] However, the nature of the spin states is still unclear as a function of temperature. The magnetic susceptibility χ shows a broad maximum around 90 K, above which it decreases like a Curie-Weiss law. It reaches a plateau around 500 K, and starts to decrease again with further increasing temperatures.[3,4] Neutron scattering experiments[5–9] have revealed that no long-range magnetic order exists down to 4.2 K, and that a transition from a nonmagnetic phase to a paramagnetic one occurs around 90 K accompanying an anomalous thermal expansion.[9] In the paramagnetic phase it was found that ferromagnetic short-range order is rather strong. In resistivity measurements, a gradual transition from semiconductor to metal was observed around 400~600 K.[3,4] According to the neutron scattering experiments,[7] this transition is not considered to be dominantly magnetic in origin. In addition, many photoemission spectroscopic studies have been reported on LaCoO$_3$.[10–17] The x-ray photoemission spectroscopy (XPS) spectra show a satellite structure below the valence band,[12,16,17] which is a hallmark of strongly correlated electron systems. There are no drastic changes until ~400 K and slight changes between 400 and 600 K in the spectra of XPS as well as oxygen 1s x-ray photoabsorption spectroscopy (XAS).[13] This behavior of photoemission spectroscopies contrasts with the remarkable change in the χ-T curve around 90 K with merely a plateau around 500 K.[3,4]

The quench of the susceptibility at low temperatures T <35 K indicates that Co trivalent ions are in the low-spin ($t_{2g}^6 e_g^0$) (LS) configuration.[3,4] The nonmagnetic-to-paramagnetic transition around 90 K has been thought to be caused by thermal excitation of ions to the high-spin ($t_{2g}^4 e_g^2$) (HS) configuration due to a very small excitation energy.[18] Recently Korotin *et al.*[19] calculated the electronic

structure using the LDA+U method, which is a generalization of the local density approximation (LDA), and found that the intermediate-spin ($t_{2g}^5 e_g^1$) (IS) configuration has an excitation energy lower than the HS configuration. They suggested that the transition to the IS state accompanying the orbital order corresponds to the transition around 90 K. The thermal expansion was expected to help this transition by reducing the excitation energy. They also suggested that a gradual collapse of the orbital order in the IS phase is responsible to the semiconductor-to-metal transition around 500 K. In their study, however, electron correlations are not properly taken into account. It is quite natural to think that the electron correlation plays an important role, since LaCoO$_3$ is considered a strongly correlated electron system. The purpose of this paper is to study the electronic structure associated with the spin-states transition by taking account of electron correlations.

Electronic structures are usually obtained from the band calculation based on the LDA. When it is applied to strongly correlated electron systems, it usually faces several problems. For LaCoO$_3$, it predicts a metal and no satellite intensities below the valence band.[15,20,21] In order to improve the LDA, the LDA+U method mentioned above has been proposed, but it is still at the level of the mean-field approximation.[19,22] Although this method correctly predicts an insulator, the energy spectra are quite different from those expected from photoemission experiments: there are no satellite intensities, and the band gap and exchange splitting are too large; the O 2p weight is exaggerated around the top of the valence band. Note that the Hartree-Fock (HF) approximation using the tight-binding model[23] gives spectra similar to those given by the LDA+U method.

The cluster model calculation is another method widely used to calculate the photoemission spectra.[15,17,24,25] Analyzing photoemission spectra on the basis of this model calculation, one can estimate several important parameters such as Racah parameters, transfer integrals, and the charge transfer energy. When this method is applied to LaCoO$_3$, it predicts
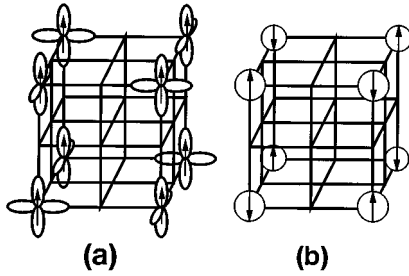
FIG. 1. (a) Spin and orbital orders for occupied e_g orbitals in the intermediate-spin phase; (b) G-type spin order in the high-spin phase. Arrows represent the spin direction of Co ions.

the HS phase as the ground state unless Coulomb interactions that are too small are assumed to work on Co sites. This indicates that the charge-transfer process beyond the cluster is important to make the LS phase the ground state. Also it is difficult to describe the O $2p$ band appropriately.

In this paper, starting with an itinerant model (tight-binding model) for LaCoO$_3$, we apply the HF approximation to the model. The ground state is given by the LS phase, where each Co atom is in the LS configuration. Then using the local three-body scattering theory, we make the self-energy correction to the HF solutions. This method has already been applied to transition-metal monoxides, resulting in good agreement with photoemission experiments.[26–28] The LS phase remains the ground state even after including the correlation effects. It is shown that the excitation spectra for the LS phase are considerably improved from those given by the HF approximation, leading to good agreement with the photoemission experiments. The band gap becomes ~ 0.5 eV. In the spectra projected onto the Co $3d$ states, a satellite structure appears below the valence band, and the intensity in the lower part of the valence band is pushed toward the upper part of the valence band, giving rise to a sharp peak of the Co t_{2g} states. The spectra projected onto the O $2p$ states are concentrated in the middle and the lower part of the valence band.

We also study several phases that have higher energies than that for the LS phase, aiming at obtaining some insights into the nonmagnetic-to-paramagnetic transition around 90 K. Since the present calculation is limited by assuming long-range spin and orbital orders at zero temperature and the present model is too simple to include the crystal distortion, we have no intention of discussing directly the spin-states transition by exhausting all possible phases. We consider only two typical phases; one is the IS phase, where each Co atom is in the IS configuration with the ferromagnetic spin order and the orbital order, as shown in Fig. 1(a);[29] the other is the HS phase, where each Co atom is in the HS configuration with antiferromagnetic spin order, as shown in Fig. 1(b). Both phases have nearly the same energies about 0.5 eV higher than that of the LS phase per CoO$_3$ formula within the HF approximation, consistent with the previous calculation by Mizokawa and Fujimori.[23] Due to the electron correlation, the energies of the IS and HS phases become more than 1.0 eV higher than that of the LS phase per CoO$_3$ formula. That value is much larger than the spin gap ~ 0.03 eV estimated from the experimental χ-T curve for $T < 100$ K.[4] This discrepancy may come from the neglect of

the lattice expansion and the lattice distortion, which usually lower the energies of the IS and HS phases. As regards the excitation spectra, a main difference between the spectra of the IS and the HS phases and that of the LS phase is that the sharp peak around the top of the valence band is split into several peaks and a part of them is pushed above the Fermi level in the IS and HS phases. This leads to a reduction of the spectral weight around the top of the valence band, if the IS or the HS phase is realized. We do not expect that the spectra are sensitive to the presence of long-range order. Experimentally the XPS spectra have not clearly changed with increasing temperatures.[13,17]

Furthermore, we study *doped* systems La$_{1-x}$Sr$_x$CoO$_3$. Since the La $5s$, $5p$, $5d$, $4f$ states and the Sr $5s$, $5p$, $4d$ states are well separated from the Co $3d$ states and the O $2p$ states, we simply assume that Sr atoms introduce holes in the network of Co and O atoms. The present calculation as well as the HF one indicate the instability of the LS phase with increasing values of x by lowering the energies of the IS and HS phases. The instability of the nonmagnetic phase is consistent with the paramagnetic behavior of the susceptibility data, which obey the Curie law down to about 30 K.[9] It is not clear whether long-range order is established or not at zero temperature. In the photoemission experiment, the spectral intensity around the top of the valence band decreases considerably, supporting the instability of the LS phase.[11] The strong ferromagnetic correlations observed by NMR and neutron scattering experiments[9,30,31] favor the IS phase, not the HS phase.

In Sec. II, we describe a model Hamiltonian and review briefly the three-body scattering theory applied to LaCoO$_3$. In Sec. III, we present the calculated results with some discussions. The last section contains concluding remarks.

II. CALCULATION METHOD

We employ a multiorbital tight-binding model, restricting the bases within Co $3d$ orbitals and O $2p$ orbitals. The effects of La atoms are implicitly included in the parameters of the tight-binding model, since the La $5s$ and $5p$ orbitals constitute core-level states deep below the Fermi level and La $5d$ and $4f$ orbitals form empty bands around 5 eV above the Fermi level.[15,20,21] Assuming the cubic symmetry and neglecting a small rhombohedral distortion along the (111) direction,[20,32] we write the Hamiltonian as

$$H = H_0 + H_I, \tag{2.1}$$

$$H_0 = T + V, \tag{2.2}$$

$$T = \sum_{\langle i,j \rangle} \sum_{\sigma lm} (t^{dp}_{im,jl} d^\dagger_{im\sigma} p_{jl\sigma} + \text{H.c.})$$
$$+ \sum_{\langle j,j' \rangle} \sum_{\sigma ll'} (t^{pp}_{jl,j'l'} p^\dagger_{jl\sigma} p_{j'l'\sigma} + \text{H.c.}), \tag{2.3}$$

$$V = \sum_{im\sigma} E^d(m) n^d_{im\sigma} + \sum_{jl\sigma} E^p n^p_{jl\sigma}, \tag{2.4}$$

TABLE I. Tight-binding parameters in units of eV.

Parameter		Parameter	
A	6.20	$pd\sigma$	1.78
B	0.14	$pd\pi$	-0.82
C	0.54	$pp\sigma$	0.66
Δ	2.03	$pp\pi$	-0.18
$10Dq$	1.20		

$$H_I = \frac{1}{2} \sum_i \sum_{\nu_1 \nu_2 \nu_3 \nu_4} g(\nu_1 \nu_2 \nu_3 \nu_4) d^\dagger_{i\nu_1} d^\dagger_{i\nu_2} d_{i\nu_4} d_{i\nu_3}.$$

$$(2.5)$$

H_0 represents the noninteracting part, where T and V are the kinetic energy and the one-body potential, respectively. Operators $d_{im\sigma}$ and $p_{jl\sigma}$ denote the annihilation of an electron with spin σ in the Co $3d$ orbital m at site i and the annihilation of an electron with spin σ in the O $2p$ orbital l at site j, respectively. Number operators $n^d_{im\sigma}$ and $n^p_{jl\sigma}$ are defined by $n^d_{im\sigma} = d^\dagger_{im\sigma} d_{im\sigma}$, $n^p_{jl\sigma} = p^\dagger_{jl\sigma} p_{jl\sigma}$. The transfer integrals, $t^{dp}_{im,jl}$, $t^{pp}_{jl,j'l'}$, are evaluated from the Slater-Koster two-center integrals, $(pd\sigma)$, $(pd\pi)$, $(pp\sigma)$, $(pp\pi)$. Different from the case of NiO,[27] the transfer integrals $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$ can be neglected between Co atoms, since their distances are larger than the ones between Ni atoms and thereby the parameter values become negligibly small in accordance with Harrison's interpolation scheme.[33] A point charge crystal-field splitting $(10Dq)$ is taken into account so that the $3d$-orbital energies are split according to $E^d(e_g) = E^d + 6Dq$, $E^d(t_{2g}) = E^d - 4Dq$. The d-level position relative to the p levels is given by the charge-transfer energy Δ (for the d^n configuration, $\Delta = E_d - E_p + nU$ with U being the average of the intra-atomic Coulomb interaction). The part H_I represents the intra-atomic Coulomb interaction on Co sites; the Coulomb interaction on O sites is neglected. The interaction matrix element $g(\nu_1 \nu_2 \nu_3 \nu_4)$ is written in terms of the Racah parameters A, B, and C, where ν_i labels both m and σ. We use the parameter values determined from the cluster-model analysis of photoemission spectra,[16,25,34] which are listed in Table I.

First we carry out the HF self-consistent band calculation by taking 512 $\mathbf{k}$ points in the first Brillouin zone. We continue the iteration until the sum of the square root of the HF self-energy converges within an error less than 10^{-7}eV. We obtain a stable solution of the LS phase with the lowest ground-state energy. In addition, we also obtain several stable solutions having slightly higher ground-state energies such as the IS phase with both a ferromagnetic spin order and an orbital order, and the HS phase triply degenerate with the G-type antiferromagnetic order (see Fig. 1). For the latter phase, a Jahn-Teller-type crystal distortion is required to lift the degeneracy, although such effects are neglected in the present calculation. We will discuss in the next section these states in detail.

Next, following the procedures of the local three-body scattering theory,[27,28] we introduce the single-particle Green's function, and calculate the self-energy $\Sigma(\omega)$ localized on Co sites by taking account of the multiple scattering between three particles excited out of the HF ground state.

We neglect the self-energy correction on O sites. This approximation has worked very well for describing the excitation spectra in transition-metal oxides.[27,28] We refer to Refs. 27 and 28 for details of the method. Once we obtain the single-particle Green's function $G(\mathbf{k},\omega)$, we can calculate the spectral density $\rho_j(\omega)$, the total number of electrons N, the local spin moment M on Co sites, and the total energy E from the following relations:

$$\rho_j(\omega) = -\operatorname{sgn}(\omega) \sum_{\mathbf{k}} \sum_{l\sigma} \frac{1}{\pi} \operatorname{Im} G_{jl\sigma,jl\sigma}(\mathbf{k},\omega) e^{i\omega\eta},$$

$$(2.6)$$

$$N = -\frac{i}{2\pi} \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} G(\mathbf{k},\omega) e^{i\omega\eta}, \qquad (2.7)$$

$$M = -\frac{i}{2\pi} \frac{1}{N_c} \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\omega \sum_{l\sigma} \sigma G_{jl\sigma,jl\sigma}(\mathbf{k},\omega) e^{i\omega\eta},$$

$$(2.8)$$

$$E = -\frac{i}{4\pi} \sum_{\mathbf{k}} \int_{-\infty}^{\infty} d\omega \operatorname{Tr}\{[\omega + H_0(k)] G(\mathbf{k};\omega) e^{i\omega\eta}\},$$

$$(2.9)$$

where $\eta \to 0^+$ and N_c is the number of unit cells. Here the Green's function $G(\mathbf{k},\omega)$ is a matrix labeled by $(jl\sigma)$, where j represents an atomic site in a unit cell, and (l,σ) labels the orbital and the spin at the site j. The matrix of one-body energy $H_0(\mathbf{k})$ in Eq. (2.9) is obtained from writing Eqs. (2.3) and (2.4) in the momentum space. The sum over $\mathbf{k}$ is restricted in the first Brillouin zone. The chemical potential μ contained in the Green's function is determined from Eq. (2.7).

III. CALCULATED RESULTS

A. The low-spin phase

Within the HF approximation, the LS phase becomes the ground state of LaCoO$_3$. The number of electrons occupied in the Co $3d$ orbitals is listed in Table II. The t_{2g} orbitals are almost fully occupied, while the e_g orbitals are partly occupied due to the strong hybridization to the O $2p$ orbitals. Taking account of the self-energy correction lowers the ground-state energy about 3.3 eV per CoO$_3$ formula. The LS phase is still found to be the ground state. As also shown in Table II, the number of electrons occupied in the Co $3d$ orbitals is little modified by the self-energy correction.

Figure 2 shows the calculated spectral densities in comparison with the photoemission spectra.[14,15] Within the HF approximation, we obtain an insulator with a band gap of as large as 3 eV. Note that the LDA+U method gives a band gap of ~ 2 eV.[19,22] These values are much larger than the experimental values, ~ 0.2 eV from the optical measurement[35] and ~ 0.6 eV from the XPS and XAS spectra.[11,17] Note that the LDA predicts a metal.[15,20,21] Above the Fermi level, a broad structure appears [denoted by (a)]. This comes mainly from the unoccupied Co e_g states, which strongly hybridize to the O $2p$ states. Around the top of the valence band, a sharp peak exists in the spectra of the Co $3d$ states. This comes mainly from the Co t_{2g} states. At the

TABLE II. Occupancies of various d orbitals and the local moment of the Co ion for the LS, IS, and HS phases.

		yz	zx	xy	$3z^2-r^2$	x^2-y^2	$m(\mu_B)$
LS HF	↑↓	1.00	1.00	1.00	0.17	0.17	0.00
HF+Σ	↑↓	0.99	0.99	0.99	0.21	0.21	0.00
IS HF	↑	1.00	1.00	1.00	0.47	0.94	2.12
	↓	1.00	1.00	0.05	0.11	0.13	
HF+Σ	↑	1.00	1.00	1.00	0.55	0.85	2.02
	↓	0.99	0.98	0.09	0.15	0.16	
HS HF	↑	1.00	1.00	1.00	0.99	0.99	3.49
	↓	1.00	0.06	0.06	0.17	0.21	
HF+Σ	↑	1.00	1.00	1.00	0.99	0.99	3.39
	↓	1.00	0.07	0.07	0.19	0.24	

same position, the spectra of the O $2p$ states have a sharp peak with the intensity larger than that of the Co $3d$ states. The large intensity is the result of a strong enhancement caused by the hybridization to the Co t_{2g} states. In the lower part of the valence band, broad peaks appear both in the spectra of the O $2p$ states [denoted by (o)] and in the spectra of Co $3d$ states [denoted by (c)]. In regard to the latter peak, most contributions come from the Co t_{2g} states and only a few come from the Co e_g states. No satellite structures are obtained within the HF approximation. These results are nearly the same as those previously obtained by Mizokawa and Fujimori.[23]

The self-energy correction due to the local three-body correlations changes considerably the spectra of the HF approximation. The band gap is greatly reduced to a value of ~ 0.5 eV in good agreement with the experiments.[11,17,35] The spectral weight of the Co $3d$ states in the lower part of the valence band in the HF approximation is now transferred to the upper part of the valence band, and thereby a sharp peak is formed around the top of the valence band [denoted by (B)]. This peak consists mainly of the Co t_{2g} states. Only a

small intensity remains in the lower part of the valence band [denoted by (C)]. As regards the spectral density projected onto the O $2p$ states, the strong intensity found in the HF approximation around the top of the valence band is now greatly suppressed, and only a small intensity remains. Thus the O $2p$ band (O) is concentrated in the middle and lower parts of the valence band, well separated from the Co t_{2g} band (B). This result is different from the cluster model calculations, where the top of the valence band has a strong O $2p$ character and the O $2p$ band is well mixed up with the Co $3d$ states. The photoemission spectra are shown in the same figure. With decreasing incident photon energies, the intensity of the peak around the top of the valence band decreases considerably. Since the cross section of the Co $3d$ states relative to that of the O $2p$ states becomes smaller with decreasing photon energies, this experimental fact gives support to the present result that the spectra around the top of the valence band consist mainly of the Co $3d$ states. The other peaks in the experimental spectra correspond well to the density of states projected onto the O $2p$ states. Below the valence band, the satellite denoted by (S) is observed around $\omega = -12$ eV.[12,17] In the present calculation we obtain a satellite denoted by (D) around $\omega = -14$ eV, about 2 eV deeper than the experimental one.[34] This discrepancy may partly come from the neglect of the screening process by the states of three holes and two electrons.

B. The intermediate-spin phase

We consider another stable HF solution, the IS phase, which has ferromagnetic spin order and the orbital order, as shown in Fig. 1(a). This state has an energy of about 0.5 eV higher than that of the LS phase per a formula of CoO_3. As listed in Table II, one of the t_{2g} orbitals is unoccupied, and the e_g orbitals are occupied by nearly 1.6 electrons per Co site. The local moment is $\sim 2 \mu_B$. The self-energy correction due to three-particle correlations lowers the energy, but its energy is about 1.2 eV higher than the ground-state energy of the LS phase. The self-energy correction modifies little the number of electrons in each $3d$ orbital.

Figure 3 shows the calculated spectral densities for the IS phase. The HF approximation gives a band gap of ~ 0.5 eV. The orbital order is responsible for opening the band gap rather than forming a broad band of the Co e_g states across the Fermi level. A sharp peak appears above the
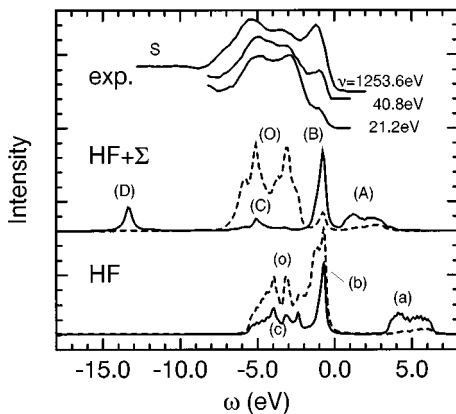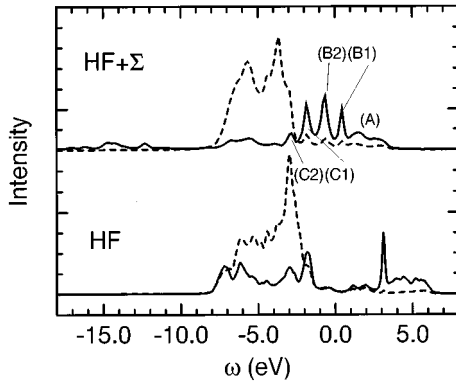

FIG. 2. Spectral densities projected onto the Co $3d$ states (solid lines) and onto the O $2p$ states (dashed lines) for the LS phase of $LaCoO_3$, within the HF approximation and by including the self-energy correction. An imaginary part of 0.1 eV is added to the HF energy eigenvalues, while a value of 0.3 eV is added to the three-particle energies when the self-energy is evaluated. The origin of the ω axis is set at the top of the valence band. Photoemission spectra are shown for several incident photon energies.

FIG. 3. Spectral densities projected onto the Co $3d$ states (solid lines) and onto the O $2p$ states (dashed lines) for the IS phase of LaCoO$_3$, within the HF approximation and by including the self-energy correction. The origin of the ω axis is set at the top of the valence band.

FIG. 4. Spectral densities projected onto the Co $3d$ states (solid lines) and onto the O $2p$ states (dashed lines) for the HS phase of LaCoO$_3$, within the HF approximation and by including the self-energy correction. The origin of the ω axis is set at the top of the valence band.

Fermi level. This corresponds to a process of adding electrons to unoccupied t_{2g} orbitals. In addition, broad structures appear below and above this sharp peak. They have the strong Co e_g character with the minority and majority spins, respectively. In the valence band, the Co $3d$ states are well mixed with the O $2p$ states.

The self-energy correction modifies greatly the spectra of the IS phase of the HF approximation. The peaks ($B1$) and ($B2$) consist of the Co t_{2g} states with minority spin, and the peaks ($C1$) and ($C2$) consist of the Co t_{2g} states with majority spin. In the lower part of the valence band, only a small spectral weight of the Co $3d$ states remains. The intensities of the Co e_g states are widely distributed to form a broad band, while those of the O $2p$ states are concentrated in the middle and lower parts of the valence band.

If the paramagnetic phase above ~ 90 K is simulated by the state where some parts of the system are in the IS phase, the peak intensity near the top of the valence band should decrease with the spin-state transition. Experimentally such a change is not clear. As regards a gradual change from semiconductor to metal between 400 and 600 K observed in transport measurements,[3,4] it has been proposed that this comes from the vanishing of the orbital order in the IS phase.[19] However, the present calculation predicts that the spectra are nearly independent of the orbital order in the IS phase, and therefore that mechanism cannot explain the remarkable change in the XPS and XAS spectra between 400 and 600 K.[13]

C. The high-spin phase

We consider the other typical stable HF solution, which has the G-type antiferromagnetic spin order, as shown in Fig. 1(b). This state has the energy 0.2 eV higher than that of the LS phase per CoO$_3$ formula. As listed in Table II, all the $3d$ orbitals with majority spin and one of t_{2g} orbitals with minority spin are fully occupied in each Co ion. The local moment is $\sim 3.5 \mu_B$. This state is triply degenerate so that a Jahn-Teller distortion may be accompanied to lift the degeneracy. The self-energy correlation lowers the energy of the
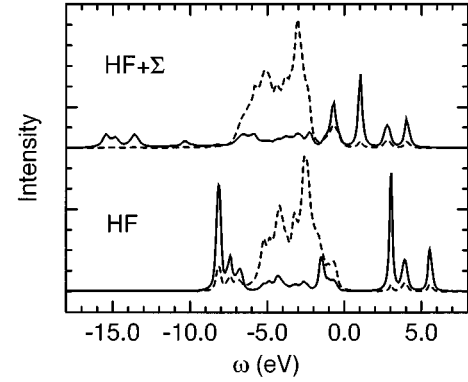
HS phase, but it is about 1.6 eV higher than that of the LS phase. The number of electrons occupied in the Co $3d$ orbitals is modified little.

Figure 4 shows the spectral density for the HS phase. The HF approximation gives the band gap of ~ 3 eV. The self-energy correction reduces the gap to as small as ~ 0.5 eV, and the satellite appears around $\omega = -14$ eV (below the valence band) and 10 eV (above the conduction band). A prominent peak in the lower part of the valence band (consisting mainly of the Co t_{2g} states) in the HF approximation disappears by the self-energy correction, and thereby the overall spectral shape becomes similar to that of the IS phase (the peak intensity around the top of the valence band is smaller than that of the IS phase). It is difficult to judge from the photoemission spectra whether the HS phase is related to the phases at high temperatures.[13]

D. Hole doping

We study the *doped* system La$_{1-x}$Sr$_x$CoO$_3$ by assuming that Sr atoms introduce holes in the network of Co and O atoms. We tentatively assume that one Sr atom introduces one hole. We consider three typical phases, the LS, IS, and
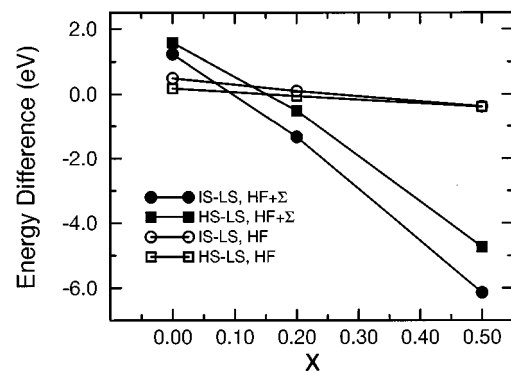

FIG. 5. Energy differences between the IS and LS phases and between the HS and LS phases, per CoO$_3$ formula in La$_{1-x}$Sr$_x$CoO$_3$. Open marks and filled marks are the values obtained by the HF approximation and by including the self-energy correction, respectively.
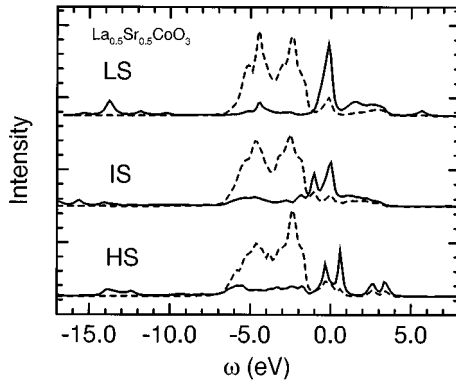
FIG. 6. Spectral densities for $La_{0.5}Sr_{0.5}CoO_3$ for the LS, IS, and HS phases. The solid lines represent the spectral density projected onto the Co $3d$ states, while the dashed lines represent the one projected onto the O $2p$ states. The origin of the ω axis is set at Fermi level.

TABLE III. Hole numbers in the Co $3d$ states per site obtained by including the self-energy correction.

x	LS	IS	HS
0.0	3.19	3.23	3.45
0.2	3.32	3.27	3.49
0.5	3.53	3.33	3.52

HS phases, which are obtained as metal for finite values of x. Figure 5 shows the energy difference between the IS phase and the LS phase and the one between the HS phase and the LS phase, as a function of x. As already mentioned, the LS phase is the most stable among the three phases at $x=0$. The LS phase is found to be unstable with increasing values of x within the HF approximation. The instability is also obtained by the self-energy correction, which makes the energy differences change more rapidly as a function of x. The instability of the nonmagnetic phase is consistent with the paramagnetic behavior of the susceptibility for $x>0.08$.[9]

Figure 6 shows the spectral densities at $x=0.5$ for the three phases. The intensity of the peak just below the Fermi level is smaller for the IS and HS phases than for the LS phase. A similar decrease is observed with increasing values of x in the XPS spectra.[11]

The Co $3d$ states should be occupied by four $3d$ holes per site for $x=0$, if the ionic picture is strictly valid. As shown in Table III, however, the occupied hole number in the Co $3d$ states is found to be less than 4 due to the hybridization to the O $2p$ states. A similar result has been obtained by the LDA+U method. When holes are introduced into the network of Co and O atoms, most of them go into the O $2p$ states. This tendency is stronger for the IS and HS phases than for the LS phase. Since the density of states just below the Fermi level is dominated by the Co $3d$ states, the above result indicates that the rigid band model does not work.

IV. CONCLUDING REMARKS

We have studied the excitation spectra of $LaCoO_3$ by using a local three-body scattering theory. Starting with the tight-binding model where its parameters are taken from the cluster model calculation, we first carry out the HF approximation, and then consider the self-energy correction by taking account of three-body scattering in the Co sites. This calculational scheme has successfully been applied to transition-metal oxides.[27,28] Although the self-energy correction up to second order with respect to U was considered for transition-metal compounds,[36] such a treatment seems insufficient because of large values of U. We have obtained the LS phase as the ground state. It is shown that the self-energy correction changes considerably the spectra of the HF approximation; a reasonable size of the band gap and the satellite are obtained, in good agreement with the XPS experiments. For more information on the spectral density projected onto the O $2p$ states, O $K\alpha$ x-ray emission experiments are desired.

Getting some insights into the nonmagnetic-to-paramagnetic transition, we have also studied the excited states, the IS phase, and the HS phase, which have long-range spin and orbital orders. We have not exhausted all possible low-energy phases. Also we have not considered the crystal distortions, since the tight-binding model seems too simple to include such effects. However, it is known that the overall spectral shape is insensitive to the long-range spin and orbital orders as well as the crystal distortions. The spectral density in the paramagnetic phase may be simulated by mixing the spectral weight of the LS, IS, and HS phases. The peak intensity around the top of the valence band is predicted to be reduced in the paramagnetic phase. In the photoemission experiment, the spectra change little around 90 K.[13] In order to make clear the relation between photoemission spectra and the spin-state transition expected from the susceptibility data, detailed photoemission experiments are desired at low temperatures well below 90 K.

In addition, we have studied doped systems, $La_{1-x}Sr_xCoO_3$ by assuming that Sr atoms introduce holes in the network of Co and O atoms. It is found that the LS phase becomes unstable under the hole doping. This is consistent with the reduction of the peak intensity around the top of the Fermi level with increasing values of x in the photoemission experiment.[11]

[1] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).

[2] J. B. Goodenough, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1971), Vol. 5.

[3] M. A. Señarís-Rodríguez and J. B. Goodenough, J. Solid State Chem. **116**, 224 (1995).

[4] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53**, R2926 (1996).

[5] W. C. Koehler and O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[6] N. Menyuk, K. Dwight, and P. M. Raccah, J. Phys. Chem. Solids **28**, 549 (1967).

[7] G. Thornton, B. C. Tofield, and D. E. Williams, Solid State Commun. **44**, 1213 (1982).

[8] G. Thornton, B. C. Tofield, and A. W. Hewat, J. Solid State Chem. **61**, 301 (1986).

[9] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J. M. Tranquada, G. Shirane, S. Higashi, Y. Okajima, and K. Kohn, Phys. Rev. B **50**, 3025 (1994).

[10] L. Richter, S. D. Bader, and M. B. Brodsky, Phys. Rev. B **22**, 3059 (1980).

[11] A. Chainani, M. Mather, and D. D. Sarma, Phys. Rev. B **46**, 9976 (1992).

[12] S. Masuda, M. Aoki, Y. Harada, H. Hirohashi, Y. Watanabe, Y. Sakisaki, and H. Kato, Phys. Rev. Lett. **71**, 4214 (1993).

[13] M. Abbate, J. C. Fuggle, A. Fujimori, L. H. Tjeng, C. T. Chen, R. Potze, G. A. Sawatzky, H. Eisaki, and S. Uchida, Phys. Rev. B **47**, 16 124 (1993).

[14] S. R. Barman and D. D. Sarma, Phys. Rev. B **49**, 13 979 (1994).

[15] M. Abbate, R. Potze, G. A. Sawatzky, and A. Fujimori, Phys. Rev. B **49**, 7210 (1994).

[16] T. Saitoh, T. Mizokawa, A. Fujimori, Y. Takeda, and M. Takano, J. Electron Spectrosc. Relat. Phenom. **78**, 195 (1996).

[17] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **55**, 4257 (1997).

[18] M. Itoh, M. Mori, M. Sugahara, T. Yamauchi, and Y. Ueda, Czech. J. Phys. **46**, 2157 (1996).

[19] M. A. Korotin, S. Y. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[20] N. Hamada, H. Sawada, and K. Terakura, *Spectroscopy of Mott Insulators and Correlated Metals*, edited by A. Fujimori and Y. Tokura, Springer Series in Solid-State Sciences (Springer-Verlag, Berlin, 1995), p. 95.

[21] D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. **75**, 1126 (1995).

[22] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).

[23] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

[24] T. Saitoh, A. E. Bocquet, T. Mizokawa, and A. Fujimori, Phys. Rev. B **52**, 7934 (1995).

[25] A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. R. Barman, K. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda, Phys. Rev. B **53**, 1161 (1996).

[26] J. Igarashi, P. Unger, K. Hirai, and P. Fulde, Phys. Rev. B **49**, 16 181 (1994).

[27] M. Takahashi and J. Igarashi, Ann. Phys. (Leipzig) **5**, 247 (1996).

[28] M. Takahashi and J. Igarashi, Phys. Rev. B **54**, 13 566 (1996).

[29] Since the neutron scattering experiment indicates a ferromagnetic correlation in the paramagnetic phase, we assume the ferromagnetic spin order for the IS phase. Of course a solution with antiferromagnetic spin order is also possible for the IS phase, as Korotin *et al.* has considered (Ref. 19).

[30] M. Itoh and I. Natori, J. Phys. Soc. Jpn. **64**, 970 (1995).

[31] M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Magn. Magn. Mater. **140-144**, 1811 (1995).

[32] P. Ganguly, P. S. A. Kumar, P. N. Santhosh, and I. S. Milla, J. Phys. Condens. Matter **6**, 533 (1994).

[33] W. A. Harrison, *Electronic Structures and the Properties of Solids– The Physics of the Chemical Bond* (W. H. Freeman and Company, San Francisco, 1979).

[34] For NiO, we have used the value of U, about 2 eV smaller than that of the cluster model analysis, in order to make the satellite position agree with the experimental one (Refs. 27 and 28). In the present calculation, we use the value of U to be the same as that of the cluster model analysis.

[35] T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B **48**, 17 006 (1993).

[36] T. Mizokawa and A. Fujimori, Phys. Rev. B **53**, R4201 (1996).