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Electronic and magnetic states in doped $LaCoO_3$

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The electronic and magnetic states in doped perovskite cobaltites, $(La,Sr)CoO_3$, are studied in the numerically exact diagonalization method on Co_2O_{11} clusters. For realistic parameter values, it is shown that a high spin state and an intermediate spin state coexist in one-hole-doped clusters due to strong p-d mixing. The magnetic states in the doped cobaltites obtained in the calculation explain various experimental results. [S0163-1829(99)06007-5]

Recently cobaltites have attracted renewed interest in connection with the so-called colossal magnetoresistaice in perovskite manganites. $La_{1-x}Sr_xCoO_3$ exhibits anomalous magnetic and transport properties that are still far from understanding.[1–4] The undoped $LaCoO_3$ is an insulator with low spin state (LS) of t_{2g}^6 configuration. At low temperatures, the magnetic susceptibility is suppressed. However, with increasing temperature (T), it increases rapidly and the magnetic moment of each Co ion seems to appear above ~100 K, where the resistivity remains still high.[5,6] Similar behavior can be seen by increasing the carrier concentration x.[7] $La_{1-x}Sr_xCoO_3$ becomes metallic at sufficiently high T ($\gtrsim 500$ K) or high x ($\gtrsim 0.3$), thus indicating that the charge gap is much larger than the spin gap.

The magnetic state in $LaCoO_3$ in the intermediate-T region ($100\ \mathrm{K} \lesssim T \lesssim 500\ \mathrm{K}$) is controversial. In the recent experiments,[8,9] it was suggested that there exists the intermediate spin state (IS) of $t_{2g}^5 e_g$ configuration rather than the high spin state (HS) of $t_{2g}^4 e_g^2$ configuration. In the intermediate x region ($0 \lesssim x \lesssim 0.3$), on the other hand, a spin glass or a cluster-glass phase has been reported to exist at low temperatures, indicating an inhomogeneous magnetic state in the doped cobaltites.[10] Recently, Tokura *et al.*[11] have reported the T and x dependence of the optical conductivity which shows that a large change in the electronic state occurs over a wide energy range in a similar way for both high T and x. These results, as well as the photoemission study,[12,13] clearly suggest the importance of the electron-electron correlation for the insulator-metal transition in the cobaltites.

Based on the LDA+U (where LDA is the local-density approximation) band calculation,[14] it has been argued that the anomalous behavior of $LaCoO_3$ may be caused by the temperature dependence of the mixing parameter between Co and O ions. A mean-field approximation of Hartree-Fock type was also applied to examine the electronic and magnetic states.[15–17]

In this paper, we perform numerically exact diagonalization calculation on small clusters in order to take the strong electron correlation, i.e., the Coulomb interaction and Hund's rule coupling, into consideration more explicitly. We adopt Co_2O_{11} clusters with zero and one hole and study how the nearly degenerate spin states change by doping. By performing the calculation for wide range of parameter values, we will show that a coexistence of HS and IS is most plausible in doped cobaltites.

The Hamiltonian consists of four terms as

$$H = H_p + H_d + H_{pd} + H_{dd}, \tag{1}$$

where H_p and H_d denote $2p$ and $3d$ energy levels on O and Co ions, respectively, H_{pd} is the $2p$-$3d$ mixing term, and H_{dd} includes Coulomb interaction between $3d$ electrons. In H_p we include only $2p_\sigma$ orbitals that are given by suitable linear combinations of atomic $2p$ orbitals to have the same symmetry with the e_g orbitals. The energy level ϵ_m of the mth $3d$ orbital takes $\epsilon_m = -4Dq$ and $6Dq$ for t_{2g} and e_g orbitals, respectively. H_{pd} includes only the overlap integral $pd\sigma$ between $2p_\sigma$ and $3d$ orbitals by assuming $pd\pi = 0$. Therefore, the t_{2g} electrons are regarded as localized spins.

The interaction term H_{dd} is given by

$$H_{dd} = U\sum_{i,m} n^d_{i,m,\uparrow} n^d_{i,m,\downarrow} + V \sum_{i,m>m'} N_{i,m} N_{i,m'} - 2J \sum_{i,m>m'} \left(\mathbf{S}_{i,m}\cdot\mathbf{S}_{i,m'} + \tfrac{1}{4} N_{i,m} N_{i,m'}\right), \tag{2}$$

where U, V, and J denote the intraorbital, and interorbital Coulomb, and exchange interactions between $3d$ electrons, $n^d_{i,m,s}$ is the number operator for $3d$ electrons on ith Co ion ($i = 1,2$) with orbital m and spin s, $N_{i,m} = n^d_{i,m,\uparrow} + n^d_{i,m,\downarrow}$ and $\mathbf{S}_{i,m}$ is the spin operator of m orbital in the ith $3d$ site. The charge-transfer energy Δ is defined as $\Delta = E(d^{N+1}) - E(d^N) - \epsilon_p$ where ϵ_p is the energy level of $2p_\sigma$ orbitals and $E(d^N)$ is the energy of $3d$ state averaged over configurations of N $3d$-electrons, and is given by $E(d^N) = (U + 8V - 4J)/9 \times N(N-1)/2$ for H_{dd} given in Eq. (2). The energy $(U + 8V - 4J)/9$ is the same as the Hubbard gap energy $\tilde{U}$ defined as $\tilde{U} = E(d^{N+1}) + E(d^{N-1}) - 2E(d^N)$.

Equation (2) has a simplified form as compared with that in the multiplet theory. We have examined the energy levels in a CoO_6 cluster using the Hamiltonian of the multiplet

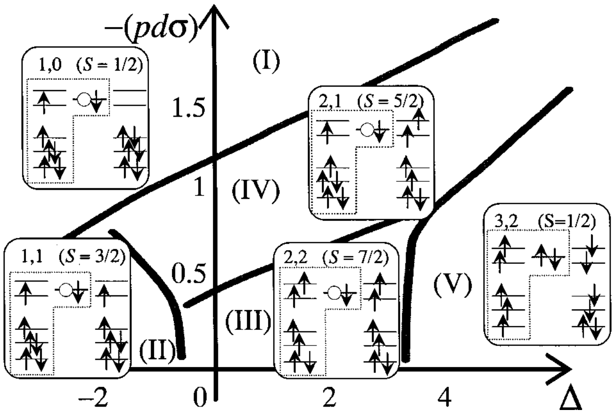

FIG. 1. Phase diagram of the ground state in one-hole-doped Co_2O_{11} cluster.

theory, and confirmed that the energy levels of LS, IS and HS states calculated by using Eq. (2) are consistent with those of $^1A_1$, $^3T_1$, and $^5T_2$ states in the multiplet theory.

There are six parameters U, V, J, $pd\sigma$, $10Dq$ and Δ in this model. We first fix the values of electron-electron interaction as $U=V=5$ eV and $J=1$ eV following the analyses of photoemission spectra. We treat $pd\sigma$, $10Dq$ and Δ as parameters under a condition that the energy of LS is the same as that of HS or IS in the undoped Co_2O_{11}, since the energy difference between LS and HS or IS is expected to be very small, i.e., about 100 K in $LaCoO_3$. In the following, the value of $10Dq$ is taken to satisfy the above condition for each set of parameter values of $pd\sigma$ and Δ except for region I shown in Fig. 1.

In Fig. 1, we show the electronic states of the ground state of one-hole-doped Co_2O_{11} for several sets of parameter values on the $pd\sigma$-Δ plane. As the value of Δ may be smaller than that of $\tilde{U}$ (~ 5 eV) for $LaCoO_3$, the value of Δ was varied from about -4 to 6 eV in the calculation. The range of $pd\sigma$ is taken to be from 0 to -2 eV, which includes the values used for the analyses of the previous experiments. The panels inserted in Fig. 1 show five $3d$ orbitals of each Co ion and one $2p_\sigma$ orbital. The arrows denote spins of the electrons. Here, only one $2p_\sigma$ orbital is drawn to represent the $2p_\sigma$ states of O ions and the circle denotes that there is one hole in four $2p_\sigma$ orbitals. The other six electrons in the $2p_\sigma$ orbitals are not shown in Fig. 1 for simplicity. Because the t_{2g} electrons are localized in this model as noted above, the number of t_{2g} electrons may characterize the electronic state of the cluster. Therefore, HS, IS, and LS of each $3d$ ion are distinguished by the number of t_{2g} holes which is written on the top-left side of each panel.[18] The total spin S of each state is also given. The electronic configurations enclosed by dotted frames in the panels are the ground states of the doped CoO_6.

The notable features in Fig. 1 are (i) the ground states of one-hole-doped CoO_6 in regions I–IV are either $t_{2g}^5e_g^1\underline{L}$ or $t_{2g}^4e_g^2\underline{L}$, while that in region V is $t_{2g}^3e_g^2$, (ii) the spins of Co ions of doped Co_2O_{11} in regions II, III and IV align ferromagnetically, while those in region V align antiferromagnetically, (iii) HS is more stable for larger values of Δ and/or smaller values of $|pd\sigma|$, and (iv) IS and HS coexist in region IV.

The strong p-d mixing makes the spins of Co ions ferromagnetic by a double exchange type interaction to gain the kinetic energy. The spins of HS and $t_{2g}^3e_g^2$ state in region V align antiferromagnetically by the superexchange interaction as the $2p_\sigma$ orbitals are occupied. It is natural that HS is more stable for larger values of Δ and/or smaller values of $|pd\sigma|$ because each Co ion prefers HS if the p-d mixing is neglected. Actually, in the ground state of the undoped Co_2O_{11}, HS is degenerate with LS in the parameter regions III–V. In contrast, in region II IS is degenerate with LS. So, we find that there is a tendency that IS or HS, which is degenerate with LS in the undoped clusters, appears in both Co ions of doped clusters except for regions IV and V. The appearance of $t_{2g}^3e_g^2$ in region V just comes from the situation that a hole is created in $3d$ orbitals because of large values of Δ. The coexistence of IS and HS in region IV is due to strong p-d mixing, i.e., a gain in the kinetic energy of e_g and p electrons. In region I, where $pd\sigma$ is large, the aforementioned condition can not be satisfied within the range of the parameter values of $pd\sigma$ and Δ in Fig. 1 for positive values of $10Dq$. Therefore, we set $10Dq=0$ so that LS is the nondegenerate ground state of the undoped clusters.

The coexistence of IS and HS in region IV is explained in the following: In the undoped case, because of large values of $|pd\sigma|$, the effective levels of the occupied ‘‘bonding’’ orbitals of e_g and $2p$ orbitals are lower in energy than those of t_{2g} orbitals, and a hole is created in t_{2g} orbitals. Therefore, the $t_{2g}^5e_g^1\underline{L}$, i.e., an apparent IS + p-hole state appears in a CoO_6 cluster upon doping. In the doped Co_2O_{11} cluster, existence of e_g electrons on both Co sites is favorable due to the strong p-d mixing to gain the kinetic energy. In addition, the spins of e_g electrons become parallel due to the double exchange type interaction. As the HS is degenerate with LS in the undoped clusters, the HS appears at neighboring Co site. The energy gain due to the alignment of the spins is 5–10 times larger than the energy difference between LS and HS in the undoped case. This means that the doped holes change the states from nonmagnetic to magnetic ones not only in the ‘‘doped’’ site, but also in the site(s) around the ‘‘doped’’ site. Thus, the p-d mixing is crucial for coexistence of IS and HS in region IV.

Following the studies of x-ray spectroscopy, we find that almost all the parameter sets belong to region IV. For example, Abbate *et al.*[12] obtained the parameters $\tilde{U}=5$ eV, $\Delta=4$ eV, and $pd\sigma=-1.5$ eV. Saitoh *et al.*[13] obtained $\tilde{U}=5.5$ eV, $\Delta=2$ eV, and $pd\sigma=-1.8$ eV. Thus, the state shown in region IV may be the most plausible one for the doped cobaltites. This state is also plausible in view of several experimental results, which is now ready to argue.

Let us consider the interaction between two Co_2O_{11} clusters connected by one O ion. If the electronic states of the clusters are those given in region IV, the magnetic interaction may be either ferromagnetic or antiferromagnetic. When two Co ions in IS state are on the near-neighbor sites, the interaction is ferromagnetic due to the itineracy of holes as shown in Fig. 2(a), the effect of which exceeds the superexchange interaction between two IS’s. On the other hand, when two Co ions in HS state are on the near-neighbor sites, the interaction is antiferromagnetic due to the superexchange interaction between HS via the occupied $2p_\sigma$ orbital, which

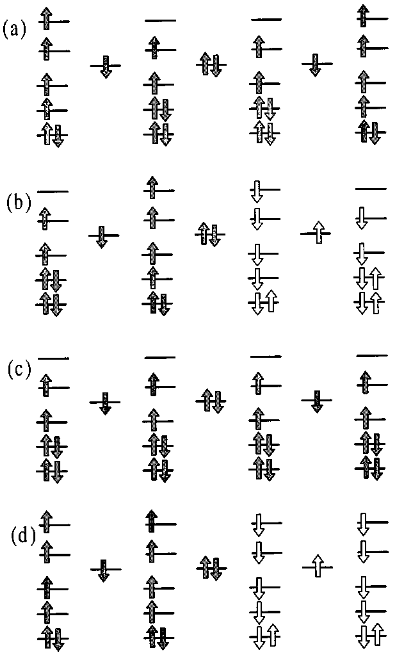

FIG. 2. Electronic states of coupled two Co_2O_{11} clusters connected by one O ion. (a) Ferromagnetic coupling of two Co_2O_{11} clusters in region IV, (b) antiferromagnetic coupling of two Co_2O_{11} clusters in region IV, (c) ferromagnetic coupling of two Co_2O_{11} clusters in region II, and (d) antiferromagnetic coupling of two Co_2O_{11} clusters in region III.

is shown in Fig. 2(b). In lightly doped cobaltites, therefore, we may expect coexistence of ferromagnetic and antiferromagnetic interaction. The coexistence of these interactions may be the origin of the spin-glass and/or cluster-glass state reported in experiments.[10]

Actually, the state shown in Fig. 2(a) is quite similar to that argued by Señaris-Rodríguez and Goodenough for relatively low *x*.[19] They argued that for low *x*, holes may be trapped at Sr^{2+} ions and form a cluster of one $t_{2g}^5 e_g^0$ Co ion and six HS Co ions. With increasing *x*, a segregation of hole-rich and hole-poor regions occurs and the hole-rich region may be ferromagnetic due to the double exchange interaction. Furthermore, they argued the hole-rich region stabilizes HS Co ions at the interfaces to the hole-poor regions, and magnetic interaction between these hole-rich regions is antiferromagnetic due to the superexchange interaction. This picture is the same as that shown in Fig. 2(a) except for the strong *p*-*d* mixing which realize an apparent IS and *p*-holes on O ions instead of $t_{2g}^5 e_g^0$ configuration. The degree of *p*-*d* mixing may be measured by electron-energy-loss spectroscopy (EELS) as done for doped manganites.[20]

The magnetic state shown in Fig. 2(a) also explains the optical conductivity in the lightly doped cobaltites. Doped holes are mobile within the ferromagnetic region, while there is no Drude part because the holes are confined within the regions. On the other hand, coupled clusters of Co_2O_{11} with the magnetic states of regions II and III in Fig. 1, which are shown in Figs. 2(c) and 2(d), respectively, do not explain the experimental results. The coupling of spins in Fig. 2(c) is ferromagnetic due to the double exchange interaction. Thus, in this case, the systems can be metallic as manganites. In contrast, the coupling of the Co_2O_{11} clusters in region III will lead to a less conductive state because of the antiferromagnetic coupling of the clusters shown in Fig. 2(d). The states made of the magnetic states in regions I and V in Fig. 1 may be ruled out due to their weak magnitude of cluster spins. Especially, holes in magnetic state in region V may be completely localized.

The magnetic state shown in the region IV in Fig. 1 has large spin $S=5/2$ for Co_2O_{11}. A doped hole induces the magnetic states not only in the ''doped'' site, but also in the sites around the ''doped'' one. Then, the spins align ferromagnetically. As the result, a large spin moment ($S=25/2$) per doped hole may occur. This is consistent with the experimental result reported by Yamaguchi *et al.* that giant magnetic moment ($S=10$–15) per doped hole appears for very small values of *x*.[21]

In conclusion, we have examined the electronic and magnetic states induced by doped holes in $LaCoO_3$ by using the numerically exact diagonalization method on Co_2O_{11} clusters. The phase diagram for the ground state of one-hole doped Co_2O_{11} cluster has been constructed. For a realistic parameter set, HS and IS coexist in a cluster due to strong *p*-*d* mixing and give rise to a large spin state. The magnetic states in doped cobaltites obtained in the calculation explain various experimental results.

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