Electronic and magnetic states in doped LaCoO$_3$

K. Tsutsui and J. Inoue

Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

S. Maekawa

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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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$_2$O$_{11}$ 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.

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Recently cobaltites have attracted renewed interest in connection with the so-called colossal magnetoresistive inhomogeneous magnetic state in the doped LaCoO$_3$. An insulator with low spin state (LS) of $t_{2g}$ configuration, the electronic and magnetic states. In this paper, we perform numerically exact diagonalization 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$_2$O$_{11}$ 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

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

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 $2p_g$ orbitals which are given by suitable linear combinations of atomic $2p$ orbitals to have the same symmetry with the $e_g$ orbitals. The energy level $\epsilon_m$ of the $m$-th 3d orbital takes $\epsilon_m = -4Dq$ and $6Dq$ for $t_{2g}$ and $e_g$ orbitals, respectively. $H_{pd}$ includes only the overlap integral $pd\pi$ between $2p_d$ and 3d orbitals by assuming $p\pi = 0$. Therefore, the $t_{2g}$ electrons are regarded as localized spins.

The interaction term $H_{dd}$ is given by

$$H_{dd} = U \sum_{i,m} n_{i,m,\uparrow} n_{i,m,\downarrow} + V \sum_{i,m>m'} N_{i,m} N_{i,m'} - 2J \sum_{i,m>m'} (S_{i,m} \cdot S_{i,m'} + \frac{1}{4} N_{i,m} N_{i,m'}),$$

where $U$, $V$ and $J$ denote the intra- and inter-orbital Coulomb, and exchange interactions between $3d$ electrons, $n_{i,m,s}$ is the number operator for $3d$ electrons on $i$-th Co ion ($i = 1, 2$) with orbital $m$ and spin $s$, $N_{i,m} = n_{i,m,+} + n_{i,m,-}$ and $S_{i,m}$ is the spin operator of $m$ orbital in the $i$-th $3d$ site. The charge-transfer energy $\Delta$ is defined as $\Delta = E(d^{N+1}) - E(d^N) - \epsilon_p$ where $\epsilon_p$ is the energy level of $2p_g$ 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 $\bar{U}$ defined as $\bar{U} = E(d^{N+1}) + E(d^{N-1}) - 2E(d^N)$.

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Eq. (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 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 $^3T_2$ states in the multiplet theory.

There are six parameters $U$, $V$, $J$, $pd\sigma$, $10Dq$ and $\Delta$ as parameters under a condition that the energy of LS is the same as that of HS or IS in the undoped CoO$_{11}$, 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 $\Delta$ except for region I shown in Fig. 1.

In Fig. 1, we show the electronic states of the ground state of one-hole doped CoO$_{11}$ for several sets of parameter values on the $pd\sigma$-$\Delta$ plane. As the value of $\Delta$ may be smaller than that of $U$ ($\sim$5 eV) for LaCoO$_3$, the value of $\Delta$ 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 3$d$ orbitals of each Co ion and one 2$p_{\sigma}$ orbital. The arrows denote spins of the electrons. Here, only one 2$p_{\sigma}$ orbital is drawn to represent the 2$p_{\sigma}$ states of O ions and the circle denotes that there is one hole in four 2$p_{\sigma}$ orbitals. The other six electrons in the 2$p_{\sigma}$ 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 3$d$ ion are distinguished by the number of $t_{2g}$ holes which is written on the top left side of each panel. 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 $t_{2g}^5e_g^1L$ or $t_{2g}^4e_g^2L$, while that in region V is $t_{2g}^3e_g^2$, ii) the spins of Co ions of doped CoO$_{11}$ in region II, III and IV align ferromagnetically, while those in region V align antiferromagnetically, iii) HS is more stable for larger values of $\Delta$ 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 $\Delta$ 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 CoO$_{11}$, 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 clus-
ters except for regions IV and V. The appearance of $t_{2g}^2e_g^0$ in region V just comes from the situation that a hole is created in 3$d$ orbitals because of large values of $\Delta$. 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 $pda$ is large, the aforementioned condition cannot be satisfied within the range of the parameter values of $pda$ and $\Delta$ in Fig. 1 for positive values of 1$0Dq$. Therefore, we set $10Dq = 0$ so that LS is the non-degenerate 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 $pda$, the effective levels of the occupied 'bonding' orbitals of $e_g$ and 2$p$ orbitals are lower in energy than those of $t_{2g}$ orbitals, and a hole is created in $t_{2g}$ orbitals. Therefore, the $t_{2g}^2e_g^0$ $L$, i.e., an apparent IS $+$ $p$-hole state appears in a CoO$_6$ cluster upon doping. In the doped CoO$_2$O$_{11}$ 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 $\sim$ 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. obtained the parameters $\tilde{U} = 5$ eV, $\tilde{\Delta} = 4$ eV, and $pda = -1.5$ eV. Saitoh et al. obtained $\tilde{U} = 5.5$ eV, $\tilde{\Delta} = 2$ eV, and $pda = -1.8$ 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 CoO$_2$O$_{11}$ 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 2$p_d$ orbital, which 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.

Actually, the state shown in Fig. 2(a) is quite similar to that argued by Rodríguez and Goodenough for relatively low $x$. They argued that for low $x$, holes may be trapped at Sr$^{2+}$ ions and form a cluster of one $t_{2g}^2e_g^0$ 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 realizes an apparent IS and $p$-holes on O ions instead of $t_{2g}^2e_g^0$ configuration. The degree of $p$-$d$ mixing may be measured by EELS as done for doped manganites.

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 CoO$_2$O$_{11}$ with the magnetic states of regions II and III in Fig. 1, which are shown in Figs. 2(c) and (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 \( \text{Co}_2\text{O}_{11} \) 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 \( \text{Co}_2\text{O}_{11} \). 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 \textit{et al.} that giant magnetic moment \( S \sim 10 \) per doped hole appears for very small values of \( x \).

In conclusion, we have examined the electronic and magnetic states induced by doped holes in \( \text{LaCoO}_3 \) by using the numerically exact diagonalization method on \( \text{Co}_2\text{O}_{11} \) clusters. The phase diagram for the ground state of one-hole doped \( \text{Co}_2\text{O}_{11} \) clusters 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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\* Present Address: Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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