Antiferromagnetic, Charge and Orbital Order in Na$_{0.5}$CoO$_2$ Based on the Two Dimensional 11 Bands d-p Model

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Abstract. The electronic state of the CoO$_2$ plane in the layered cobalt oxide Na$_{0.5}$CoO$_2$ is investigated on the basis of the 11 band d-p model on a two dimensional triangular lattice, where the tight-binding parameters are determined so as to fit the LDA band structure and an effective one dimensional potential is added so as to include the effect of the Na order. We treat the Coulomb interaction on a Co site: the intra- and inter-orbital direct terms $U$ and $U'$, the exchange coupling $J$ and the pair-transfer $J'$, within the Hartree-Fock approximation. It is found that the metallic antiferromagnetic order takes place for $T_c^2 < T < T_c^1$ and the coexistent state of the antiferromagnetic, orbital and charge orders takes place for $T < T_c^2$ where the system becomes insulator. The obtained results are consistent with the successive phase transitions observed in Na$_{0.5}$CoO$_2$.

1. Introduction
Na$_{0.5}$CoO$_2$ exhibits remarkable successive phase transitions at $T_{c1} \sim 87$ K and $T_{c2} \sim 53$ K [1]: the itinerant antiferromagnetism is realized below $T_{c1}$ and the system becomes insulator below $T_{c2}$. The magnetic susceptibility $\chi$ shows kinks at $T_{c1}$ and $T_{c2}$. The resistivity $\rho$ exhibits only a tiny anomaly at $T_{c1}$, while it rapidly increases below $T_{c2}$. From the NMR and the neutron measurements, Yokoi et al. [2] have proposed the magnetic structure of Na$_{0.5}$CoO$_2$ below $T_{c1}$, where chains of Co$^{3.5-\delta}$ with larger staggered moments within the CoO$_2$ (ab) plane and chains of Co$^{3.5-\delta}$ with smaller moments along the $c$ axis align alternatively on the $ab$ plane. The ordering of the $c$ axis oriented moments on the Co$^{3.5-\delta}$ chains has not been distinguished whether ferromagnetic or antiferromagnetic [2], and has not been detected by polarized neutron measurements [3]. The charge disproportionation of the Co sites into chains of Co$^{3.5-\delta}$ and Co$^{3.5-\delta}$ is closely related to the ordered pattern of Na ions which form one dimensional zigzag chains below room temperature [4, 5].

The purpose of this paper is to investigate the electronic state of the CoO$_2$ plane including the successive phase transition of Na$_{0.5}$CoO$_2$, particularly focused on the effect of the one dimensional Na order on the antiferromagnetism. For this purpose, we take into account of an effective one dimensional potential on the CoO$_2$ plane due to the effect of the Na order.
2. Model

To investigate the electronic states of the CoO$_2$ plane in the layered cobalt oxides Na$_x$CoO$_2$, we employ the two dimensional triangular lattice $d$-$p$ model [6, 7, 8, 9] which includes 11 orbitals: $d_{3z^2-r^2}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{yz}$, $d_{zx}$ of Co and $p_{1x}$, $p_{1y}$, $p_{1z}$ ($p_{2x}$, $p_{2y}$, $p_{2z}$) of O in the upper (lower) side of the Co plane. The model is given by the following Hamiltonian:

$$
H = \sum_{n,m,\sigma} \varepsilon_n^d d_{n,m,\sigma}^d d_{n,m,\sigma} + \sum_{k,m,m',\sigma} t_{km,m'}^d d_{k,m,\sigma}^d d_{k,m',\sigma} + \varepsilon_p \sum_{k,j,ll',\sigma} P_{k,j,l}^p P_{k,j} d_{k,j,l,\sigma}^l d_{k,j,l',l,\sigma}^l + U \sum_{n,m,m',\sigma} n_{n,m}^d n_{n,m,m'}^d + U' \sum_{n,m,m',\sigma} n_{n,m}^d n_{n,m,m'}^d + J \sum_{n,m,m',\sigma} d_{n,m,\sigma}^d d_{n,m,m',\sigma}^d d_{n,m,m',\sigma}^d d_{n,m,m',\sigma}^d + J' \sum_{n,m,m',\sigma} d_{n,m,\sigma}^d d_{n,m,m',\sigma}^d d_{n,m,m',\sigma}^d d_{n,m,m',\sigma}^d,
$$

where $d_{k,m,\sigma}^d$ ($d_{n,m,\sigma}^d$) is a creation operator for a Co 3d electron with wave vector $k$ = $(k_x, k_y)$ (site $n$ = $(n_x, n_y)$), orbital $m$ = $(3z^2-r^2, x^2-y^2, xy, yz, zx)$ and spin $\sigma$ = ($\uparrow$, $\downarrow$), and $P_{k,j,l}^p$ is a creation operator for a oxygen 2p electron with wave vector $k$, site $j$ = $(1, 2)$, orbital $l$ = $(x, y, z)$ and spin $\sigma$, respectively; $n_{n,m}^d = d_{n,m,\sigma}^d d_{n,m,\sigma}^d$ and $n_{n,m,m'}^d = \sum_\sigma n_{n,m}^d$. The transfer integrals $t_{km,m'}^d$ and $t_{k,j,l,m}^d$, which are written by the Slater-Koster parameters, together with the atomic energies $\varepsilon_p$ and $\varepsilon_m^d$ are determined so as to fit the tight-binding energy bands to the LDA bands for Na$_{0.5}$CoO$_2$ [10]. As the six hole pockets near the $K$ points predicted by the LDA [10] have not been observed by ARPES experiments [11], we employ the energy bands without the hole pockets where the tight-binding parameters relating to the trigonal distortion are slightly modified.

In the Hamiltonian eq. (1), we consider the effects of the Coulomb interaction at a Co site: the intra- and inter-orbital direct terms $U$ and $U'$, the exchange coupling $J$ and the pair-transfer $J'$. Here and hereafter, we assume the rotational symmetry yielding the relations: $U' = U - 2J$ and $J = J'$, and we set $J = U/10$ for simplicity. We also consider the effect of the Na order at $x = 0.5$, where Na ions form one dimensional chains along the X-direction below room temperature, by taking into account an effective one dimensional potential on the CoO$_2$ plane [6, 7]:

$$
\varepsilon_{n,m}^d = \begin{cases} 
\varepsilon_m^d - \Delta \varepsilon_d & \text{for odd } n_y \\
\varepsilon_m^d + \Delta \varepsilon_d & \text{for even } n_y 
\end{cases}
$$

(2)

with the effective potential $\Delta \varepsilon_d$ due to the Na order. In this paper, we set $\Delta \varepsilon_d = 1.0$ eV. Due to the effect of $\Delta \varepsilon_d$, the band structure becomes quasi one dimensional and the Fermi surface nesting is enhanced resulting in the antiferromagnetic order[6, 7].

3. Result

Now we discuss the possible ordered states of the Hamiltonian eq. (1) within the Hartree-Fock approximation, where we assume that the order parameters are diagonal with respect to the orbital $m$ and the spin $\sigma$. We note that the charge order in X-direction is different from the charge order of Co$^{3.5+\delta}$ and Co$^{3.5-\delta}$ in Y-direction due to the effect of the one dimensional Na order.
Figure 1. The sublattice magnetization $(n_↑ - n_↓)/2$, the orbital order $n_{yz} - n_{zx}$, the charge order $\eta$, the resistivity $\rho$ and the density of states at the Fermi level $D_F$ as functions of $U$ for $\Delta\varepsilon_d = 1.0$ eV at $T = 20$ K.

Figure 1 shows the sublattice magnetization $(n_↑ - n_↓)/2$, the orbital order $n_{yz} - n_{zx}$, the charge order $\eta$, the density of states at the Fermi level $D_F$ and the resistivity $\rho$ as functions of $U$ at $T = 20$ K. When $U$ is larger than a critical value $U_c \sim 1.45$ eV, we observe the coexistence state of antiferromagnetism, charge order and orbital order (AFM+CO+OO). When $U$ increases for $U > U_c$, both the sublattice magnetization $(n_↑ - n_↓)/2$ and the orbital order $n_{yz} - n_{zx}$ increase, while the density of states $D_F$ decreases and finally becomes zero for $U > 1.7$ eV. The resistivity $\rho$ rapidly increases for $U > U_c$ and becomes almost infinity for $U > 1.7$ eV. Due to the structure of the orbital order, the charge order $\eta$ is induced by the orbital order although the amount of $\eta$ is vary small or zero as shown in Fig. 1.

Figure 2. The temperature dependence of the sublattice magnetization $(n_↑ - n_↓)/2$ (a), the orbital order $n_{yz} - n_{zx}$ (b), the charge order $\eta$ (c) and the resistivity $\rho$ (d) for $\Delta\varepsilon_d = 1.0$ eV at $U = 1.5$ eV (solid lines), $U = 1.6$ eV (dotted lines) and $U = 1.7$ eV (dashed lines).
We plot the temperature dependence of the order parameters together with the resistivity for several values of $U$ in Figs. 2 (a)-(d). We observe the successive phase transitions at $T_{c1}$ and $T_{c2}$ which increase with $U$. Below $T_{c1}$, the sublattice magnetization $(n_{↑} - n_{↓})/2$ becomes finite and the AFM is realized as shown in Fig. 2 (a). Below $T_{c2}(< T_{c1})$, the orbital order $n_{zz} - n_{xx}$ and the induced tiny charge order $\eta$ become finite and the coexistence state of AFM+CO+OO is realized as shown in Figs. 2 (b) and (c). The sublattice magnetization is enhanced due to the effect of the orbital order below $T_{c1}$, while it rapidly increases with decreasing $T$ resulting the insulating grand state as shown in Fig. 2 (d). On the other hand, in the cases with small $U = 1.5$ eV, the resistivity shows kinks at both $T_{c1}$ and $T_{c2}$ resulting the metallic grand state. We note that, for larger value of $U > 1.8$ eV, $T_{c1}$ merges with $T_{c2}$ and the direct transition from the paramagnetic state (PM) to the coexistence state of AFM+CO+OO is observed.

4. Summary
In summary, we investigated the electronic states of the CoO$_2$ plane in the layered cobalt oxides Na$_{0.5}$CoO$_2$ by using the 11 band $d$-$p$ model on the two dimensional triangular lattice within the Hartree-Fock approximation. What we have found are; (1) The system shows the successive phase transitions where the AFM state is realized below $T_{c1}$ and the coexistence state of AFM+CO+OO is realized below $T_{c2}$ ($< T_{c1}$). (2) The effect of the one dimensional potential due to the Na order is crucial for the successive phase transitions. (3) The resistivity shows a small anomaly at $T_{c1}$, while it rapidly increases with decreasing $T$ resulting the insulating grand state for large $U$. (4) In the coexistence state of AFM+CO+OO, the charge order is induced by the orbital order and is extremely small.

The obtained results are qualitatively consistent with the experimental results for the successive phase transitions in Na$_{0.5}$CoO$_2$. The effect of the strong correlation, which was neglected in the Hartree-Fock approximation, is considered to be important for quantitative discussions. Such calculations are now under way.

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