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 $T_{c2} < T < T_{c1}$ and the coexistent state of the antiferromagnetic, orbital and charge orders takes place for $T < T_{c2}$ 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 χ shows kinks at T_{c1} and T_{c2}. The resistivity ρ 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 $\mathrm{CoO_2}$ plane in the layered cobalt oxides $\mathrm{Na}_x\mathrm{CoO_2}$, 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:

$$\begin{aligned}H =& \sum_{\mathbf{n},m,\sigma} \varepsilon^d_{\mathbf{n}m} d^\dagger_{\mathbf{n}m\sigma} d_{\mathbf{n}m\sigma} + \sum_{\mathbf{k},m,m',\sigma} t^{dd}_{\mathbf{k}mm'} d^\dagger_{\mathbf{k}m\sigma} d_{\mathbf{k}m'\sigma} \\ &+ \varepsilon_p \sum_{\mathbf{k},j,l,\sigma} p^\dagger_{\mathbf{k}jl\sigma} p_{\mathbf{k}jl\sigma} + \sum_{\mathbf{k},j,j',l,l',\sigma} t^{pp}_{\mathbf{k}jj'll'} p^\dagger_{\mathbf{k}jl\sigma} p_{\mathbf{k}j'l'\sigma} + \sum_{\mathbf{k},j,l,m,\sigma} (t^{pd}_{\mathbf{k}jlm} p^\dagger_{\mathbf{k}jl\sigma} d_{\mathbf{k}m\sigma} + \mathrm{h.c.}) \\ &+ U \sum_{\mathbf{n},m} \hat{n}^d_{\mathbf{n}m\uparrow} \hat{n}^d_{\mathbf{n}m\downarrow} + U' \sum_{\mathbf{n},m>m'} \hat{n}^d_{\mathbf{n}m} \hat{n}^d_{\mathbf{n}m'} \\ &+ J \sum_{\mathbf{n},m>m',\sigma,\sigma'} d^\dagger_{\mathbf{n}m\sigma} d^\dagger_{\mathbf{n}m'\sigma'} d_{\mathbf{n}m\sigma'} d_{\mathbf{n}m'\sigma} + J' \sum_{\mathbf{n},m>m',\sigma} d^\dagger_{\mathbf{n}m\sigma} d^\dagger_{\mathbf{n}m-\sigma} d_{\mathbf{n}m'-\sigma} d_{\mathbf{n}m'\sigma}, \end{aligned} \tag{1}$$

where $d^\dagger_{\mathbf{k}m\sigma}$ ($d^\dagger_{\mathbf{n}m\sigma}$) is a creation operator for a Co $3d$ electron with wave vector $\mathbf{k} = (k_x, k_y)$ (site $\mathbf{n} = (n_x, n_y)$), orbital $m(= 3z^2 - r^2, x^2 - y^2, xy, yz, zx)$ and spin $\sigma(=\uparrow, \downarrow)$, and $p^\dagger_{\mathbf{k}jl\sigma}$ is a creation operator for a oxygen $2p$ electron with wave vector $\mathbf{k}$, site $j(= 1, 2)$, orbital $l(= x, y, z)$ and spin σ, respectively; $\hat{n}^d_{\mathbf{n}m\sigma} = d^\dagger_{\mathbf{n}m\sigma} d_{\mathbf{n}m\sigma}$ and $\hat{n}^d_{\mathbf{n}m} = \sum_\sigma \hat{n}^d_{\mathbf{n}m\sigma}$. The transfer integrals $t^{pp}_{\mathbf{k},j,j',l,l'}$, $t^{pd}_{\mathbf{k},j,l,m}$ and $t^{dd}_{\mathbf{k},m,m'}$, which are written by the Slater-Koster parameters, together with the atomic energies ε_p and ε^d_m are determined so as to fit the tight-binding energy bands to the LDA bands for $\mathrm{Na_{0.5}CoO_2}$ [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 on X-direction below room temperature, by taking into account an effective one dimensional potential on the $\mathrm{CoO_2}$ plane [6, 7] :

$$\varepsilon^d_{\mathbf{n},m} = \begin{cases} \varepsilon^d_m - \Delta\varepsilon_d & \begin{array}{c}\text{for odd } n_y \\ \text{(on Na ordered lines)}\end{array} \\ \varepsilon^d_m + \Delta\varepsilon_d & \begin{array}{c}\text{for even } n_y \\ \text{(out of Na ordered lines)}\end{array} \end{cases} \tag{2}$$

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 σ. We note that the charge order in X-direction is different from the charge order of $\mathrm{Co}^{3.5+\delta}$ and $\mathrm{Co}^{3.5-\delta}$ in Y-direction due to the effect of the one dimensional Na order.

Figure 1 shows the sublattice magnetization $(n_\uparrow - n_\downarrow)/2$, the orbital order $n_{yz} - n_{zx}$, the charge order η, the density of states at the Fermi level D_F and the resistivity ρ as functions of U at

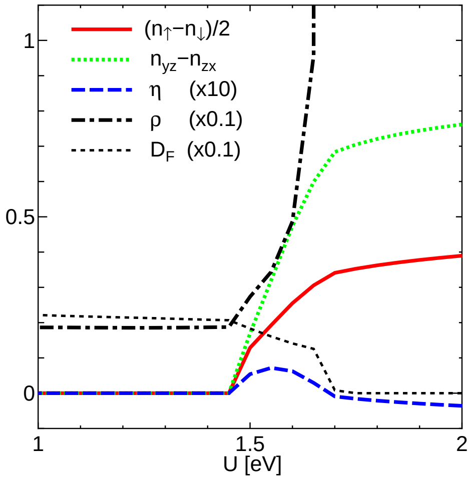

Figure 1. The sublattice magnetization $(n_\uparrow - n_\downarrow)/2$, the orbital order $n_{yz} - n_{zx}$, the charge order η, the resistivity ρ and the density of states at the Fermi level D_F as functions of U for $\Delta\varepsilon_d = 1.0$ eV at $T = 20$ K.

$T = 20$ 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 $(n_\uparrow - n_\downarrow)/2$ 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 ρ 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 η is induced by the orbital order although the amount of η is vary small or zero as shown in Fig. 1.

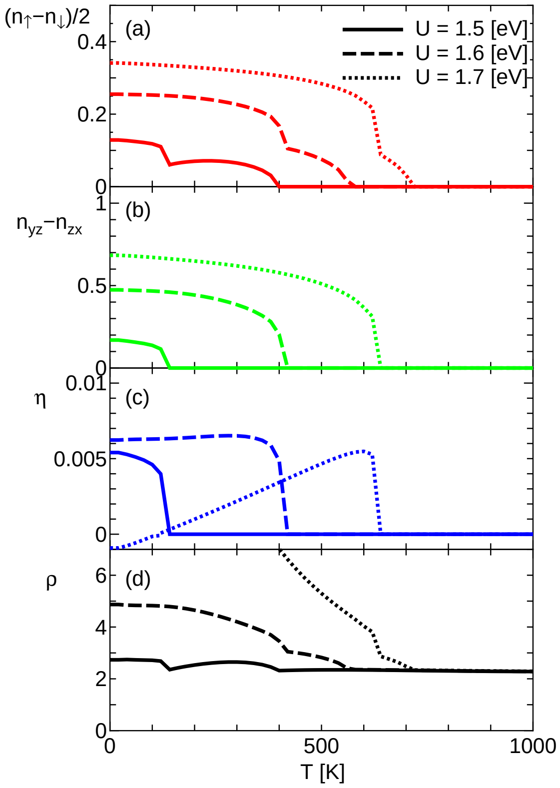

Figure 2. The temperature dependence of the sublattice magnetization $(n_\uparrow - n_\downarrow)/2$ (a), the orbital order $n_{yz} - n_{zx}$ (b), the charge order η (c) and the resistivity ρ (d) for $\Delta\varepsilon_d = 1.0$ eV at $U = 1.5$ eV (solid lines), $U = 1.6$ eV (dotted lines) and $U = 1.7$ 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 $(n_\uparrow - n_\downarrow)/2$ becomes finite and the AFM is realized as shown in Fig. 2 (a). Below $T_{c2}(< T_{c1})$, the orbital order $n_{yz} - n_{zx}$ and the induced tiny charge order η 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_{c2} as shown in Fig. 2 (a). In the case with large $U = 1.7$ eV, the resistivity ρ shows a small anomaly at 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 $U = 1.5$ and 1.6 eV, ρ 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 the way.

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