Effects of ferromagnetic fluctuations on the electric and thermal transport properties in Na_xCoO_2

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Abstract. We investigate the electronic states and the transport properties of the CoO_2 plane in Na_xCoO_2 on the basis of the two-dimensional triangular lattice 11-band d-p model by using the fluctuation exchange approximation, where we consider the Coulomb interaction between the t_{2g} electrons on a Co site. It is found that all of the effective mass of quasiparticles, the resistivity, the thermoelectric power and the uniform spin susceptibility increase with increasing x for $x > 0.6$. This implies that the ferromagnetic fluctuations play significant roles on determining the electronic states. These results are qualitatively consistent with the experiments.

1. Introduction

The layered cobalt oxide Na_xCoO_2 has been intensively investigated as a promising thermoelectric material due to the large thermoelectric power (TEP) together with the low resistivity for $x > 0.7$[1]. In addition to the large TEP, this compound shows rich physical properties. For $x \geq 0.75$, a weak magnetic order appear below $T_m = 22$K[2], where the ferromagnetic ordered CoO_2 planes couple antiferromagnetically with each other. For $0.6 < x < 0.75$, the anomalous metallic behavior is observed, where the temperature dependence of the uniform spin susceptibility is Curie-Weiss-like[3, 4] and the thermoelectric power S, the resistivity ρ and the electronic specific coefficient γ increase with increasing x towards the magnetic ordered region[3, 5].

Some theoretical studies on Na_xCoO_2 in Na-rich region have been performed. For example, Koshibae *et al.* studied the TEP in the atomic limit by using the Heikes formula focusing on the large spin-orbital degeneracy of Co^{3+} and Co^{4+}[6]. Effects of the band structure, however, are not considered there. Kuroki *et al.* investigated the transport properties based on the single band Hubbard model and found that the peculiar shape of the band structure called "pudding mold" plays important roles on the TEP together with the low resistivity. Effects of the electron correlation, however, are not explicitly taken into account[7]. Therefore, the microscopic theory including both effects of the band structure and the electron correlation is highly desired.

In the present study, we investigate the electronic states and the transport properties of the CoO_2 plane in Na_xCoO_2 by using the multi-orbital formula of the fluctuation exchange (FLEX) approximation[8, 9] on the basis of the two-dimensional triangular lattice 11-band d-p model[9, 10, 11, 12].

2. Model and Formulation

Our model includes $3d$ orbitals $(d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx})$ of Co atoms on the two-dimensional triangular lattice and $2p$ orbitals (p_x, p_y, p_z) of O atoms which lie on the upper and the lower plane of the Co plane, and is given by the following Hamiltonian

$$
\begin{aligned}
H = & \sum_{i,\ell,\sigma} \varepsilon^d_{\ell\ell'} d^\dagger_{i\ell\sigma} d_{i\ell\sigma} + \sum_{i,m,\sigma} \varepsilon^p_m p^\dagger_{im\sigma} p_{im\sigma} + \sum_{i,j,\ell,\ell',\sigma} t^{dd}_{i,j,\ell,\ell'} d^\dagger_{i\ell\sigma} d_{j\ell'\sigma} \\
& + \sum_{i,j,m,m',\sigma} t^{pp}_{i,j,m,m'} p^\dagger_{im\sigma} p_{jm'\sigma} + \sum_{i,j,\ell,m,\sigma} t^{dp}_{i,j,\ell,m} d^\dagger_{i\ell\sigma} p_{jm\sigma} + h.c. \\
& + H_{\text{int}},
\end{aligned}
\tag{1}
$$

where $d_{i\ell\sigma}$ is the annihilation operator for a Co-$3d$ electron with spin σ in the orbital ℓ at site i and $p_{im\sigma}$ is the annihilation operator for a O-$2p$ electron with spin σ in the orbital m at site i. In eq. (1), the transfer integrals $t^{dd}_{i,j,\ell,\ell'}$, $t^{pp}_{i,j,m,m'}$, $t^{dp}_{i,j,\ell,m}$ and the atomic energies $\varepsilon^d_{\ell\ell'}$, ε^p_m are determined so as to fit the energy bands obtained from the tight-binding approximation to those from the band calculation[13] and are listed in ref. 9. The band calculation predicted that the large hole Fermi surface around the Γ-point and the six small hole pockets near the K-points[13]. However, the six small hole pockets have not been observed in the ARPES measurments[14]. Thus, we introduce the change of the crystal field energy $\sum_{i,\ell\neq\ell'\in t_{2g},\sigma} V'_t d^\dagger_{i\ell\sigma} d_{i\ell'\sigma}$ and then set $V'_t = 0.15\text{eV}$ to sink those below the Fermi level in the present study[9]. H_{int} is the Coulomb interaction Hamiltonian for the t_{2g} orbitals of Co atoms and characterized by the parameters: the intra(inter)-orbital direct terms $U(U')$, the Hund's rule coupling J and the pair transfer J'[9].

In the FLEX approximation, the spin (charge-orbital) susceptiblity $\hat{\chi}^s(q)$ ($\hat{\chi}^c(q)$) is given as follows

$$
\hat{\chi}^s(q) = (\hat{1} - \hat{\chi}^{(0)}(q)\hat{S})^{-1}\hat{\chi}^{(0)}(q), \quad \hat{\chi}^c(q) = (\hat{1} + \hat{\chi}^{(0)}(q)\hat{C})^{-1}\hat{\chi}^{(0)}(q),
\tag{2}
$$

where $q = (\mathbf{q}, i\omega_m = i2m\pi T)$. In the above, $\hat{\chi}^{(0)}(q)$ and $\hat{S}(\hat{C})$ are the matrices whose components are given by

$$
\chi^{(0)}_{\ell_1\ell_2,\ell_3\ell_4}(q) = -\frac{T}{N} \sum_k G_{\ell_3\ell_1}(k) G_{\ell_2\ell_4}(k+q),
\tag{3}
$$

$$
S_{\ell_1\ell_2,\ell_3\ell_4}\ (C_{\ell_1\ell_2,\ell_3\ell_4}) = \begin{cases} U\ (U) & (\ell_1 = \ell_2 = \ell_3 = \ell_4) \\ U'\ (-U' + 2J) & (\ell_1 = \ell_3 \neq \ell_2 = \ell_4) \\ J\ (2U' - J) & (\ell_1 = \ell_2 \neq \ell_3 = \ell_4) \\ J'\ (J') & (\ell_1 = \ell_4 \neq \ell_2 = \ell_3) \\ 0 & (\text{otherwise}) \end{cases},
\tag{4}
$$

where $k = (\mathbf{k}, i\varepsilon_n = i(2n+1)\pi T)$, $\hat{G}(k) = (\{\hat{G}^{(0)}(k)\}^{-1} - \hat{\Sigma}(k))^{-1}$ and $\hat{G}^{(0)}(k)$ is the noninteracting Green's function. The self-energy $\hat{\Sigma}(k)$ is given by

$$
\Sigma_{\ell\ell'}(q) = \frac{T}{N} \sum_{q,\ell_1,\ell_2} G_{\ell_1\ell_2}(k-q) V^{\text{eff}}_{\ell_1\ell,\ell_2\ell'}(q),
\tag{5}
$$

where the effective interaction is $\hat{V}^{\text{eff}}(q) = \frac{3}{2}\hat{V}^s(q) + \frac{1}{2}\hat{V}^c(q)$ with $\hat{V}^s(q) = \hat{S}\hat{\chi}^s(q)\hat{S} - \frac{1}{2}\hat{S}\hat{\chi}^{(0)}(q)\hat{S}$ and $\hat{V}^c(q) = \hat{C}\hat{\chi}^c(q)\hat{C} - \frac{1}{2}\hat{C}\hat{\chi}^{(0)}(q)\hat{C}$. We solve the above equations (2)-(5) self-consistently to obtain $\hat{G}(k)$, $\hat{\chi}^s(q)$ and $\hat{\chi}^c(q)$, and then calculate ρ and S based on the linear responce theory, where we neglect the vertex corrections. For simplicity, we assume $U' = U - 2J$, $J = J'$ and set $U = 1.5\text{eV}$, $J = 0.15\text{eV}$ in the present study. In the numerical calculation, we use the 64×64 $\mathbf{k}$-points and 256 Matsubara frequencies.
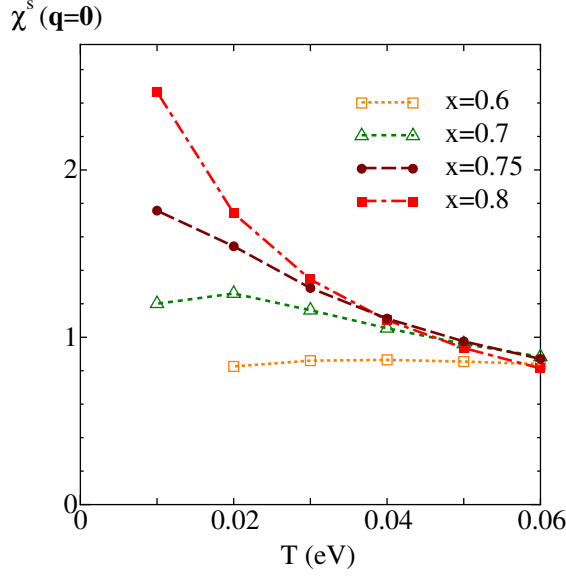
Figure 1. Temperature dependence of the uniform spin susceptibility χ^s.
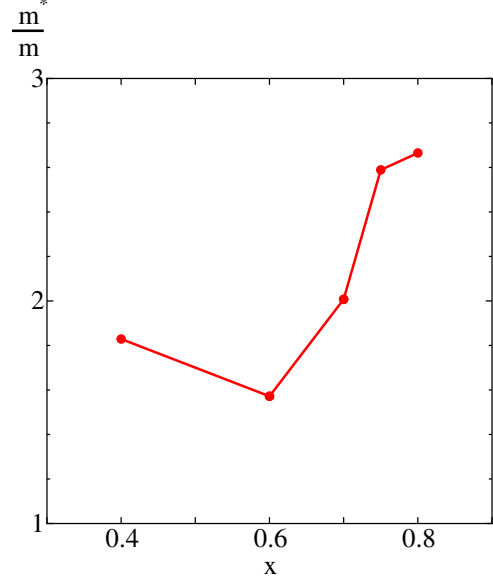
**Figure 2.** Doping dependence of the effective mass of quasiparticles m^*/m

3. Results

We show the temperature dependence of the uniform spin susceptibility $\chi^s = \sum_{\ell\ell'} \chi^s_{\ell\ell,\ell'\ell'}(\mathbf{q} = \mathbf{0}, i\omega_m = 0)$ in Figure 1. For $x \geq 0.75$, χ^s shows the Curie-Weiss-like behavior, while for $x \leq 0.7$, it shows the weak pseudogap like behavior at low temperatures. At the low temperature, χ^s increases with the doping x due to the effect of the flat dispersion near the Γ-point ($\mathbf{k}$=(0,0)) which approaches the Fermi level with increasing x.

Figure 2 shows the doping dependence of the effective mass of quasiparticles, $m^*/m = z_{k_F}^{-1} = 1 - \frac{\partial \mathrm{Re}\Sigma^{\mathrm{R}}_\alpha(k_F,\varepsilon)}{\partial \varepsilon}\Big|_{\varepsilon=0}$, where $\Sigma^{\mathrm{R}}_\alpha(\mathbf{k},\varepsilon)$ is the retarded self-energy in the band basis which is obtained by the unitary transformation and the numerical analytic continuation of $\Sigma_{\ell\ell'}(\mathbf{k}, i\varepsilon_n)$ from the upper half plane to the real axis with use of the Padé approximation. In the present paper, all of the numerical calculations are performed for $T \geq 0.01$eV. Then, we obtaine the extrapolated value of z_{k_F} at $T = 0$eV from the data at $T = 0.01 - 0.06$eV by using the third order polynomial fit. For $x \geq 0.6$, m^*/m increases with increasing x, as observed in experiments[3]. The increase in m^*/m with the doping x is considered due to the effect of the ferromagnetic fluctuations as shown in χ^s at the low temperature.

Finally, we turn to the transport properties. Figure 3. (a) shows the temperature dependence of ρ. We find that ρ increases with increasing x, and shows concave downward temperature dependence for $x \geq 0.7$. Figure 3. (b) shows the temperature dependence of S. S is always positive and increases with increasing x. The increases in both ρ and S with the doping x are qualitatively consistent with experiments[5].

4. Summary and Discussion

We have investigated the electronic states and the transport properties of the CoO_2 plane in $Na_x CoO_2$ on the basis of the two-dimensional triangular lattice 11-band d-p model by using the FLEX approximation. It is found that the temperature dependence of χ^s shows the Curie-Weiss-like behavior for $x \geq 0.75$ and m^*/m, ρ, S and χ^s increase with increasing x for $x \geq 0.6$. This implies that the ferromagnetic fluctuations play significant roles on determining the electronic
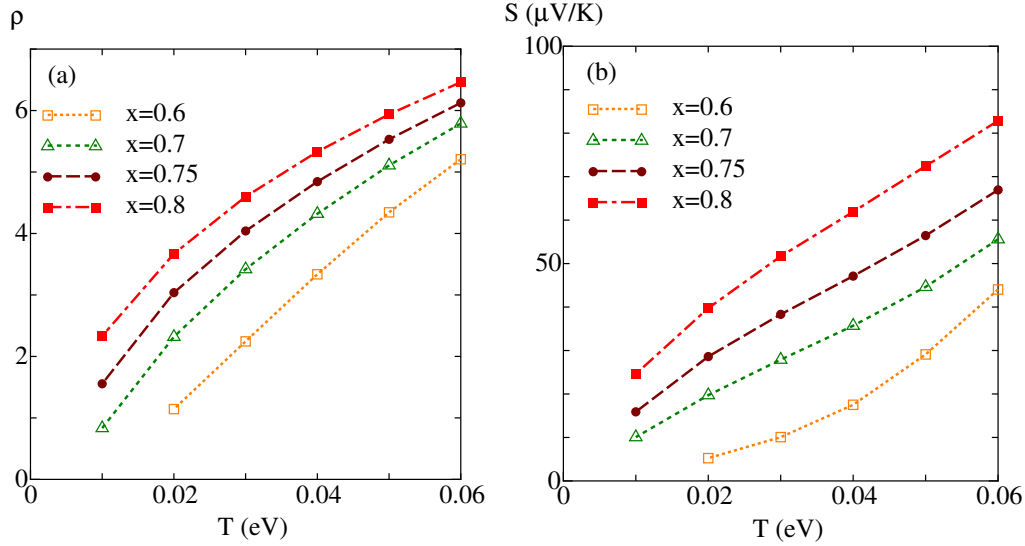
Figure 3. Temperature dependence of (a) the resistivity ρ and (b) the thermoelectric power S.

states. These results are qualitatively consistent with experimental results[3, 4, 5].

However, we cannot reproduce the hump of the temperature dependence of S at $T \sim 50 - 150K$[5] and the absolute value of S obtained by our numerical calculation is less than a half of that observed in experiments[1, 5]. This seems to be due to the underestimate of the ferromagnetic fluctuations. The FLEX approximation does not include the mode-mode coupling effect due to the vertex correction which can be important in the nearly ferromagnetic metals and as a result, underestimate the ferromagnetic fluctuations[15]. The self-consistent renormalization theory[15] may improve our results.

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