Effects of ferromagnetic fluctuations on the electric and thermal transport properties in Na$_x$CoO$_2$

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Abstract. We investigate 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 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$_x$CoO$_2$ 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 $\rho$ and the electronic specific coefficient $\gamma$ increase with increasing $x$ towards the magnetic ordered region[3, 5].

Some theoretical studies on Na$_x$CoO$_2$ 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$_x$CoO$_2$ 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 \((d_{z^2-r^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{xz})\) 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

\[
H = \sum_{i,\ell,\sigma} \varepsilon_{d\ell} d_{i\ell\sigma}^\dagger d_{i\ell\sigma} + \sum_{i,m,\sigma} \varepsilon_{p\sigma} p_{i\sigma}^\dagger p_{i\sigma} + \sum_{i,j,\ell,\ell',\sigma} t_{d\ell,j\ell'}^d d_{i\ell\sigma}^\dagger d_{j\ell'\sigma} + \sum_{i,j,m,\sigma} t_{p\sigma}^{p\ell} d_{i\ell\sigma}^\dagger p_{j\sigma} + h.c. + H_{\text{int}},
\]

where \(d_{i\ell\sigma}\) is the annihilation operator for a Co-3d electron with spin \(\sigma\) in the orbital \(\ell\) at site \(i\) and \(p_{i\sigma}\) is the annihilation operator for a O-2p electron with spin \(\sigma\) in the orbital \(m\) at site \(i\). In Eq. (1), the transfer integrals \(t_{d\ell,j\ell'}^d\), \(t_{p\sigma}^{p\ell}\), and the atomic energies \(\varepsilon_{d\ell}\), \(\varepsilon_{p\sigma}\) 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 the large hole Fermi surface around the \(\Gamma\)-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 measurements[14]. Thus, we introduce the change in the crystal field energy \(\sum_{i,\ell,\ell'\neq\ell,\sigma} V'_{\ell,\ell'} \delta d_{i\ell\sigma}^\dagger d_{i\ell'\sigma}\) and then set \(V' = 0.15 eV\) to sink those below the Fermi level in the present study[9]. \(H_{\text{int}}\) is the Hamiltonian of the Coulomb interaction between the \(2p\) electrons on the Co atom and characterized by the following 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) susceptibility \(\hat{\chi}^s(q)\) (\(\hat{\chi}^c(q)\)) is given as follows

\[
\hat{\chi}^s(q) = \hat{\chi}^{(0)}(q)\hat{S}^{-1}(q), \quad \hat{\chi}^c(q) = \hat{\chi}^{(0)}(q)\hat{C}^{-1}(q),
\]

where \(\hat{\chi}^{(0)}(q)\) and \(\hat{S}(\hat{C})\) are the matrices whose components are given by

\[
\chi_{\ell_1\ell_2\ell_3\ell_4}^{(0)}(q) = -\frac{T}{N} \sum_{k} G_{\ell_1\ell_4}(k) G_{\ell_2\ell_3}(k+q),
\]

\[
S_{\ell_1\ell_2\ell_3\ell_4}^{(C)}(q) = \begin{cases} \frac{U}{2} (\ell_1 = \ell_2 = \ell_3 = \ell_4) \\ \frac{U'}{2} (\ell_1 \neq \ell_2 = \ell_3 = \ell_4) \\ \frac{J}{2} (\ell_1 \neq \ell_2 \neq \ell_3 = \ell_4) \\ 0 \\ \frac{J'}{2} (\ell_1 \neq \ell_2 \neq \ell_3 \neq \ell_4) \\ \frac{J'}{2} (\ell_1 \neq \ell_2 \neq \ell_3 \neq \ell_4) \end{cases},
\]

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

\[
\Sigma_{\ell\ell'}(q) = \frac{T}{N} \sum_{k} G_{\ell_1\ell_2}(k-q) V_{\ell_1\ell_2\ell_3\ell_4}^{\text{eff}}(q),
\]

where the effective interaction is \(V_{\ell\ell'}^{\text{eff}}(q) = \frac{\sqrt{2}}{2} \hat{V}_s(q) + \frac{\sqrt{2}}{2} \hat{V}_c(q)\) with \(\hat{V}_s(q) = \hat{\chi}^s(q)\hat{S} - \frac{1}{2} \hat{\chi}^{(0)}(q)\hat{S}\) and \(\hat{V}_c(q) = \hat{\chi}^c(q)\hat{C} - \frac{1}{2} \hat{\chi}^{(0)}(q)\hat{C}\). 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 \(\rho\) and \(S\) based on the linear response theory,

\[
\sigma = \frac{1}{N} \sum_{k} \int_{-\infty}^{\infty} \frac{d\varepsilon}{\pi} \text{Tr} \{ \text{Im}(\tilde{\varepsilon}_{\ell}^{(0)}(k)) \hat{G}(k, \varepsilon + i\delta) \tilde{\varepsilon}_{\ell}^{(0)}(k) \hat{G}(k, \varepsilon - i\delta) \},
\]

\[
S = -\frac{1}{NT\sigma} \sum_{k} \int_{-\infty}^{\infty} \frac{d\varepsilon}{\pi} \text{Tr} \{ \text{Im}(\varepsilon \tilde{\varepsilon}_{\ell}^{(0)}(k)) \hat{G}(k, \varepsilon + i\delta) \tilde{\varepsilon}_{\ell}^{(0)}(k) \hat{G}(k, \varepsilon - i\delta) \},
\]
where we neglect the vertex corrections and \( \hat{w}_z^{(0)}(k) \) is the bare velocity. 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 \( k \)-points and 256 Matsubara frequencies.

3. Results

We show the temperature dependence of the uniform spin susceptibility \( \chi^s = \sum_{ll'} \chi_{ll',ll'}^s(q=0, i\omega_m = 0) \) in Figure 1. For \( x \geq 0.75 \), \( \chi^s \) 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, \( \chi^s \) increases with the doping \( x \) due to the effect of the flat dispersion near the \( \Gamma \)-point \( (k=(0,0)) \) which approaches the Fermi level with increasing \( x \).

Figure 2 shows the doping dependence of the effective mass of quasiparticles, \( m^*/m = z_{k_F}^{-1} = 1 - \left. \frac{\partial \text{Re} \Sigma_R(k, \epsilon)}{\partial \epsilon} \right|_{\epsilon = 0} \), where \( \Sigma_R(k, \epsilon) \) is the retarded self-energy in the band basis which is obtained by the unitary transformation and the numerical analytic continuation of \( \Sigma_{l'l'}(k, i\varepsilon_n) \) 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 \( T \geq 0.01\text{eV} \). Then, we obtain the extrapolated value of \( z_{k_F} \) at \( T = 0\text{eV} \) from the data at \( T = 0.01 - 0.06\text{eV} \) 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 \( \chi^s \) at the low temperature.

Finally, we turn to the transport properties. Figure 3. (a) shows the temperature dependence of \( \rho \). We find that \( \rho \) 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 \( \rho \) 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 has been found that the temperature dependence of $\chi^s$ shows the Curie-Weiss-like behavior for $x \geq 0.75$ and $m^s/m$, $\rho$, $S$ and $\chi^s$ increase with increasing $x$ for $x \geq 0.6$ due to the effects of the ferromagnetic fluctuations. These results are qualitatively consistent with experimental results[3, 4, 5].

However, we failed to reproduce the hump in the temperature dependence of $S$ experimentally observed at $T \sim 50 - 150$K[5]. In addition, the absolute value of $S$ obtained from our calculation is less than a half of that from experiments[1, 5]. These results seem to be caused by underestimation of the ferromagnetic fluctuations in the FLEX approximation. The effects of the mode-mode coupling due to the vertex corrections, which are considered to play crucial roles for the nearly ferromagnetic metals as shown in the self-consistent renormalization theory[15], are neglected in the FLEX approximation and will be discussed in the subsequent paper.

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