Origin of the Weak Pseudo-gap Behaviors in Na$_{0.35}$CoO$_2$:
Absence of Small Hole Pockets

Keiji YADA and Hiroshi KONTANI
Department of Physics, Nagoya University, Furo-cho, Nagoya 464-8602, Japan.
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We analyze the normal electronic states of Na$_{0.35}$CoO$_2$ based on the effective d-p model with full d-orbital freedom using the fluctuation-exchange (FLEX) approximation. They sensitively depend on the topology of the Fermi surfaces, which changes as the crystalline electric splitting (CES) due to the trigonal deformation. We succeed in reproducing the weak pseudo-gap behaviors in the density of states (DOS) and in the uniform magnetic susceptibility below 300K, assuming that six small hole-pockets predicted by LDA band calculations are absent. When they exist, on the contrary, then “anti-pseudo-gap behaviors” should inevitably appear. Thus, the present study strongly supports the absence of six small hole-pockets in Na$_{0.35}$CoO$_2$, as reported by recent ARPES measurements. A large Fermi surface around the Γ-point would account for the superconductivity in water-intercalated samples.

Na$_{0.35}$CoO$_2$·1.3H$_2$O is the first Co-oxide superconductor ($T_c \approx 4.7$K) with a triangular lattice structure [1]. Below $T_c$, the coherent peak in 1/$T_1$T by NMR/NQR is absent (or very tiny even if it exists) [2, 3, 4], and the Knight shift is finite both for $\mathbf{H} \perp \mathbf{c}$ [5] and $\mathbf{H} \parallel \mathbf{c}$ [6]. Moreover, the specific heat data below $T_c$ cannot be explained by an isotropic s-wave BCS theory; one should assume an anisotropic s-wave gap or a gap with line-nodes to fit the observed data, depending on samples [6]. These experiments suggest that the superconductivity (SC) in Na$_{0.35}$CoO$_2$·1.3H$_2$O is not an isotropic s-wave superconductor.

Precise knowledge about the shape of the Fermi surfaces (FS’s) is indispensable in analyzing the origin of the unconventional SC. As for Na$_{0.35}$CoO$_2$, however, even the topology of FS’s is still uncertain unfortunately. The LDA band calculation performed by Singh predicted that a large hole-like FS composed of $a_{1g}$-orbital around Γ-point, surrounded by six small hole-pockets composed of $e'_g$-orbitals [7]. The latter give major contribution to the density of states (DOS) at the Fermi level. The crystalline electric splitting (CES) of Co 3d-orbitals is shown in Fig. 1. Based on the Singh’s FS’s, various theoretical groups have predicted unconventional SC’s due to the Coulomb interaction by using the RPA [8, 9], the perturbation theory [10, 11], and the fluctuation-exchange (FLEX) approximation [12, 13]. When the d-orbital freedom is taken into account, d-wave SC due to antiferromagnetic (AF) fluctuations are dominant when the exchange coupling $J$ is relatively small [8], whereas $f$(p)-wave SC due to ferromagnetic (FM) fluctuations mediated by small hole-pockets occurs for larger $J$ [11, 12, 14]. However, only a large $a_{1g}$-like FS is observed by ARPES measurements by several groups [13, 15]. Therefore, we have to solve this conflict on the FS’s before studying the mechanism of the SC.

We stress that the electronic properties in the normal states should be analyzed in detail before discussing the mechanism of the SC. In the normal state of Na$_{0.35}$CoO$_2$·1.3H$_2$O, the Knight shift [16], the uniform magnetic susceptibility ($\chi$) [17] and the DOS measured by PES [18] moderately decrease below 300K. This “weak pseudo-gap behaviors”, which is also observed in high-$T_c$ cuprates below $T_\omega \approx 700$K and above the strong pseudo-gap temperature $T^* \approx 200$K [19, 20], suggest the occurrence of strong AF-fluctuations [20].

In the present work, we study the normal electronic states of Na$_{0.35}$CoO$_2$ to find out the topology of the FS. Based on the FLEX approximation, the appropriate weak pseudo-gap behaviors are well reproduced under the condition that (i) six small hole-pockets composed of $e'_g$-orbitals should be absent, and (ii) the exchange coupling $J$ should be about one order smaller than $U$. To obtain an appropriate magnitude of the pseudo-gap, the top of six small hole-pockets, $E_{top}$, should be just below the chemical potential ($\sim -0.1$eV) which is consistent with ARPES measurements in Na$_{0.35}$CoO$_2$ [14, 15]. The pseudo-gap in DOS becomes larger in water-intercalated samples [15], which would be understood if $E_{top}$ is raised slightly (but still $E_{top} < \mu$), result of the trigonal deformation of CoO$_6$-octahedron by water-intercalation.

The FLEX approximation is a self-consistent spin-fluctuation theory [21]. It can reproduce various non-

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FIG. 1: CES between $a_{1g}$ and $e'_g$ is caused by the trigonal deformation of CoO$_6$-octahedron. $V''$ is introduced additionally in the present study.
Fermi-liquid like behaviors in high-$T_c$ cuprates above $T^*$ [24]. For example, weak pseudo-gap behaviors below $T_0$ in the DOS, $\chi^e$ and the specific heat are well reproduced, are caused by the strong AF-fluctuations. Here, we analyze the role of the spin fluctuations on the electronic states of Na$_2$CoO$_2$, using the FLEX approximation. We note that the FLEX approximation for systems with orbital degree of freedom is so complicated that only a few works have been performed previously [12, 13].

Here we explain in detail the $d$-$p$ model Hamiltonian and the formalism of the FLEX approximation with orbital degree of freedom. The unit of energy is eV hereafter. The kinetic term of the Hamiltonian is

$$H_0 = \sum_{i,j,\sigma} \sum_{i'j',\sigma'} t_{ij}^{\sigma\sigma'} c_{i\sigma}^\dagger c_{j'\sigma'}$$

where

$$c_{ij} = \begin{cases}
  d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2} : \text{Co} \\
  P_{1x}, P_{1y}, P_{1z} : \text{O}(1) \\
  P_{2x}, P_{2y}, P_{2z} : \text{O}(2)
\end{cases}$$

Here, $t_{ij}^{\sigma\sigma'}$ in eq. (1) is given by the following Slater-Koster parameters: $(pd\overline{p}) = 0.78$, $(pd\overline{s}) = -1.7$, $(pp\overline{p}) = 0.18$ and $(pp\overline{s}) = -0.48$ for nearest-neighbor transfers, $(pp\overline{p})_2 = 0.11$ and $(pp\overline{s})_2 = -0.26$ for next-nearest ones. $10Dq = 1.1$ is the CES between $t_{2g}$ and $e_g$, and $\Delta = 1.8$ is the $d$-$p$ charge transfer energy. Reflecting the trigonal deformation, furthermore, $3V = -0.18$ is the CES between $a_{1g}$ and $e_g$, $c_t = 1.3$ is the ratio of the inter-layer $pp$ transfer to the intra-layer one, and $(pd)_t = 0.31$ is the $pd$ transfer emerged by the deviation of O-Co-O angle from $\pi$. They are determined by fitting the Singh's LDA-band structure [3].

Here we introduce $V_i'$ to express the change of the CES. The FS's given by the FLEX approximation are shown in Figs. 2, where the density of hole is fixed at 0.65. $V_i' = 0$ corresponds to the original Singh's FS's. The shape of FS's is sensitive to $V_i'$. The small hole-pockets disappear when $V_i' \geq 0.1$, whose band-structure is similar to the experimental results by ARPES measurements [14, 15]. We find that the deformation of the FS's due to the interaction is tiny in the present model, which is consistent with the analysis by the Gutzwiller approximation [23].

In addition to $H_0$, we treat the on-site correlation in $t_{2g}$-orbitals, which is expressed in a symmetric form as

$$H' = \frac{1}{4} \sum_{\ell} \sum_{\ell'} \sum_{\sigma} \sum_{\sigma'} \Gamma_{\ell\ell',\sigma\sigma'}^{(0)} c_{\ell\sigma}^\dagger c_{\ell'\sigma'}$$

where $\ell \equiv (l, \sigma)$. $\Gamma^{(0)}$ is given by

$$\Gamma_{\ell\ell',\sigma\sigma'}^{(0)} = -\frac{1}{2} \tilde{S}_{\ell\ell',\sigma\sigma'}^{(0)} + \frac{1}{2} \tilde{C}_{\ell\ell',\sigma\sigma'}^{(0)},$$

where $U \ (U')$ is the intra-orbital (inter-orbital) direct Coulomb interaction, and $J, J'$ represent the exchange interactions. We put $J = J'$ hereafter.

In the FLEX approximation, the spin and charge susceptibility are given by

$$\chi^s(q) = \left(1 - \tilde{S}^{(0)}(q)\right)^{-1} \tilde{\chi}^{(0)}(q),$$

$$\chi^c(q) = \left(1 + \tilde{C}^{(0)}(q)\right)^{-1} \tilde{\chi}^{(0)}(q),$$

where $q = (q, \omega_n = 2\pi T \ell)$. $\tilde{\chi}^{(0)}(q)$ is given by

$$\tilde{\chi}^{(0)}(q) = -\frac{T}{N} \sum_k G_{\ell\ell',k}(k + q)G_{\ell\ell',k}(k),$$

where $k = (k, \epsilon_n = \pi T(2n + 1))$. $\tilde{G}(k) = \left(\tilde{\chi}^{(0)}(k)\right)^{-1}$, and $\tilde{\chi}^{(0)}(k) = (\omega + \mu - 2\tilde{\chi}^{(0)}(q))^{-1}$. The self-energy is given by

$$\Sigma_{\ell\ell',\epsilon}(k) = -\frac{T}{N} \sum_q \sum_{\ell\ell'} G_{\ell\ell',k}(k + q) V_{\ell\ell',\ell\ell',q},$$

where $V_{\ell\ell',\ell\ell',q} = \frac{3}{2} \tilde{V}^s(q) + \frac{1}{2} \tilde{V}^c(q)$;

$$\tilde{V}^s(q) = \tilde{S}^{(0)}(q)\tilde{\chi}^{(0)}(q)\tilde{S}(q) - \frac{1}{2} \tilde{S}^{(0)}(q)\tilde{\chi}^{(0)}(q)\tilde{S}^{(0)}(q),$$

$$\tilde{V}^c(q) = \tilde{C}^{(0)}(q)\tilde{\chi}^{(0)}(q)\tilde{C}(q) - \frac{1}{2} \tilde{C}^{(0)}(q)\tilde{\chi}^{(0)}(q)\tilde{C}^{(0)}(q).$$

We solve eqs. (1) - (7) self-consistently. In the numerical study, we use 4096 $k$-meshes and 256 Matsubara frequencies.
Hereafter, we present the results by the FLEX approximation for 0 ≤ V′ ≤ 0.15. We will see that the appropriate weak pseudo-gap behaviors are reproduced only for V′ ≥ 0.1, where a large single FS around the Γ-point exists. Note that V′ will “decrease” by water-intercalation because trigonal deformation, which raise the ℓ′_g-level, is promoted further [24]. In the present study, we put J/U = 1/3, J = 0.13 (U = U′ + 2J = 1.56), where AF-fluctuations dominate the FM-ones as shown below. We have checked that similar results are obtained if we put J = 0.26. On the other hand, ref. [13] reports that strong FM-fluctuations occur when J/U = 1/5 (i.e., J/U′ = 1/3). These results are consistent with the magnetic phase diagram in the present model obtained by the RPA [8]: U promotes the AF-fluctuations whereas J promotes the FM-ones.

Figure 3 shows the temperature dependences of the DOS, ρ(ω) = \sum_k Tr{ImG_k(ω - iδ)/ω}. ω = 0 corresponds to the chemical potential. First, we discuss the case of V′ ≤ 0.075; then, the DOS without interaction, ρ^0(ω), is very large at ω = 0 due to six small hole-pockets. In the presence of interaction, ρ(0) at higher temperatures is small because huge ImΣ_k(0) by the FLEX approximation smears the steep ω-dependence of ρ^0(ω). As the temperature decreases, the DOS obtained by the FLEX approximation approaches ρ^0(ω) because the quasiparticles become coherent. As a result, ρ(0) increases as the temperature decreases, which may be called the “anti-pseudo-gap behavior”.

In case of V′ ≥ 0.1, on the other hand, ρ^0(0) is small because six small hole-pockets sink below μ. Therefore, ImΣ_k(0) by the FLEX approximation is relatively small. Then, ρ(0) in the presence of interaction slightly decreases as T → 0, reflecting the reduction of the DOS around the “hot-spot” on the FS, where ImΣ_k(0) takes the maximum value due to strong AF-fluctuations. Each hot-spot is connected with others by the nesting vector. We find that the hot-spot lays on the cross-point of a large FS and a Γ-K line for V′ ≥ 0.1. As a result, ρ(0) slightly decreases as the temperature decreases, which we call the “weak pseudo-gap behavior”. We note that the FLEX approximation tends to underestimates the size of the pseudo-gap; the vertex corrections for Σ_k(ω) might recover its correct size [25].

Figure 4 shows the temperature dependences of the spin susceptibility χ^s(q, 0) = Trχ^s(q, 0) for several values of V′. When small hole-pockets exist (V′ ≤ 0.075), both the FM-fluctuations (at q = 0) as well as the AF-fluctuations with q = ΓM = (0, 2π/√3) grow as the temperature decreases. The latter come from the nesting of small hole-pockets between neighboring Brillouin zones, whereas the former is caused by each small hole-pockets. Thus, small hole-pockets govern the magnetic fluctuations when V′ ≤ 0.075. On the other hand, when small hole-pockets are absent (V′ ≥ 0.1), AF-fluctuations with q = ΓK = (4π/3, 0), which come from the nesting of a large FS around the Γ-point, dominate the fluctuations with q = (0, 2π/√3). On the contrary, the uniform sus-
duced that small hole-pockets are absent and $\text{Na}_0$ are almost unchanged by the water-intercalation. /T Knight shift, the specific heat, and $1/T_{\chi}$ slightly decrease below 100K, which suggests the emergence of strong AF-fluctuations \cite{16} as well as the analysis by the Gutzwiller approximation \cite{23}. On the contrary, weak pseudo-gap does not emerge for larger $J$ where FM-fluctuations are dominant, which is inconsistent with experiments. In later works, the mechanism of the SC should be studied based on the model established in the present work, with only a single FS composed of $a_{1g}$-orbital. We will also perform the study below 100K in future.

As a result, experimental weak pseudo-gap behaviors are qualitatively reproduced only when the small hole-pockets are absent ($V'_t \geq 0.1$). Because the pseudo-gap phenomena are caused by strong AF-fluctuations, they cannot be reproduced when $J/U$ is so large that FM-fluctuations dominates. Thus, we conclude that (i) small hole-pockets are absent, and (ii) $J/U \sim O(1/10)$.

Here we discuss the effect of water-intercalation. Experimentally, both for $\text{Na}_{0.35}\text{CoO}_2$ and $\text{Na}_{0.35}\text{CoO}_2\cdot1.3\text{H}_2\text{O}$, the uniform susceptibility \cite{17} as well as the Knight shift \cite{18} slightly decrease below room temperatures, if impurity effect is subtracted. In water-intercalated samples, the size of the pseudo-gap in DOS is larger \cite{18}, and prominent Curie-Weiss behavior of $1/T_{\chi}$ is observed below 100K, which suggests the emergence of strong AF-fluctuations \cite{17}. Comparing these experimental facts with the theoretical results, we infer that $\text{Na}_{0.35}\text{CoO}_2$ and $\text{Na}_{0.35}\text{CoO}_2\cdot1.3\text{H}_2\text{O}$ correspond to $V'_t = 0.15$ and 0.1, respectively. Note that $V'_t$ will be reduced by the water-intercalation, as discussed before. However, small hole-pockets are still absent ($V'_t \geq 0.1$) even in $\text{Na}_{0.35}\text{CoO}_2\cdot1.3\text{H}_2\text{O}$, because Knight shift, the specific heat, and $1/T_{\chi}$ above 100K are almost unchanged by the water-intercalation.

In summary, we analyzed the $d$-$p$ Hubbard model for $\text{Na}_{0.35}\text{CoO}_2$ using the FLEX approximation, and deduced that small hole-pockets are absent: When $J$ is relatively small ($J \sim U/10$), strong AF-fluctuations due to the nesting emerge. Thanks to the AF-fluctuations, experimental weak pseudo-gap behaviors below room temperature are well reproduced, only when top of six small hole-pockets is just below the Fermi level. Then, the obtained mass-enhancement ratio ($\sim 2$) is consistent with the renormalization of bandwidth observed by ARPES \cite{14, 15} as well as the analysis by the Gutzwiller approximation \cite{23}. On the contrary, weak pseudo-gap does not emerge for larger $J$ where FM-fluctuations are dominant, which is inconsistent with experiments. In later works, the mechanism of the SC should be studied based on the model established in the present work, with only a single FS composed of $a_{1g}$-orbital. We will also perform the study below 100K in future.

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FIG. 4: Obtained $\chi^s(q,0)$ for several values of $V'_t$. When $V'_t \leq 0.075$ ($V'_t \geq 0.1$), the uniform susceptibility decreases (increases) as $T \to 0$, and $\chi^s(q,0)$ takes the maximum value at $q = (0, 2\pi/\sqrt{3})$ ($q = (4\pi/3, 0)$).
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