Electronic theory for itinerant in-plane magnetic fluctuations in Na$_x$CoO$_2$

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(Dated: October 31, 2018)

Starting from $ab$-initio band structure for Na$_x$CoO$_2$, we derive the single-electron energies and the effective tight-binding description for the $t_{2g}$ bands using a projection procedure. We find that due to the presence of the next-nearest-neighbor hoppings a local minimum in the electronic dispersion close to the $\Gamma$ point of the first Brillouin zone forms. Therefore, in addition to a large Fermi surface an electron pocket close to the $\Gamma$ point emerges at high doping concentrations. The latter yields the new scattering channel resulting in a peak structure of the itinerant magnetic susceptibility at small momenta. This indicates itinerant in-plane ferromagnetic state above certain critical concentration $x_m$, in agreement with neutron scattering data. Below $x_m$ the magnetic susceptibility shows a tendency towards the antiferromagnetic fluctuations. We estimate the value of $0.56 < x_m < 0.68$ within the rigid band model and within the Hubbard model with infinite on-site Coulomb repulsion consistent with the experimental phase diagram.

PACS numbers: 31.15.Ar; 74.70.-b; 71.10.-w; 75.40.Cx

1. The diverse physical properties of the cobaltate Na$_x$CoO$_2$ attracted much attention after the discovery of the unconventional superconductivity in its hydrated counterpart, Na$_x$CoO$_2$·yH$_2$O [1]. The phase diagram of this compound, with varying electron doping $x$ and water intercalation $y$, is rich and complicated; in addition to superconductivity, it exhibits magnetic and charge orders, and some other structural transitions [2, 3, 4, 5]. Parent compound, Na$_x$CoO$_2$, is a quasi-two-dimensional system with Co in CoO$_2$ layers forming a triangular lattice where Co-Co in-plane distance three times smaller than the inter-plane one. Na ion resides between the CoO$_2$ layers and gives additional $x$ electrons to the layer, lowering Co valence from Co$^{3+}$ (3d$^9$ configuration) to Co$^{3+}$ (3d$^6$ configuration) upon $x$ changing from 0 for virtual compound CoO$_2$ to 1 for NaCoO$_2$. The hole in the d-orbital occupies one of the $t_{2g}$ levels, which are lower than $e_g$ levels by about 2 eV [2]. The degeneracy of the $t_{2g}$ levels is partially lifted by the trigonal distortion which splits it into the higher $a_{1g}$ singlet and the lower two $e'_g$ states.

First principle LDA (local density approximation) and LDA+U band structure calculations predict Na$_x$CoO$_2$ to have a weak intra-plane itinerant ferromagnetic (FM) state for almost all Na concentrations, $0.3 \leq x \leq 0.7$ [12]. On the contrary, neutron scattering finds the A-type antiferromagnetic order implying the ferromagnetic order within Co-layer only for $0.75 \leq x \leq 0.9$ with ordering temperature $T_m \approx 22$ K, and with inter-plane $J_c$ and intra-plane $J_{ab}$ exchange constants to be 12 meV and -6 meV, respectively [13, 14, 15].

In this letter we derive an effective low-energy model describing the bands crossing the Fermi level on the basis of the LDA band structure calculations. Due to the FS topology, inferred from LDA band structure, the magnetic susceptibility $\chi_0(q, \omega = 0)$ reveals two different regimes for different dopings: for $x < 0.58$ it shows pronounced peaks at antiferromagnetic (AFM) wave vector $Q_{AFM}$ = $\{2\pi/\sqrt{3}, 2\pi/\sqrt{3}, 0\}$ resulting in the tendency towards the in-plane 120° AFM order, while for $x > 0.58$ the peaks at small momenta near the $Q_{FM}$ = $(0, 0, 0)$ form, clearly demonstrating the tendency of the system towards the itinerant in-plane FM ordered state. We find that the formation of the electron pocket around the $\Gamma$ point is crucial for the in-plane FM ordering at high doping concentrations.

2. The band structure of Na$_{0.33}$CoO$_2$ (Fig. 1) was obtained within the LDA [16] in the framework of TB-LMTO-ASA (Tight Binding approach to the LMTO using Atomic Sphere Approximation) [17] computation scheme. The crystal structure parameters were taken from [18]. The bands crossing the Fermi level have mostly $a_{1g}$ character, consistent with previous LDA findings [2]. Note, the small FS pockets near the K point with $e'_g$-
bands \([6, 21]\). For simplicity we have enumerated site partial density of states (PDOS) for Na.

\(\varepsilon\) is the separation of the bands crossing the Fermi level in terms of the projection procedure and the LDA bands shown in Fig. 1, \(e\) the correspondence between in-plane vectors and index \(t\) obtained by projection on the manifold we apply the projection procedure \([19, 20]\). The indices \(n\) and the obtained single-electron energies \(\varepsilon\) are equal to (in eV, relative to \(\varepsilon_{\text{Fermi}}\)): \(\varepsilon_{\alpha\pi} = 0\), \(\varepsilon_{\alpha\sigma} = -0.053\).

An agreement between the bands obtained using projection procedure and the LDA bands shown in Fig. 1 that confirms the Co-\(t_2g\) nature of the near-Fermi level bands \([4, 21]\). For simplicity we have enumerated site pairs, \(t_{fg} \rightarrow t_{ng}\), with \(n = 0, 1, 2, \ldots\) (see Fig. 2a) and the correspondence between in-plane vectors and index \(n\) in the Table 1. Due to \(C_3\) symmetry of the cobaltate lattice, the following equalities are present: \(t_{g1} = t_{g3}, t_{a1} = t_{a3}, t_{a2} = t_{a4}\). In addition \(t_{1} = t_{2} = t_{3}\) for \(a_{1g} \rightarrow a_{1g}\) hoppings, which, however, does not hold for \(e_{g1,2}\) orbitals. Thus, since the hybridization of the \(a_{1g}\) and the \(e_{g}\) bands is not small, a simplified description of the bands crossing the Fermi level in terms of the \(a_{1g}\) band only (neglecting \(e_{g}\) band and corresponding hybridizations, see e.g. \([22]\) may lead to a incorrect result due to its higher symmetry. In the following we neglect the inter-layer splitting present for \(k_z = 0\) plane because of its subtle effect on the topology of the FS \([6]\).

Then the free electron Hamiltonian for CoO\(_2\)-plane in a hole representation is given by:

\[
H_0 = - \sum_{k, \alpha, \sigma} (\varepsilon - \mu) n_{k\alpha\sigma} - \sum_{k, \sigma} \sum_{\alpha, \beta} t_{\alpha\beta} d_{k\alpha\sigma}^\dagger d_{k\beta\sigma}. \tag{1}
\]

where \(d_{k\alpha\sigma}\) (\(d_{k\alpha\sigma}^\dagger\)) is the annihilation (creation) operator for hole with momentum \(k\), spin \(\sigma\) and orbital index \(\alpha\), \(n_{k\alpha\sigma} = d_{k\alpha\sigma}^\dagger d_{k\alpha\sigma}\), and \(t_{\alpha\beta}\) is the Fourier transform of the hopping matrix element. Introducing matrix notations, \(\langle t_{k}\rangle = t_{\alpha\beta}^\alpha\), and \(\langle t_{g}\rangle = t_{\alpha\beta}^\alpha\), the hoppings matrix elements in the momentum representation are given by:

\[
\langle t_{k}\rangle = 2t_{1} \cos k_{z} + 2t_{2} \cos k_{3} + 2t_{3} \cos k_{1} + 2t_{4} \cos (k_{1} + k_{3}) + 2t_{5} \cos (k_{2} + k_{1}) + 2t_{6} \cos (k_{1} - k_{2}) + 2t_{7} \cos 2k_{2} + 2t_{8} \cos 2k_{3} + 2t_{9} \cos 2k_{1}, \tag{2}
\]

where \(k_{1} = \frac{\pi}{a_{z}} k_{x} - \frac{1}{2} k_{y}, k_{2} = \frac{\pi}{a_{z}} k_{y}, k_{3} = \frac{\pi}{a_{z}} k_{x} + \frac{1}{2} k_{y}\).

Within this rigid band approximation the doping-dependent evolution of the electronic dispersion, the density of states (DOS) and the FS is shown in Fig. 3. We notice, that already at \(x = 0.48\) the FS \(e_{g}\) hole pockets are absent. Most importantly we find another interesting feature. Namely, the local minimum of the band dispersion around the \(\Gamma\) point yields the appearance of the second FS contour centered around this point. This electron FS pocket becomes larger upon increasing doping \(x\).

As was shown in Ref. \([23]\) for the Hubbard model on a triangular lattice, the main reason for the local minimum around the \(\Gamma\) point is the presence of the next-nearest-neighbor hoppings, which also enter in our calculations. Although this minimum is not yet directly observed in ARPES experiments, the presence of the associated second FS contour would reduce the FS volume and resolve an issue why the volume of the FS observed in ARPES is larger than it is expected from Luttinger’s theorem \([24]\).

Furthermore, an emergence of this pocket would influence the Hall conductivity at high doping concentrations which is interesting to check experimentally.

3. To analyze a possibility of the itinerant magnetism we calculate the magnetic susceptibility \(\chi_{0}(q, \omega = 0)\) based on the Hamiltonian \(H_0\). The doping-dependent evolution of the peaks in \(\text{Re} \chi_{0}(q, 0)\) is shown in Fig. 4. At \(x = 0.45\) the \(e_{g}\) bands are below the Fermi level, and the FS has the form of the rounded hexagon. It results in a number of nesting wave vectors around the antiferromagnetic wave vector \(Q_{AFM}\). The corresponding broad
TABLE I: The in-plane hopping integrals $t_{\alpha\beta}^n$ for different in-plane vectors $n = (f, g)$ for Na$_x$CoO$_2$, $x = 0.33$.

| $n = (f, g)$: | (0, 1) | ($\sqrt{3}/2, -1/2$) | ($\sqrt{3}/2, 1/2$) | (0, 2) | ($\sqrt{3}/2, 3/2$) | (0, 1) | ($\sqrt{3}/2, -3/2$) | ($\sqrt{3}/2, -1/2$) | ($\sqrt{3}/2, 1/2$) |
|--------------|-------|-----------------|-----------------|-------|-----------------|-------|-----------------|-----------------|-----------------|
| $a_{1g} \rightarrow a_{1g}$ | 0.123 | 0.123 | 0.123 | -0.022 | -0.021 | -0.025 | 0.025 | -0.025 | -0.025 |
| $a_{1g} \rightarrow e_{g1}$ | -0.044 | 0.089 | -0.044 | 0.010 | 0.021 | 0.042 | 0.042 | -0.021 | -0.021 |
| $a_{1g} \rightarrow e_{g2}$ | -0.077 | 0.000 | 0.077 | 0.018 | 0.018 | 0.000 | 0.000 | 0.036 | 0.036 |
| $e_{g1} \rightarrow e_{g1}$ | -0.069 | -0.005 | -0.069 | 0.018 | 0.018 | -0.026 | -0.017 | -0.085 | -0.017 |
| $e_{g1} \rightarrow e_{g2}$ | 0.037 | 0.000 | -0.037 | -0.026 | 0.026 | 0.000 | 0.039 | 0.000 | 0.039 |
| $e_{g2} \rightarrow e_{g2}$ | -0.026 | -0.090 | 0.027 | -0.011 | 0.011 | 0.033 | 0.062 | -0.062 | 0.006 |

peaks in the Re$\chi_0(q, 0)$ appear around $Q_{AFM}$, indicating the tendency of the electronic system towards the 120° AFM ordered state [25]. Upon increasing doping, the Fermi level crosses the local minimum at the $\Gamma$ point, resulting in the second almost circle FS contour. As soon as this change of the FS topology takes place, the scattering at the momentum $Q_{AFM}$ is quickly suppressed, and vanishes already at $x_m \approx 0.56$. Most importantly, a new scattering vector, $Q_1$, appears. This wave vector is small and yields peaks in the magnetic susceptibility at small momenta, indicating the tendency of the magnetic system to shift towards itinerant FM order. For larger $x$ the inner FS contour increases leading to a further decrease of the $Q_1$. In the case of $x \approx 0.88$ the FS topology changes again, resulting in a six distant FS contours, yielding even smaller length of $Q_1$. The obtained scattering at small momenta in the magnetic susceptibility for $x > x_m$ is qualitatively consistent with the scattering around $Q_{FM} = (0, 0)$, observed in the neutron scattering experiments [13, 14, 15].

Since obtained magnetic susceptibility depends mostly on the topology of the FS one expects that the behavior shown in Fig. 4 will be valid even if one includes an interaction term $H_{int}$ into account, at least in the case if it is the on-site Hubbard interaction $U$. The only dif-
ference would be a shift of the critical concentrations $x_m$, at which the FS topology changes and tendency to the AFM order changes towards the FM ordered state. To check this, we have taken the strong electron correlations into account by adding the on-site Hubbard interaction terms to the $H_0$, similar to Refs. [24, 27]. The effective on-site Hubbard repulsion $U_{\text{eff}} \approx 4$ eV on Co sites is much larger than the bare bandwidth $W \approx 1.2$ eV, and, thus, it is possible to project doubly occupied states out and formulate an effective model equivalent to the Hubbard model with infinite value of $U$.

In the atomic limit local low-energy states on the Co sites are the vacuum state $|0\rangle$ and the single-hole states $|\alpha\sigma\rangle$, $|\varepsilon_1\sigma\rangle$, $|\varepsilon_2\sigma\rangle$. The simplest way to describe the quasiparticle excitations between these states is to use the projective Hubbard-X operators [28]: $X^{\mu\nu}_f \leftrightarrow X^{\mu\nu}_p \equiv |p\rangle \langle q|$, where index $m \leftrightarrow (p, q)$ enumerates quasiparticles. There is a simple correspondence between X-operators and single-electron creation-annihilation operators: $d_{f\alpha\sigma} = \sum m \gamma_{\alpha\sigma}(m) X^m_f$, where $\gamma_{\alpha\sigma}(m)$ determines the partial weight of a quasiparticle $m$ with spin $\sigma$ and orbital index $\alpha$. In these notations the Hamiltonian of the Hubbard model in the limit $U \to \infty$ has the form:

$$H = - \sum_{f,p} (\varepsilon^p - \mu) X^p_f - \sum_{f \neq g} \sum_{m,m'} t_{fg}^{m,m'} X^m_f X^{m'}_g. \tag{3}$$

In the so-called Hubbard-I approximation within the generalized Dyson equation for the X-operators [29, 50, 51] the quasiparticle bands formed by the $a_{1g} \to a_{1g}$ hoppings will be renormalized by the $(1 + x)/2$ factor, while the quasiparticle bands formed by the $e_g$ hoppings will be renormalized by $x$.

In Fig. 3 the quasiparticle spectrum is shown. One finds within Hubbard-I approximations the bands become narrower with lowering $x$ due to doping dependence of the quasiparticle’s spectral weight. Most importantly, the doping evolution of the FS is qualitatively the same as in the rigid-band picture. Thus, a bandwidth reduction and a spectral weight renormalization do not change the topology of the FS. Therefore, the presence of the strong electronic correlations do not change qualitatively our results for the bare susceptibility. Quantitatively, the critical concentration $x_m$ shifts towards higher values and within Hubbard-I it becomes $x_m \approx 0.68$.

5. To conclude, we have shown that in the model with ab-initio calculated parameters the magnetic susceptibility is doping dependent. At the critical doping concentration, $x_m$, the electron pocket on the FS in the center of the Brillouin zone well develops. For $x < x_m$, the system shows tendency towards the $120^\circ$ AFM ordered state, while for $x > x_m$ the peak in the magnetic susceptibility is at small wave vectors indicating strong tendency towards the itinerant FS state. Within the tight-binding model $x_m$ is estimated to be around 0.56. Analyzing the influence of the strong Coulomb repulsion and the corresponding reduction of the bandwidth and the quasiparticle spectral weight in the strong-coupling Hubbard-I approximation, we show that the critical concentration changes to the $x_m \approx 0.68$. At the same time, the underlying physics of the formation of the itinerant FS state remains the same.

We would like to thank G. Bouzerar, W. Brenig, P. Fulde, S.G. Ovchinnikov, D. Singh, and Ziqiang Wang for useful discussions, I. Mazin and N.B. Perkins for the careful reading of the manuscript, and S. Borisenko for sharing with us the experimental results prior to publication. The work of M.M.K. was supported by INTAS YS (Grant 05-109-4891) and RFBR (Grants 06-02-16100 and 06-02-90537-BNATS), A.S. and V.I.A. acknowledge the financial support from RFBR (Grants 04-02-16096, 06-02-81017), and NWO (Grant 047.016.005).

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