Role of electronic correlations in the Fermi surface formation of Na$_x$CoO$_2$

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Band structure of metallic sodium cobaltate Na$_x$CoO$_2$ ($x=0.33$, 0.48, 0.61, 0.72) has been investigated by local density approximation+Hubbard $U$ (LDA+$U$) method and within Gutzwiller approximation for the Co-$t_{2g}$ manifold. Correlation effects being taken into account results in suppression of the $e'_g$ hole pockets at the Fermi surface in agreement with recent angle-resolved photo-emission spectroscopy (ARPES) experiments. In the Gutzwiller approximation the bilayer splitting is significantly reduced due to the correlation effects. The formation of high spin (HS) state in Co $d$-shell was shown to be very improbable.

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Introduction. Puzzling properties of sodium cobaltate Na$_x$CoO$_2$ are the topic of many recent theoretical and experimental investigations. This material holds much promise for thermoelectronics due to its large thermopower and the charge and magnetic in Na at holistic magnetic field. Anomalous Hall effect and a drop of the thermopower indicates for the correlated behavior come from the data on electronic correlations in these oxides. Other evidences for the correlated behavior come from the data on anomalous Hall effect and a drop of the thermopower in all three states due to spin-polarization, resulting in a spin polarized Fermi surface with an area twice as large as that observed through ARPES. Moreover, the long range ferromagnetic order has been set by hand because of limitation of LDA+$U$. The predicted large local magnetic moments as well as the splitting of bands can be considered as artifacts of the L(S)DA+$U$ method.

Although LDA+$U$ method is usually applied to describe insulators, there are some achievement in investigation of metals and metallic compounds. To analyze the effect of electronic correlations on the Fermi surface formation in sodium cobaltate we employ both LDA+$U$ method and a Gutzwiller approximation.

Co $d$-level splits by crystal field of oxygen octahedron in lower $t_{2g}$ and higher $e_g$ bands. The deficiency of Na in Na$_x$CoO$_2$ introduces additional holes in the system. Cobalt, having $d^6$ configuration and filled $t_{2g}$ shell in parent NaCO$_2$, is nonmagnetic. But in nonstoichiometric compound part of Co ions become magnetic with local moment about 1$\mu_B$. This value is provided by bilayer $d^6$ configuration and one hole in $t_{2g}$ shell. However, intensive investigations by several ARPES groups reveal absence of six small pockets in both Na$_x$CoO$_2$·H$_2$O and its parent compound Na$_x$CO$_2$. The disagreement between ARPES spectra and ab initio calculated band structure points to the importance of the electronic correlations in these oxides. Other evidences for the correlated behavior come from the data on anomalous Hall effect and a drop of the thermopower in all three states due to spin-polarization, resulting in a spin polarized Fermi surface with an area twice as large as that observed through ARPES. Moreover, the long range ferromagnetic order has been set by hand because of limitation of LDA+$U$. The predicted large local magnetic moments as well as the splitting of bands can be considered as artifacts of the L(S)DA+$U$ method.

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First, we have verified the possibility of HS state formation on Co d-shell. For this purpose the unit cell of Na$_{0.61}$CoO$_2$ with two Co atoms was considered. We have started from a saturated A-type antiferromagnetic configuration with five electrons on the t$_{2g}$ and one on the e$_g$ shells. Small $U=2.67$ eV does not stabilize such magnetic configuration and LS state was obtained. Increasing $U$ up to 5 eV however results in HS state with large local magnetic moment about 1.96 $\mu_B$. Nevertheless, this HS state has the total energy about 1.75 eV higher then the energy of a LS state. This large difference in total energy of both considered spin states arises form hexagonal structure of cobaltates where the angle of Co-O-Co bond is close to 90° in contrast to almost 180° for, e.g., RCoO$_3$ (R=La, Ho). In the later case the e$_g$ band has the width about 3-5 eV and its bottom lies just above the Fermi level. The system wins energy of 2$J$ forming a HS state overcoming the gap energy which is less than 1 eV. Due to this fact difference between LS and intermediate spin states in RCoO$_3$ is less then 250 meV$^{21}$. The angle of Co-O-Co bond is close to 90° in cobaltates and results in a weak overlap between e$_g$ orbitals and hence in a narrow e$_g$ band with larger gap between it and the t$_{2g}$ band. Our calculation confirms that formation of HS in Na$_{0.6}$CoO$_2$ is rather improbable and cannot be stabilized by any distortion of crystal structure or clusterization proposed in Ref.$^{11}$. Local magnetic moments on Co sites can arise only due to holes doping due to Na atoms deficiency. Those holes order on Co atoms and form nonmagnetic Co$^{3+}$ and magnetic Co$^{4+}$ ions with d$^0$ and d$^5$ configurations, respectively. In the further calculations only the LS state was considered.

The ordering of holes on t$_{2g}$ shell and corresponding long-range magnetic and charge order for Na$_{0.5}$CoO$_2$ arise probably due to specific arrangement of Na atoms. This arrangements were observed experimentally$^{22}$ for several doping concentrations including $x=0.5$. Proper description of such order within “unrestricted Hartree-Fock” gives strong spin and orbital polarization and local magnetic moment of about 1$\mu_B$ on Co$^{3+}$ sites as well as insulating ground state with sizable gap. To describe non-ordered systems the implementation of “re-
stricted Hartree-Fock" method is more suitable. In the later starting from non-magnetic configuration of d-shell with equal number of spin-up and spin-down electrons LDA+U method gives non-magnetic solution without spin or orbital polarization. Note, that the gap does not open and Na₈CoO₂ remains metallic for all Na concentration.

Obtained band structure of Na₈CoO₂ for x=0.33, 0.48, 0.61, and 0.72 are shown in Fig. 1. Dashed (black) lines correspond to LDA results whereas solid (red) lines are the bands obtained by LDA+U method. Cobalt d and oxygen p states are separated by a small gap of about -1.25 eV for x=0.61 and x=0.72. However, this gap disappears for lower doping concentration since the d band goes down when the number of d electrons decreases. The presence of the two CoO₂ layers within a unit cell due to alternation of the oxygen arrangement results in a bonding-antibonding (bilayer) splitting, also present in Fig. 1.

The degeneracy of the t₂g levels is partially lifted by the trigonal crystal field distortion which splits the former into the higher lying a₁g singlet and the lower two e′g states. However, slight difference in occupation numbers of a₁g and e′g orbitals (0.714 and 0.886 respectively for x=0.33) results in significant difference in LDA+U band structure in respect to LDA one. The energy of the less occupied a₁g orbital increases for both spins, whereas all e′g bands go down (the total a₁g-e′g splitting becomes 0.21 eV for x=0.33). This makes six e′g Fermi surface hole pockets to disappear for small x values. Note, for all Na concentration LDA+U predicts large a₁g pocket of Fermi surface centered around the Γ point in excellent agreement with ARPES spectra for x < 0.7. The additional electron pocket close to the Γ point appears in both LDA and LDA+U methods for a large doping concentrations. It was discussed in our previous work²³,²⁴ in connection with the electronic theory for the itinerant magnetism of this compound.

*Gutzwiller approximation.* The free electron Hamiltonian for CoO₂-plane in a hole representation is given by:

\[
H_0 = - \sum_{\mathbf{r}, \alpha, \sigma} (\varepsilon^\alpha - \mu) n_{\mathbf{r} \alpha \sigma} - \sum_{\mathbf{g}, \alpha, \beta} \sum_{\sigma} t_{\mathbf{g} \alpha \beta} d_{\mathbf{g} \alpha \sigma}^\dagger d_{\mathbf{g} \beta \sigma}.
\]  

where \(d_{\mathbf{r} \alpha \sigma} (d_{\mathbf{r} \alpha \sigma}^\dagger)\) is the annihilation (creation) operator for the \(t_{2g}\) hole at Co site \(\mathbf{r}\), spin \(\sigma\) and orbital index \(\alpha\), \(n_{\mathbf{r} \alpha \sigma} = d_{\mathbf{r} \alpha \sigma}^\dagger d_{\mathbf{r} \alpha \sigma}\), and \(t_{\mathbf{g} \alpha \beta}\) is the hopping matrix element, \(\varepsilon^\alpha\) is the single-electron energies, and \(\mu\) is the chemical potential. All in-plane hoppings and single-electron energies were derived previously²³,²⁴ from the *ab-initio* LDA calculations. Since LDA-calculated hoppings and single-electron energies do not depend much on doping concentration, we used here parameters for Na₈CoO₂ from Table I of Ref.²⁴. To take bilayer splitting into account, we also consider here the hoppings \(t_{2g}^\beta\) between adjacent CoO₂ planes. Their values were also derived from LDA results and are equal to \(g_{z}^\alpha a_{1g} = -0.0121\), \(e_{z}^\alpha e_{z}^\alpha = 0.0080\), and \(e_{z}^\alpha e_{z}^\alpha = -0.0086\).

The Gutzwiller approximation²⁵–²⁷ for the Hubbard model provides a good description for the correlated metallic system. Its multiband generalization was formulated in Ref.²⁸. In this approach, the Hamiltonian describing the interacting system far from the metal-insulator transition for \(U \gg W\), \(J = 0\):

\[
H = H_0 + \sum_{\mathbf{r}, \alpha} U_{\alpha} n_{\mathbf{r} \alpha \uparrow} n_{\mathbf{r} \alpha \downarrow},
\]

is replaced by the effective non-interacting Hamiltonian:

\[
H_{\text{eff}} = - \sum_{\mathbf{r}, \alpha, \sigma} (\varepsilon^\alpha + \delta \varepsilon^{\alpha \sigma} - \mu) n_{\mathbf{r} \alpha \sigma} - \sum_{\mathbf{g}, \alpha, \beta} \sum_{\sigma} t_{\mathbf{g} \alpha \beta} d_{\mathbf{g} \alpha \sigma}^\dagger d_{\mathbf{g} \beta \sigma} + C.
\]
Here, $t_{\alpha\beta} = \frac{t_{\alpha\beta}}{\sqrt{a_{\alpha} \sqrt{b_{\beta}}}}$ is the renormalized hopping between two lattice sites connected by the spatial vector $(f-g)$, $t_{\alpha\beta} = \frac{1}{n_{\alpha\beta}}$, $n_{\alpha\beta} = \langle \Psi | H_{f\alpha\beta} | \Psi \rangle \equiv \langle \Psi | H_{f\alpha\beta} | \Psi \rangle_0$ is the orbital's filling factors, $x = 1 - \sum n_{\alpha\beta}$ is the equation for the chemical potential. $\delta^{\alpha\beta}$ are the Lagrange multipliers yielding the correlation induced shifts of the single-electron energies. The constant $C = \sum_{\alpha, \beta} \delta^{\alpha\beta} n_{\alpha\beta}$ was determined from the condition that the ground state energy is the same for both Hamiltonians, $\langle \Psi | H_{f\alpha\beta} | \Psi \rangle_0 = \langle \Psi | H \ | \Psi \rangle_0$, where $| \Psi \rangle_0$ is the wave function of the free electron system (3), and $| \Psi \rangle$ is the Gutzwiller wave function for the Hamiltonian (2). The Lagrange multipliers are determined by minimizing the energy $\langle \Psi | H_{f\alpha\beta} | \Psi \rangle_0$ with respect to the orbital filling factors $n_{\alpha\beta}$. This results in the following expression for the single-electron energies renormalization:

$$\delta^{\alpha\beta} = \frac{1}{2(1-x)} \sum_{f,g,\beta} t_{f\alpha\beta}^3 \left\langle d_{f\alpha\beta}^g d_{g\beta}^* \right\rangle_0.$$  \hspace{1cm} (4)

It is this energy shift that forces the $e_g'$ bands to sink below the Fermi energy. This is clearly seen in the doping-dependent evolution of the quasiparticle dispersion within Gutzwiller approximation in Fig. 2. To obtain these figures we solved self-consistently Eq. (4) and the equation on the chemical potential $\mu$.

The comparison of the Gutzwiller approximation results with the LDA+$U$ dispersion reveals few very interesting conclusions. First, both approximations result in a suppression of $e_g'$ hole pockets of the FS. Second, the bilayer splitting is strongly doping dependent and significantly reduced for Gutzwiller quasiparticles in comparison with the LDA+$U$ quasiparticles because the renormalization coefficient, $\sqrt{a_{\alpha} \sqrt{b_{\beta}}}$, occurs not only for the intra-plane hoppings, but also for the interlayer hoppings $t_{2g}$. Third, when both bonding and antibonding $t_{2g}$ bands do not cross the Fermi level around the $\Gamma$ point, the FS crossings are the same in both approximations (see Fig. 2a). It is the simple consequence of the Luttinger theorem which holds for both approaches. But for large $x$ due to the larger bilayer splitting in LDA+$U$ the Fermi surfaces become different, while the Luttinger theorem is still preserved. With increase of the doping concentration $x$ the bandwidth of the Gutzwiller quasiparticles becomes closer to the LDA+$U$ ones because band renormalization factor $\sqrt{a_{\alpha} \sqrt{b_{\beta}}}$ comes closer to unity.

Dynamical Mean Field Theory (DMFT) calculations\cite{Ref31,Ref32} show that for the small $U$ and non-zero $J$, $e_g'$ FS pockets can be stabilized. On the other hand, DMFT calculations of Ref.\cite{Ref30} confirm results of the Gutzwiller approximation provided that $U$ and the crystal field splitting are large.

**Conclusion.** In the present work employing *ab-initio* constrained LDA method we obtained Coulomb repulsion parameter $U=2.67$ eV for $t_{2g}$ orbitals taking into account the screening by $e_g$-electrons in addition to the screening by itinerant $s$- and $p$-electrons. Hund's exchange parameter was found equal to $J=1.07$ eV.

Also, we have shown that due to the Co-O-Co bond angle close to $90^\circ$ in Na$_8$CoO$_2$ the energy gap between LS and HS states is too large to be overcome by clusterization or reasonable distortions of crystal structure. Thus we conclude that realization of HS state is highly improbable in this particular substance.

Then, to analyze the effect of electronic correlations on the Fermi surface topology of Na$_8$CoO$_2$ we use two approaches, non-magnetic LDA+$U$ and Gutzwiller approximation for the Hubbard-type model based on the LDA band structure. Within LDA+$U$ the energy of the less occupied $a_{\sigma}$ orbital increases for both spins, whereas all $e_g'$ bands go down. This makes six $e_g'$ FS hole pockets to disappear for small $x$ values, in agreement with ARPES for $x < 0.7$. Gutzwiller approximation also resulted in a suppression of $e_g'$ hole pockets at the FS. Moreover, the bilayer splitting was found to be strongly doping dependent and significantly reduced for Gutzwiller quasiparticles in comparison with LDA+$U$ quasiparticles.

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