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Role of electronic correlations in the Fermi surface formation of Na_xCoO_2

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Band structure of metallic sodium cobaltate Na_xCO_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.

1. Introduction. Puzzling properties of sodium cobaltate Na_xCO_2 are the topic of many recent theoretical and experimental investigations [1]. This material holds much promise for thermoelectronics due to its large thermopower [2] together with the relatively low resistivity [3]. The discovery of superconductivity with T_c about 5 K in $Na_{0.33}CoO_2{\cdot}1.3H_2O$ [3] revived the interest in lamellar sodium cobaltates. Moreover, the charge and magnetic long range orders on the frustrated triangular lattice of cobaltate is of the fundamental interest. The band theory predict the complicated Fermi surface (FS) with one large hole pocket around the $\Gamma = (0,0,0)$ point and six small pockets near the $K = (0, \frac{4\pi}{3}, 0)$ points of the hexagonal Brillouin zone at least for $x < 0.5$ [4, 5]. However, intensive investigations by several ARPES groups reveal absence of six small pockets in both $Na_xCO_2{\cdot}yH_2O$ and in its parent compound Na_xCO_2 [6 – 10].

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 an anomalous Hall effect and a drop of the thermopower in holistic magnetic field [11].

The six hole pockets are absent in the L(S)DA+U calculations [12, 13]. However, in this approach, the insulating gap is formed by a splitting of the local single-electron 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 [14], there are some achievement in investigation of metals and metallic compounds [15, 16]. To analyze the effect of electronic correlations on the Fermi surface formation in sodium cobaltate we employ non-magnetic LDA+U method. Then, we use a Gutzwiller approximation to display the effect of correlations on the bilayer splitting and compare it with LDA+U results.

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_xCO_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 d^5 configuration and one hole in t_{2g} shell. However, the experiments revealed the magnetic susceptibility at room temperature that is much higher than it was expected for dilute magnetic impurity in non-magnetic solvent. Explanation of this anomaly was suggested in Ref. [17] as transition from low-spin (LS) state with six d-electrons on t_{2g} shell to high-spin (HS) state with five d-electrons on t_{2g} shell and one electron on e_g. The possibility of such transition will be discussed below.

2. LDA+U results. $Na_{0.61}CoO_2$ crystallize in the hexagonal unit cell ($P6_3/mmc$ space group) with $a = 2.83176(3)$ Å and $c = 10.8431(2)$ Å at 12 K Ref [18]. Displacement of Na atoms from their ideal sites $2d$ $(1/3, 2/3, 3/4)$ on about $0.2\mathring{A}$ are observed in nonstoichiometric cobaltates for both room and low temperatures. This is probably due to the repulsion of a randomly distributed Na atoms, locally violating hexagonal

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symmetry [18]. In the present investigation Na atoms are shifted back to their 2d ideal sites. In order to avoid charge disproportionation which can arises from some Na distribution if the supercell is used in calculation, the change in the Na concentration has been considered in virtual crystal approximation (VCA) where each 2d site is occupied by virtual atoms with fractional number of valence electrons x and a core charge $10 - x$ instead of Na. Note, that all core states of virtual atom are left unchanged and corresponds to Na ones. We have chosen $4s$, $4p$, and $3d$ states of cobalt, $2s$, $2p$, and $3d$ states of oxygen, and $3s$, $3p$, and $3d$ states of Na as the valence states for TB-LMTO-ASA computation scheme [19]. The radii of atomic spheres where 1.99 a.u. for Co, 1.61 a.u. for oxygen, and 2.68 a.u. for Na. Two classes of empty spheres (pseudo-atoms without core states) were added to fill the unit cell volume.

Crystal field of oxygen octahedron splits Co d-band into doubly degenerate e_g and triply degenerate t_{2g} subbands (without taking spin into account). LDA calculations shows that those manifolds are separated by about 2 eV [4]. Here partially filled t_{2g} subband crosses the Fermi level whereas e_g subband due to strongly hybridization with nearest oxygen atoms is positioned well above the Fermi level. The procedure proposed in Ref. [20] allows one to calculate the Coulomb repulsion parameter U taking into account the screening of localized d-shell by itinerant s- and p-electrons. Resulting U is equal to 6.7 eV. However, the presence of the t_{2g}–e_g splitting give the reason to take into account an additional screening channel provided by the less localized e_g electrons. The value of $U = 2.67$ eV for t_{2g} orbitals was calculated using the "constrained LDA" method [21], where the screening by the e_g electrons is also taken into account. This value was used in the present calculation for all doping concentrations x. Hund's exchange parameter J depends weakly on screening effects due to its "on-site" character. Its value was also calculated within the "constrained LDA" method and was found to be 1.07 eV.

First, we have verified the possibility of HS state formation on Co d-shell. For this purpose the unit cell of $Na_{0.61}CO_2$ 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 the hexagonal structure of cobaltates where the angle of Co-O-Co bond is close to 90° in contrast to almost 180° in, e.g., $RCoO_3$ (R=La, Ho). In the latter case the e_g band has the width of about 3–5 eV and its bottom lies just above the Fermi level. The system wins energy of $2J$ forming a HS state overcoming the gap energy which is less than 1 eV. Due to this fact the difference between the LS and intermediate spin states in $RCoO_3$ is less then 250 meV [22]. The angle of Co-O-Co bond is close to 90° in cobaltates and it 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 the HS state in Na_xCoO_2 is rather improbable and cannot be stabilized by any distortion of crystal structure or clusterization proposed in Ref. [17]. Local magnetic moments on Co sites can arise only because of the doped holes due to Na atoms deficiency. Those holes order on Co atoms and form nonmagnetic Co^{3+} and magnetic Co^{4+} ions with d^6 and d^5 configurations, respectively. In the following, we consider only the LS state.

The ordering of holes on t_{2g} shell and corresponding long-range magnetic and charge orders in $Na_{0.5}CoO_2$ arise probably due to specific arrangement of Na atoms. These arrangements were observed experimentally [23] for several doping concentrations including $x = 0.5$. Proper description of such order within the "unrestricted Hartree-Fock" gives strong spin and orbital polarization and local magnetic moment of about $1\mu_B$ on Co^{4+} sites as well as the insulating ground state with a sizable gap. To describe the non-ordered systems, the implementation of the "restricted Hartree-Fock" method is more suitable. In the latter, starting from the non-magnetic configuration of the d-shell with the equal number of spin-up and spin-down electrons, LDA+U method gives the non-magnetic solution without spin or orbital polarization. Note, that the gap does not open and Na_xCoO_2 remains metallic for all Na concentration.

Obtained band structure of Na_xCoO_2 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 CoO_2 layers within the 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 t_{2g} levels is partially lifted by the trigonal crystal field distortion which splits them into the higher lying a_{1g} singlet and the two lower lying e'_g states. However, slight difference in occupation numbers of a_{1g} and e'_g orbitals (0.714 and 0.886 respectively for $x = 0.33$) results in a significant difference

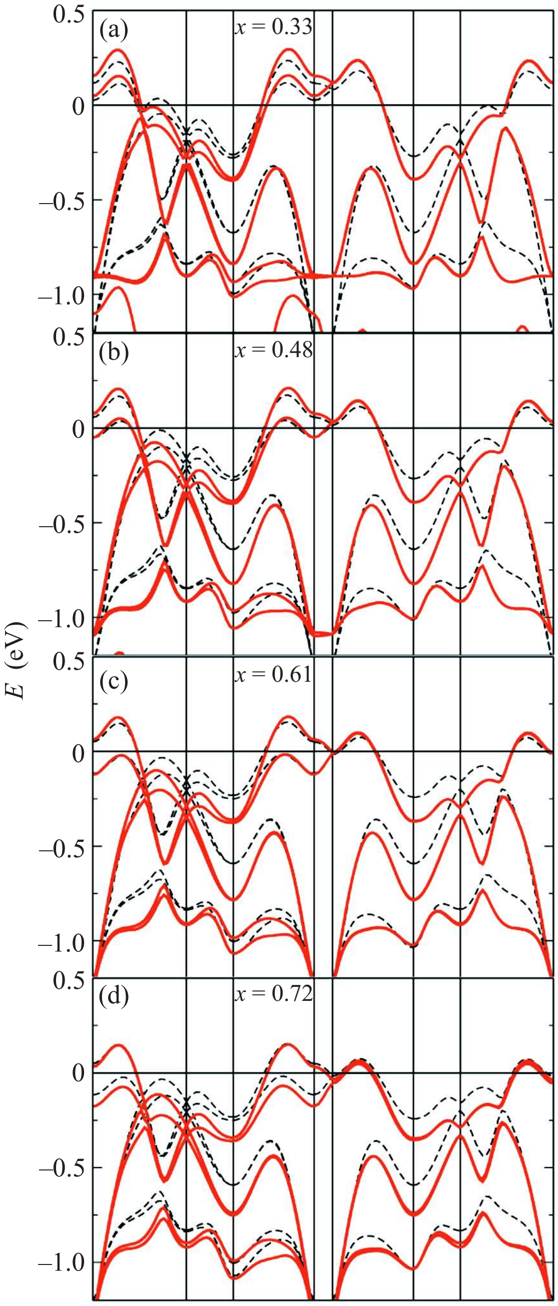

Fig.1. Band structure of Na_xCoO_2 for x equal to 0.33 (a), 0.48 (b), 0.61 (c), and 0.72 (d), obtained within LDA is shown by the black (dashed) curves. Band structures for the same doping concentrations within LDA+U are shown by the red (solid) curves

between the LDA+U and LDA band structures. The energy of the less occupied a_{1g} orbital increases for both spins, whereas all e'_g bands go down (the total a_{1g}–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 that for all Na concentration LDA+U predicts large a_{1g} Fermi pocket centered around the Γ point in excellent agreement with the 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 work [24, 25] in connection with the electronic theory for the itinerant magnetism of highly doped compounds.

3. Gutzwiller approximation. For the small doping concentrations, $x \approx 0.3$, sodium cobaltate displays a canonical Fermi-liquid behavior both in resistivity [26] and in NMR relaxation rate [27]. Transport measurements [28] on single crystals with $x = 0.7$ also revealed Fermi-liquid behavior at low temperatures. However, this behavior is characterized by the enormous electron-electron scattering. The Gutzwiller approximation [29–31] for the Hubbard model recommended itself as a good tool to describe low-energy quantities such as the FS and a ground state energy in the correlated metallic system. We will use the multiband generalization of this approximation [32] to investigate the effect of correlations on the bilayer splitting and compare it with the LDA+U results.

Hamiltonian for CoO_2-plane in a hole representation is given by:

$$H = -\sum_{\mathbf{f},\alpha,\sigma} \varepsilon^{\alpha} n_{\mathbf{f}\alpha\sigma} - \sum_{\mathbf{fg},\alpha,\beta,\sigma} t_{\mathbf{fg}}^{\alpha\beta} d_{\mathbf{f}\alpha\sigma}^{\dagger} d_{\mathbf{g}\beta\sigma} + + \sum_{\mathbf{f},\alpha} U_{\alpha} n_{\mathbf{f}\alpha\uparrow} n_{\mathbf{f}\alpha\downarrow}, \qquad (1)$$

where $d_{\mathbf{f}\alpha\sigma}$ ($d_{\mathbf{f}\alpha\sigma}^{\dagger}$) is the annihilation (creation) operator for the t_{2g} hole at Co site $\mathbf{f}$, spin σ and orbital index α, $n_{\mathbf{f}\alpha\sigma} = d_{\mathbf{f}\alpha\sigma}^{\dagger} d_{\mathbf{f}\alpha\sigma}$, and $t_{\mathbf{fg}}^{\alpha\beta}$ is the hopping matrix element between two lattice sites connected by the spatial vector $(\mathbf{f} - \mathbf{g})$, ε^{α} is the single-electron energies in which the chemical potential μ is included. Since LDA-calculated hoppings and single-electron energies do not depend much on doping concentration [24, 25], we use here parameters for $Na_{0.33}CoO_2$ form Table I of Ref. [25]. To take the bilayer splitting into account, we also consider hoppings $t_z^{\alpha\beta}$ between the adjacent CoO_2 planes. Their values were also derived from LDA results and are equal to $t_z^{a_{1g}a_{1g}} = -0.0121$, $t_z^{e'_{g1}e'_{g1}} = 0.0080$, and $t_z^{e'_{g2}e'_{g2}} = -0.0086$.

Within the Gutzwiller approximation the Hamiltonian describing the interacting system far from the metal-insulator transition for $U \gg W$, $J = 0$, is replaced by the effective non-interacting Hamiltonian:

$$H_{\text{eff}} = -\sum_{\mathbf{f},\alpha,\sigma} (\varepsilon^{\alpha} + \delta\varepsilon^{\alpha\sigma} - \mu) n_{\mathbf{f}\alpha\sigma} - - \sum_{\mathbf{f}\neq\mathbf{g},\sigma} \sum_{\alpha,\beta} \tilde{t}_{\mathbf{fg}}^{\alpha\beta} d_{\mathbf{f}\alpha\sigma}^{\dagger} d_{\mathbf{g}\beta\sigma} + \sum_{\alpha,\sigma} \delta\varepsilon^{\alpha\sigma} n_{\alpha\sigma}. \qquad (2)$$

Here, $\tilde{t}^{\alpha\beta}_{\mathbf{fg}} = t^{\alpha\beta}_{\mathbf{fg}}\sqrt{q_{\alpha\sigma}}\sqrt{q_{\beta\sigma}}$ is the renormalized hopping, $q_{\alpha\sigma} = \frac{x}{1-n_{\alpha\sigma}}$, $n_{\alpha\sigma} = \langle n_{\mathbf{f}\alpha\sigma}\rangle_0$ is the orbital's filling factors, $x = 1 - \sum\limits_{\alpha\sigma} n_{\alpha\sigma}$ is the equation for the chemical potential. $\delta\varepsilon^{\alpha\sigma}$ are the Lagrange multipliers yielding the correlation induced shifts of the single-electron energies. They are determined by minimizing the energy $\langle H_{eff}\rangle_0$ with respect to the orbital filling factors $n_{\alpha\sigma}$. It is this energy shift $\delta\varepsilon^{\alpha\sigma}$, that forces the e'_g bands to sink below the Fermi level [33]. This is clearly seen in the doping-dependent evolution of the quasiparticle dispersion within the Gutzwiller approximation in Fig.2. To obtain these figures we self-consistently solved equations on $\delta\varepsilon^{\alpha\sigma}$ and on the chemical potential μ.

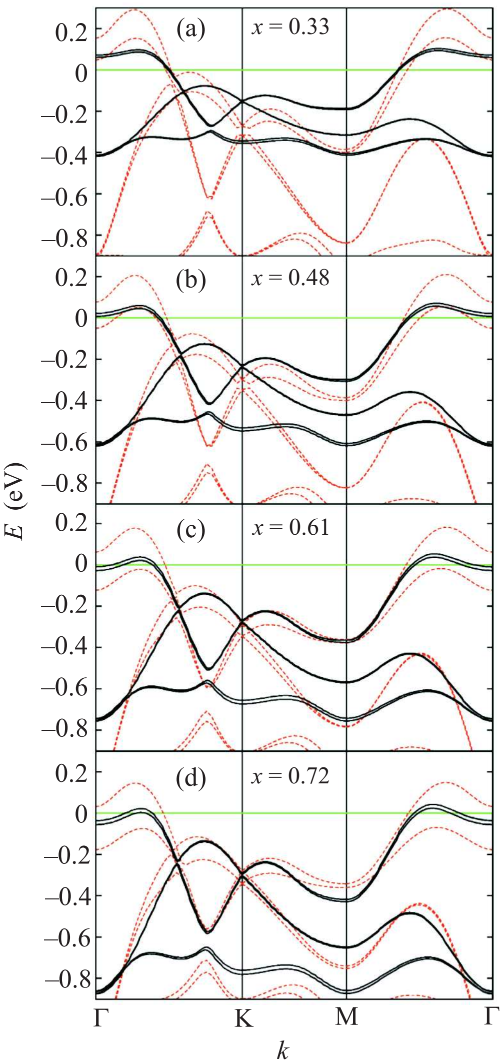

Fig.2. Band structure of Na_xCoO_2 for x equal to 0.33 (a), 0.48 (b), 0.61 (c), and 0.72 (d), obtained in LDA+U is shown by the dashed (red) curves. Dispersion within the Gutzwiller approximation is shown by the solid (black) curves

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 the Gutzwiller quasiparticles in comparison with the LDA+U quasiparticles because the renormalization coefficient, $\sqrt{q_{\alpha\sigma}}\sqrt{q_{\beta\sigma}}$, occurs not only for the in-plane hoppings, but also for the interlayer hoppings $t^{\alpha\beta}_z$. Third, when both bonding and antibonding t_{2g} bands do not cross the Fermi level around the Γ point, the FS crossings are the same in both approximations (see Fig.2a). It is a simple consequence of the Luttinger theorem which holds for both approaches. But for large x due to the larger bilayer splitting in the LDA+U approach, the Fermi surfaces become different, while the Luttinger theorem is again preserved. With increase of the doping concentration x, the bandwidth of the Gutzwiller quasiparticles becomes closer to the LDA+U because the band renormalization factor $\sqrt{q_{\alpha\sigma}}\sqrt{q_{\beta\sigma}}$ comes closer to unity.

Now we will discuss the correlations between our results and a more rigorous theory, namely, the Dynamical Mean Field Theory (DMFT). Generally, within DMFT the band structure of a Hubbard model consist of three parts: two incoherent Hubbard subbands and a coherent near-Fermi-level quasiparticle band. Since U is not very large in sodium cobaltates, Hubbard subbands loose their spectral weight and are almost merged with the coherent band. Thus, low-energy excitations are determined mostly by this quasiparticle band. And it is this band that revealed within the Gutzwiller approximation, even if we formally in the limit of $U \gg W$.

In the case of Na_xCoO_2, DMFT calculations show that for the small U and a non-zero J, e'_g FS pockets can by stabilized [34, 35]. On the other hand, more recent DMFT calculations of Ref. [36] confirms results of the Gutzwiller approximation provided that the crystal field slitting Δ is about 50 meV. This value is in agreement with our value of $\Delta = 53$ meV [25], so our results are consistent with DMFT.

4. 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 the e_g-electrons in addition to the screening by the itinerant s- and p-electrons. Hund's exchnage parameter was found to be J=1.07 eV.

Also we have shown that due to the Co-O-Co bond angle being close to 90° in Na_xCoO_2, the energy gap between the LS and HS states is too large to be overcome by the clusterization or reasonable distortions of the crystal structure. Thus we conclude that realization of the HS state is highly improbable in these particular substance.

To analyze the effect of electronic correlations on the Fermi surface topology of Na_xCoO_2 we use two approaches, non-magnetic LDA+U and the Gutzwiller approximation for the Hubbard-type model based on the LDA band structure. Physically, the reason of e'_g FS pockets disappearance is quite clear. Within LDA+U the energy of the less occupied a_{1g} 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. Most importantly, the bilayer splitting was found to be strongly doping dependent and significantly reduced for the Gutzwiller quasiparticles in comparison with the LDA+U quasiparticles. This may explain why the bilayer splitting is not observed in ARPES though it is very pronounced in the LDA band structure.

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