Electronic structure and Fermi surface topology of Na$_2$CoO$_2$  

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We construct an effective Hamiltonian for the motion of $T_{2g}$ highly correlated states in Na$_2$CoO$_2$. We solve exactly a multiband model in a CoO$_6$ cluster with electronic occupation corresponding to a nominal Co valence of either +3 or +4. Using the ensuing ground states, we calculate the effective O mediated hopping $t = 0.10$ eV between many-body $T_{2g}$ states, and estimate the direct hopping $t' \sim 0.04$ eV. The trigonal splitting $3D = 0.315$ eV is taken from recent quantum chemistry calculations. The resulting effective Hamiltonian is solved using a generalized slave-boson mean-field approximation. The results show a significant band renormalization and a Fermi surface topology that agrees with experiment, in contrast to predictions using the local-density approximation.

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The doped layered hexagonal cobaltates Na$_2$CoO$_2$ have attracted considerable interest in the last few years. The exceptionally high thermopower and at the same time low thermal conductivity and resistivity for $0.5 < x < 0.9$ makes the system attractive because of its potential technological applications. Wider attention has been triggered by the discovery of superconductivity in hydrated Na$_{0.35}$CoO$_2$–1.3 H$_2$O. Because of the hexagonal structure of the system which frustrates competing magnetic interactions, a possible natural explanation of the superconductivity seemed to be a resonance-valence-bond state in an effective one-band model. However, based on geometrical and physical arguments, Koshibae and Maekawa pointed out that it is more realistic to start from a three-band model of degenerate Co 3$d$ $t_{2g}$ orbitals with an indirect hopping over interstitial O orbitals. This leads to four independent interpenetrating Kagomé sublattices. On the other hand, local-density approximation (LDA) calculations predict a Fermi surface (FS) with a large portion around the $\Gamma$ point of the Brillouin zone, and six pockets near the $K$ points. However, angle-resolved photoemission (ARPES) revealed only a single hole like FS around $\Gamma$ and no hole pockets. Recent experiments with X-ray absorption spectroscopy (XAS) and their interpretation show a strong Co–O covalency. In particular, the amount of the 3$d^9$ configuration in a CoO$_6$ cluster is smaller than the total amount of 3$d^{n+1}L$ states ($L$ denotes a ligand O 2$p$ hole) for both, nominal Co$^{3+}$ ($n = 6$) and Co$^{4+}$ ($n = 5$). Ab initio quantum chemical calculations also obtain a large Co–O hybridization.

It has been suggested that the discrepancy between the LDA calculations and the Fermi surface measured by ARPES can be explained as an effect of the correlations, which are absent in LDA and LDA+U approaches, even in the most sophisticated treatments. However, the effective Hamiltonian used is unjustified and differs from that we have derived (see below). Moreover, the dispersion relation along $\Gamma$–$K$ differs from the experimentally observed one, and the results contradict those obtained using dynamical mean field theory, which actually obtain an enhancement of the hole pockets. Another recently proposed explanation is a localization of the hole pockets by disorder. However this localization is not expected to alter the small volume enclosed by the main portion of the LDA Fermi surface around $\Gamma$, while according to the more recent ARPES experiments, this portion contains all holes in a way consistent with Luttinger theorem.

This discussion shows the need of further studies of the electronic structure of Na$_x$CoO$_2$, and the starting point should take into account the strong Co–O covalency. This is the purpose of this Letter. We start from the exact solution of the appropriate multiband Hamiltonian for Co 3$d$ and O 2$p$ holes in the basic CoO$_6$ octahedron, with the hole content corresponding to $x = 1$ (nominal Co$^{3+}$) and with one additional hole (nominal Co$^{4+}$ as for $x = 0$). The parameters of the multiband model are fixed by a previous fitting of the polarization dependent XAS spectra. The resulting ground states are mapped onto the corresponding states of an effective three-band model for...
(fictitious) $3d$ $t_{2g}$ orbitals on Co sites. The eigenstates of the cluster are used to calculate the hopping in the effective model. The procedure has some similarities to the derivation of an effective $t-J$ model in the cuprates using non-orthogonal Zhang-Rice singlets [20, 21]. The trigonal splitting is taken from recent difference-dedicated configuration interaction (DDCI) calculations [15] in a distorted CoO$_6$ cluster. The DDCI are quantum chemistry calculations, particularly suited to calculate excitation energies in strongly correlated systems [15, 22]. The effective model is solved in a slave-boson mean-field approximation [23, 24]. The results reproduce the essential results of ARPES, in particular the shape of the FS and the quasiparticle dispersion near the Fermi energy $\epsilon_F$.

It might seem that the procedure mentioned above, which eliminates the O $2p$ states from the low-energy physics, is not valid when the Co–O hopping is larger or of the order of the Co and O on-site energy difference $\Delta$. However, calculations in the cuprates [25, 26] and other systems [27] using the cell perturbation method showed that this is not the case. In fact as the hopping increases, the $d$ states are replaced by hybrid states of the same symmetry which remain well separated from the other states. Using the mapping procedure it is even possible to calculate the O spectral density at low energies with the effective model which does not contain explicitly O states [26].

The Hamiltonian for the CoO$_6$ cluster contains Co $3d$ and O $2p$ holes and includes the splitting between $3d$ $e_g$ and $t_{2g}$ orbitals, Co–O and O–O hoppings and all interactions between $3d$ holes. Spin-orbit interaction is neglected. Details are given in Ref. [14]. We assume octahedral $O_h$ symmetry. This assumption greatly reduces the size of the matrices to be diagonalized and has a very small effect on the resulting many-body eigenstates [14].

The ground state of the cluster with four holes (nominal Co$^{3+}$) $|A_{1g}\rangle$ is a singlet with $A_{1g}$ symmetry. We use capital letters to denote the irreducible representations of many-body states. For the parameters that fit the polarization dependent XAS spectra, it has been found that $|A_{1g}\rangle$ consists mainly of $30\%$ of the state with four $3d$ $e_g$ holes and $47\%$ of states with three $3d$ $e_g$ holes and one $2p$ hole, in a linear combination of $e_g$ symmetry [14]. For one additional hole, the ground state of the cluster is a spin doublet with $T_{2g}$ symmetry (six-fold degenerate). These states will be denoted as $|\gamma, \sigma\rangle$, where $\gamma = xy, yz$ or $zx$ and $\sigma = \uparrow$ or $\downarrow$. As a first approximation, they can be constructed adding a $3d$ $t_{2g}$ hole to $|A_{1g}\rangle$.

In this work, to represent the movement of holes in the system between different CoO$_6$ clusters, we map the state $|i, A_{1g}\rangle$ where $i$ is a site index, onto the vacuum (absence of holes) at site $i$, and the states $|i, \gamma, \sigma\rangle$ onto the corresponding states $h_{i\gamma\sigma}^\dagger |0\rangle$ of the effective three-band model, where $h_{i\gamma\sigma}^\dagger$ creates a hole at site $i$, orbital $\gamma$ and spin $\sigma$. The most important effective hopping is the one mediated by O orbitals. Geometrical considerations show that a hole in the state $|i, \gamma, \sigma\rangle$ can hop only to some nearest Co atoms (building the state $|j, \gamma', \sigma\rangle$) through an intermediate O $2p$ orbital. Fig. 1 illustrates this indirect hopping, which can be well approximated by

$$ -t = \langle j, xx, \uparrow | i, A_{1g} | H_{\text{hop}} | j, yz, \uparrow \rangle | j, A_{1g} \rangle $$

(1)

$H_{\text{hop}}$ is the sum of Co–O and O–O hopping terms of both clusters. For the parameters that fit the XAS spectra we obtain $t = 0.10$ eV. This agrees with previous estimations [3]. Considering all possible indirect hoppings leads to the picture of four interpenetrating Kagomé sublattices for the degenerate $|\gamma, \sigma\rangle$ orbitals (see Refs. [3, 4] and Fig. 1).

![FIG. 1: (Color online)](image)

Orbitals involved in the effective hopping of a hole with symmetry $yz$ to a neighboring state with symmetry $xx$, through a $p_z$ orbital of an intermediate O site.

While $t$ is the more important hopping process [3], the direct hopping $t_1$ between $d$ electrons might be important for a realistic description of the band structure [5, 16]. Unfortunately, since this hopping is not included in the calculation of the CoO$_6$ cluster used to fit the XAS spectra, it cannot be extracted using this experimental information. Taking the value $t_1 = -44.6$ meV obtained from a fit of the band structure in Ref. [16], we obtain $t' = 36$ meV > 0 for the effective hopping between highly correlated hole states

$$ t' = \langle j, xy, \uparrow | i, A_{1g} | -t_1 d_{i \gamma \sigma}^\dagger d_{j \gamma' \sigma} | i, xy, \uparrow \rangle | j, A_{1g} \rangle $$

(2)

Here $i$ and $j$ refer to two nearest-neighbor clusters in the $(1,1,0)$ direction.

In presence of a trigonal distortion, the point symmetry is reduced to $D_{3d}$ and the $T_{2g}$ states are split into $A'_{1g}$ and $E''_g$ states. The prime denotes irreducible representations of $D_{3d}$. This splitting, which is an essential parameter of the effective model, is beyond the reach of our cluster calculation in $O_h$ symmetry. Fortunately, recent accurate DDCI calculations give a splitting $3D = 0.315$ eV between the many-body ground state
Due to the large Co–O hybridization, the effect of the distortion of the CoO octahedra is stronger than in previous multiband approaches, but not so strong to justify a one-band model based on localized $a'_{1g}$ orbitals.

In the following, we test the ability of $H_{eff}$ with parameters fixed as explained above, to explain the ARPES experiments. We solve it using a generalization to the multiband case of the slave boson treatment of Kotliar and Ruckenstein in mean field, which is equivalent to the Gutzwiller approximation. The three-band case of $t_{2g}$ orbitals with only one relevant spin and the general multiband case were considered before.

The basic idea is to enlarge the Fock space to include bosonic states which correspond to each state in the fermionic description. The vacuum state at site $i$ is now represented as $e_i^\dagger |0\rangle$, a state with one hole as $s_i^\dagger |\gamma\rangle$, a state with two holes as $d_{i\gamma\gamma'}^\dagger h_{i\gamma\sigma}^\dagger |0\rangle$, etc., where $e_i^\dagger$, $s_i^\dagger$, $d_{i\gamma\gamma'}^\dagger$ are bosonic operators corresponding to empty, singly occupied, doubly occupied sites and so on. In our case, with $U \to \infty$, only the first two bosons are relevant and from now on we neglect the others in the description that follows to simplify it. The boson operators should satisfy the constraints

$$e_i^\dagger e_i + \sum_{i,\gamma} s_i^\dagger s_i = 1; \quad h_{i\gamma\sigma}^\dagger h_{i\gamma\sigma} = s_i^\dagger s_i$$

The first ones states that there is only one boson at each site and the second that counting states with one hole in the fermionic or bosonic representations should lead to the same result. In the hopping terms involving different sites ($i \neq j$ in Eq. (3)), the fermion creation operators should be accompanied by their respective bosonic part

$$h_{i\gamma\sigma}^\dagger \rightarrow h_{i\gamma\sigma}^\dagger (1 - e_i^\dagger e_i)^{-\frac{1}{2}} s_i^\dagger s_i e_i (1 - s_i^\dagger s_i)^{-\frac{1}{2}}$$

Here the root operators are identical to one if treated exactly. They are introduced to reproduce the non-interacting limit $U = 0$ in the mean-field treatment.

To use the slave boson theory, we first diagonalize the on-site part of $H_1$, introducing hole operators $h_{k\alpha\sigma}$ with $a'_{1g}$ and $e'_g$ symmetry. In the new basis $\{ \alpha \} = \{ |a'_{1g}\rangle, |e'_g1\rangle, |e'_g2\rangle \}$, the Hamiltonian for holes becomes

$$H_1 = \sum_{k} \sum_{\alpha,\alpha',\sigma} (\tilde{e}_{\alpha\alpha'}(k) + \tilde{D}_{\alpha\alpha'} h_{k\alpha\sigma}^\dagger h_{k\alpha'\sigma})$$

with $\tilde{e}_{\alpha\alpha'}(k) = 2t' \begin{pmatrix} 0 & \cos \theta_3 & \cos \theta_1 \\ \cos \theta_3 & 0 & \cos \theta_1 \\ \cos \theta_1 & -\cos \theta_3 & 0 \end{pmatrix}$ and $\tilde{D}_{\alpha\alpha'}$, where here $k_z$ refers to the direction of two nearest-neighbor Co atoms ($-1,0,1$ in Fig. 1). We believe that $H_{eff}$ is the starting point for the description of the low-energy physics of the cobaltates. While it is similar to previous proposals, the most important parameters $D$ and $t$ are derived from cluster calculations that properly take into account the important effects of Co–O covalency and all correlations inside the Co 3d shell.
values of which are determined self-consistently minimizing the total energy under the given constraints. For a homogeneous paramagnetic phase we have two different slave bosons for singly occupied sites, \( s_{i\alpha\sigma} = s_a \) for \( a_{1g} \) and \( s_{i\beta\sigma} = s_e \) for \( e_{g\alpha} \). Eqs. (6) imply

\[
e^2 + 2s^2_a + 4s^2_e = 1; \quad \langle n \rangle = 2s^2_a + 4s^2_e = 1 - x \quad (8)
\]

with \( \langle n \rangle \) the total hole occupancy per site. From Eq. (6), the hopping terms become renormalized as \( t_a(k) \rightarrow q_a t_a(k) \), \( t_e(k) \rightarrow q_e t_e(k) \) and \( t_{ae}(k) \rightarrow \sqrt{q_a q_e} t_{ae}(k) \), where \( q_a = x/(1 - s_a^2) \).

In Fig. 2 we show the resulting dispersion relation for electrons (instead of holes to facilitate comparison with previous works) for three different values of \( x \) near to those measured by ARPES, and the corresponding FS. A comparison with the case \( U = 0 \) in the effective model (not shown), for which the band width is near 0.9 eV, renders it clear the effect of the band narrowing as a consequence of the remaining correlations in the effective model. This renormalized bandwidth is stronger as the Mott insulating limit \( x \to 0 \) is approached. As a consequence of both, the relatively strong trigonal splitting due to the large Co–O covalency and the band renormalization, the hole pockets near the Brillouin zone boundary disappear. We want to stress that if only one of these effects were present, these pockets would remain. In agreement with the most recent ARPES measurements [11], the feature that would give rise to hole-pockets near the \( \Gamma \) point is minimum in the \( \Gamma \) direction (\( \sim 31\% \)) and maximum in the \( \Gamma M \) direction (\( \sim 47\% \)). This indicates that although only one band crosses the \( \epsilon_F \), its character is strongly mixed and cannot be derived from states of \( a_{1g} \) symmetry only.

In summary, we have derived an effective Hamiltonian \( H_{eff} \) to describe the low-energy physics of \( Na_2CoO_2 \), starting from the ground state of \( CoO_6 \) clusters, and calculating the effective hopping between different clusters. Previous calculations of the trigonal distortion and fitting of the XAS experiment using \( CoO_6 \) clusters fixes the parameters of \( H_{eff} \). This \( H_{eff} \) without any new adjustable parameter is able to reproduce the main features of the ARPES experiments.

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\[\begin{align*}
\text{Fig. 2: (Color online) Renormalized band-structures for doping } x = 0.3, 0.5, 0.7 \text{ and corresponding FS in red, green, blue respectively. Larger FS corresponds to lower doping } x.
\end{align*}\]
[27] P. Petrone and A. A. Aligia, Phys. Rev. B 66, 104418 (2002).