Low energy electronic states and triplet pairing in layered cobaltates

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The structure of the low-energy electronic states in layered cobaltates is considered starting from the Mott insulating limit. We argue that the coherent part of the wave-functions and the Fermi-surface topology at low doping are strongly influenced by spin-orbit coupling of the correlated electrons on the $t_{2g}$ level. An effective $t$-$J$ model based on mixed spin-orbital states is radically different from that for the cuprates, and supports unconventional, pseudospin-triplet pairing.

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The layered cobalt oxides Na$_x$CoO$_2$ exhibit a number of remarkable properties with potential applications. At large $x$, they are unconventional metals showing a large thermopower (suppressed by magnetic field) and also signatures of localized magnetic states. Such a mixture of itinerant transport and Curie-Weiss magnetism (“Curie-Weiss metal”) is not easy to reconcile, and there is growing evidences that special charge/orbital ordering correlations are at work at large $x$, 8. Static charge ordering is observed at $x = 0.5$, 2. These observations are not totally unexpected, as a rich interplay between spin/charge/orbital degrees of freedom is a common phenomenon in transition metal oxides. Yet a real surprise and new challenge for theory was the recent discovery of superconductivity at $T_c \sim 5$ K in water-intercalated cobaltates with low sodium content about $x \sim 0.3$. It is believed that the superconductivity of the cobaltates emerges from a correlated metallic state with enhanced electronic mass, and it may have an unconventional, possibly spin-triplet pairing symmetry.

Theoretically, regarding Na$_x$CoO$_2$ as spin 1/2 Mott insulator doped by spinless charge carriers, a $t$-$J$ model similar to that for the high-$T_c$ cuprates has been considered. However, the predicted time reversal violating $d_{1x} + d_{2y}$ singlet state is not supported by experiment, and other proposals employing Fermi-surface nesting and/or charge-density fluctuations have been discussed in favor of spin-triplet pairing.

In this Letter, we show that the relevant $t$-$J$ model for the cobaltates is in fact qualitatively different from its simplest version used in Refs. [10, 11, 12, 13]. The key point is that the low-energy electronic states of the CoO$_2$ layer are derived from the Kramers pseudospin doublets of the Co$^{4+}$-ion with mixed spin and orbital quantum numbers. The projection of the (initially spin-antiferromagnetic) $J$-interaction on the pseudospin states has nontrivial consequences for the internal structure of the Cooper-pairs, leading to novel pseudospin-triplet pairing.

The basic structural element of Na$_x$CoO$_2$ are CoO$_2$ layers, which consist of edge sharing CoO$_6$ octahedra slightly compressed along the trigonal axis. The Co ions form a 2D triangular lattice, sandwiched by oxygen layers. Sodium doping is believed to introduce spinless Co$^{3+}$ states into the spin 1/2 Co$^{4+}$ background.

A minimal model for the cobaltates should include the orbital degeneracy of the Co$^{4+}$-ion, where a hole in the $d^8(t_{2g})$-shell has the freedom to occupy one out of three orbitals $a = d_{xy}$, $b = d_{x^2-y^2}$, $c = d_{yz}$. The degeneracy is partially lifted by trigonal distortion, which stabilizes the $A_{1g}$ electronic state $(a + b + c)/\sqrt{3}$ over the $E'_{g}$-doublet $(e^{\pm i\phi}a + e^{\mp i\phi}b + c)/\sqrt{3}$ (hereafter $\phi = 2\pi/3$). $H_{\Delta} = \Delta[p(E') - 2n(A_{1g})]/3$. The value of $\Delta$ is not known; Ref. [16] estimates it $\sim 25$ meV, while the band structure calculations for a related structure give $\sim 100$ meV.

In terms of the effective angular momentum $l_{eff} = 1$ of $t_{2g}$-shell, the functions $A_{1g}$ and $E'_{g}$ correspond to the $|l_z = 0\rangle$ and $|l_z = \pm 1\rangle$ states, respectively. Therefore, a hole residing on the $E'_{g}$ orbital doublet will experience an unquenched spin-orbit interaction $H_{\lambda} = -\lambda(\vec{l} \cdot \vec{s})$. The constant $\lambda$ for Co$^{4+}$ is about 640 cm$^{-1} \sim 80$ meV. Although $\lambda$ is somewhat smaller than the bare hopping matrix element $t \sim 0.1$ eV in cobaltates (inferred from the free-electron bandwidth $\sim 1$ eV), the spin-orbit coupling strongly affects the coherent motion of the fermions when the quasiparticle bandwidth is reduced by correlation effects to much smaller values $\sim 0.1$ eV.

At $x = 0$, $H = H_{\Delta} + H_{\lambda}$ is diagonalized by a transformation:

$$
\alpha_{\sigma} = \frac{1}{\sqrt{3}} \left[ c_{\sigma} e^{-i\sigma \psi_{\alpha}} f_{\alpha}^+ + i s_{\sigma} f_{\sigma} + e^{i\sigma \psi_{\alpha}} g_{\sigma} + s_{\sigma} e^{-i\sigma \psi_{\alpha}} h_{\sigma} - ic_{\sigma} h_{\sigma}\right] / \sqrt{3},
$$

where $c_{\sigma} = \cos \theta$, $s_{\sigma} = \sin \theta$, $\alpha = (a, b, c)$, and $\psi_{\alpha} = (\phi, -\phi, 0)$, correspondingly. The angle $\theta$ is determined from $\tan 2\theta = 2\sqrt{2\lambda}/(\lambda + 2\Delta)$. As a result, one obtains three levels, $f_{\sigma}, g_{\sigma}, h_{\sigma}$ [see Fig. 1(a)], each of them are Kramers doublets with pseudospin one-half $\bar{\sigma}$. The highest, $f$-level, which accommodates a hole in the $t_{2g}$-shell, is separated from the $g$-level by $\epsilon_f - \epsilon_g = \lambda + \frac{1}{2}(\lambda + 2\Delta)(1/\cos 2\theta - 1)$. This splitting is $\sim 3\lambda/2$ at $\lambda \gg \Delta$, and $\sim \lambda$ in the opposite limit. It is important to observe
that the pseudospin $f_\sigma$ states

$$
|\bar{\uparrow}\rangle_f = i c_\sigma + 1\rangle \downarrow - s_\sigma | 0\rangle \uparrow, \\
|\bar{\downarrow}\rangle_f = i c_\sigma - 1\rangle \uparrow + s_\sigma | 0\rangle \downarrow
$$

(2)

are coherent mixtures of different orbital and spin states, and this will have important consequences for the symmetry of the intersite interactions, as we see below.

We model the band motion by the following Hamiltonian suggested by the edge-shared structure [17]:

$$
H_{t}^{ij} = t(a_{i\sigma}^\dagger \beta_{j\sigma} + \beta_{j\sigma}^\dagger a_{i\sigma}) - t' \gamma_{i\sigma} \gamma_{j\sigma} + h.c.,
$$

(3)

where $t = t_{pd}/\Delta_{pd}$ originates from the $d$-$p$-$d$ process via the charge-transfer gap $\Delta_{pd}$, and $t' > 0$ is the direct $d$-$d$ hopping. On each bond, there are two orbitals ($\alpha, \beta$) active in $d$-$p$-$d$ process, while the third one ($\gamma$) is transferred via the direct $d$-$d$ channel [Fig.1(b)]. The hopping geometry in real situation could, of course, be more complicated (e.g., include $p$-$p$ hoppings). The $t, t'$-model is the simplest possibility chosen for illustrative purposes.

The quasiparticle band structure is obtained within a slave boson approach, where the electron operator is represented as $a_{i\sigma} \Rightarrow e_{i\sigma}^\dagger \xi_{i\sigma} \Rightarrow \sqrt{x} a_{i\sigma} + \text{incoherent part}$. The last equation implies that we consider a fermi-liquid regime, where holons (described by the $e_{i\sigma}$ operator) are condensed, while the $\xi_{i\sigma}$ operators represent coherent fermionic quasiparticles. On the mean-field level (the incoherent part being discarded), this leads to $t \rightarrow t_{coh} \simeq xt$, and one obtains a renormalized hopping Hamiltonian $H_{t}^{coh} \simeq x H_{t}$. While such a Gutzwiller-type approximation fails to capture high-energy electronic processes far from the Fermi level, it is believed to provide a qualitatively correct description of the low-energy states.

Under the transformation (1), the hopping Hamiltonian obtains a rather complicated matrix structure in the full spin/orbital space, and the elements of this matrix sensitively depend on the angle $\theta$. The Hamiltonian $H_{\Delta} + H_{\lambda} + H_{t}^{coh}$ has been diagonalized in momentum space numerically. The obtained quasiparticle dispersion curves are shown in Fig.2(a). The first part to notice is that even for a substantial doping level, $x = 0.3$, there is a clear separation of bands which can be traced back to the on-site level structure discussed above. In particular, we find at small doping that the states near the Fermi level are derived dominantly from the $f$-pseudospin states; therefore, they are dispersive modes with mixed spin-orbital quantum numbers. The "$f$"-band has the bottom at the $\Gamma$-point [23], and shows flat portions near the $K$-points in the Brillouin zone of the triangular lattice, which lead to a singular density of quasiparticle states near the Fermi level [Fig.2(a,b)]. An interesting doping evolution of the Fermi surface (FS) [Fig.2(c)] is also related to the presence of these flat portions. The overall energy window, covered by three quasiparticle bands, is reduced to about $3t$ by correlation effects. The high energy, incoherent electronic states, extending up to a free-electron scale $\sim 9t$, are beyond the present approximation. The consideration of the incoherent part of the electronic motion, which is a difficult task in correlated models in general, is further complicated here because of the additional orbital degrees of freedom.

As far as the low-energy physics at small doping is concerned, we arrived in fact at a single-band picture for states near the FS. However, this band has little to do with a conventional single-orbital band of $A_{1g}$ symmetry suggested by a free-electron band calculations [21] and taken in Refs.[10-13] as a starting point to develop $t$-$J$ model physics for cobaltates. The crucial difference

![FIG. 1:](image1)

![FIG. 2:](image2)
here is that the quasiparticle wave-functions are made of states which do not conserve neither spin nor orbital angular momentum separately; rather, they are build on eigenstates of the total angular momentum, as reflected in Eq. (2). This unusual situation results from the interplay between strong spin-orbit coupling of Co$^{2+}$ ion and the quasiparticle kinetic energy reduced by correlation effects. The main message is that spin-orbit coupling becomes increasingly effective near the Mott insulating limit and is thus essential for the formation of the quasiparticle bands, and hence for the FS topology. This implies that the FS shape at low doping may 

not necessarily be similar to that given by a free-electron picture, as one would expect in single-band systems like the cuprates. In a more general context, the outlined picture might be relevant also to other transition metal oxides, where narrow quasiparticle bands are derived from (quasi)degenerate $t_{2g}$-states with strong spin-orbit coupling, such as compounds based on late-3d, 4d and 5d-ions.

Now we turn to the superexchange interactions which, in analogy with high-$T_c$ cuprates, could be one of the relevant interactions responsible for superconducting pairing. When the FS states are derived from pseudospin states with mixed spin and orbital quantum numbers, an important question arises about implications of such a mixing for the pairing symmetry. Projected on the pseudospin states, the superexchange interactions may in fact give nontrivial pairing channels, which were not present in the original, pure-spin Heisenberg model.

A superexchange Hamiltonian in orbitally degenerate systems reads in general as

$$H_f = J[(\vec{S}_i \cdot \vec{S}_j) \hat{A}_{ij} + \hat{K}_{ij}]$$

The energy scale is $J = 4t^2/E$, where the virtual charge excitation energy $E$ is determined either by the on-site Coulomb $U_d$ or the charge-transfer energy $\Delta_{pd}$, depending on which one is lower. The operators $\hat{A}_{ij}$, $\hat{K}_{ij}$ represent the orbital degrees of freedom. Without orbital degeneracy (e.g., in the cuprates) $\hat{A}_{ij} = 1$, $\hat{K}_{ij} = -1/4$, and $H_f$ supports uniquely singlet pairing. In the present situation, one has to: (i) derive a full structure of the orbital operators $\hat{A}_{ij}$ and $\hat{K}_{ij}$ (which usually depends on the $\langle ij \rangle$-bond orientation in crystal via the hopping geometry [24]), and (ii) project the obtained $H_f$ onto the active pseudospin $f_o$-subspace given by Eq. (2). Details of this lengthy derivation [24] will be presented elsewhere; for our purpose, the result can be conveniently represented in the following form:

$$H_f^{ij} = -Jf \kappa_s \bar{s}^{\dagger}_{ij} s_{ij} - Jf \kappa_s T_{ij}^{\dagger} T_{ij}.$$

Here, $J_f = J/9$ with $J = 4t^2/\Delta_{pd}$. In equation (4), the interactions are separated into pseudospin singlet and triplet channels, namely, $s_{ij} = (f_{ij} f_{ij}^\dagger - f_{ij}^\dagger f_{ij})/\sqrt{2}$, while

$$T_{ij} = a_z t_{ij,0} + a_{xy}(e^{i\phi_3} t_{ij,1} + e^{-i\phi_3} t_{ij,-1})/\sqrt{2},$$

with $t_{ij,0} = i(f_{ij}^\dagger f_{ij}^\dagger + f_{ij} f_{ij}^\dagger)/\sqrt{2}$, $t_{ij,1} = f_{ij}^\dagger f_{ij}^\dagger$ and $t_{ij,-1} = f_{ij} f_{ij}^\dagger$. The phase $\phi_3$ in Eq. (5) and below depends on the $\langle ij \rangle$-bond direction $\delta$: $\phi_3 = (0, \phi, -\phi)$ on $\delta = (12, 23, 13)$-bonds (see Fig.1b), respectively. The relative weights of the different components ($M = 0, \pm 1$ projections of the total pseudospin of the pair) are controlled by the angle $\theta$, defined above, via $a_z = (1 + \cos 2\theta)/2$ and $a_{xy} = \sin 2\theta$. Finally, a constant

$$\kappa_s = 1/2 \left[ \frac{3 \cos 2\theta - 1}{2} \right]^2 + \frac{\Delta_{pd}}{U_d} \left( \frac{3 \cos 2\theta - 1}{2} + t' \right)^2,$$

while for the triplet channel one has $\kappa_t = 3/2$.

In general, the interaction (11) supports both singlet and triplet pairings on the fermi-surface. Certainly, there are also some other pairing forces in the cobaltates; yet it is interesting to explore the outcome of the superexchange interactions alone. We have therefore calculated the mean-field superconducting transition temperatures as function of the parameters involved in our effective $t$-$J$ model for the "$f$"-pseudospin band.

In the singlet channel, it is known [10, 11, 12, 13] that pairing on the triangular lattice is optimized by a complex order parameter $\langle s_{ij} \rangle = D e^{i\phi_3}$ (the degenerate conjugate state is obtained by $\phi_3 \to -\phi_3$). In momentum space, the gap function is determined by $\gamma_d(\vec{k}) = \gamma_1(\vec{k}) + i\gamma_2(\vec{k})$, where $\gamma_1 = \cos k_x - \cos k_y/\cos \sqrt{3}k_z$ and $\gamma_2 = \sqrt{3}\sin k_x \sin \sqrt{\frac{3}{2}}k_y$. This state breaks the time-reversal symmetry.

As suggested by the very form of Eq. (5), the bond dependence of the triplet order parameter is best parametrized according to the projection $M$ of the Cooper-pair pseudospin. Namely, a positive interference among the different $M$-channels is achieved by

$$\langle t_{ij,0} \rangle = d_z, \quad \langle t_{ij,\pm 1} \rangle = d_{xy} e^{\mp i\phi_3}.$$

The pairing amplitudes $d_z$, $d_{xy}$ are proportional to $a_z$ and $a_{xy}$, respectively. The bond arrangement of the phases $e^{-iM\phi_3}$ translates in momentum space into the formfactors $\gamma_z(\vec{k})$ and $\gamma_{xy}(\vec{k}) = \pm \gamma_x(\vec{k}) + i\gamma_y(\vec{k})$, where

$$\gamma_z(\vec{k}) = \sin k_x - 2 \sin k_x \cos \frac{\sqrt{3}k_y}{2},$$

$$\gamma_x(\vec{k}) = \sqrt{3} \cos \frac{k_x}{2} \sin \frac{3k_y}{2},$$

$$\gamma_y(\vec{k}) = \sin k_x + \sin \frac{k_x}{2} \cos \frac{3k_y}{2}. $$

The gap function has no nodes (apart from the $\Gamma$- and $M$-points), and the superconducting gap anisotropy is given by $\Delta(\vec{k}) \propto \sqrt{|a_z \gamma_z|^2 + |a_{xy} \gamma_{xy}|^2}$ which depends on angle $\theta$. Remarkably, the pseudospin-triplet state is nondegenerate and thus respects the time-reversal symmetry. This is because the orbital currents associated with $M = +1$ and $M = -1$ components flow in opposite directions (observe $\pm$ signs in above equations), and the orbital angular momentum of the Cooper-pair is quenched.
The mean-field $T_c$ for the triplet state (assuming the holons are already condensed) is obtained from

$$1 = J_f \sum_{\vec{k}} \frac{|a_{\gamma} \vec{\gamma}|^2 + |a_{\chi} \vec{\gamma}|^2}{2\xi_k} \tanh \frac{\xi_k}{2T_c}, \quad (11)$$

where $\xi_k$ is a "f"-quasiparticle energy. To obtain $T_c$ in the singlet channel, one simply has to replace the numerator in this equation by $(\frac{\xi_k}{\gamma} |\vec{n}_d(\vec{k})|^2$).

Numerical calculations show that for $t' < t$ and $\Delta_{pd}/U_d < 1$ (relevant for cobalt oxides [26]) the triplet state is always favored. Shown in Fig.3 are some plots for $T_c$, calculated for an effective exchange parameter $J_f = 0.05t$ (implying $\sim 5$ meV for $t \sim 0.1$ eV). Nonmonotonic dependences of $T_c$ on doping and the orbital splitting (induced by $c$-axis compression) are due to sensitive variations of the quasiparticle band near the $K$-points of Brillouin zone (Fig.2). We note that the obtained $T_c$-values ($\sim 5$ K for $t \sim 0.1$ eV) and their dependences are qualitatively consistent with experimental data [14,15].

The superexchange driven triplet state is interesting on its own. This state is stabilized by spin-orbit coupling acting on the low-energy states of doped Mott insulator with $t_{2g}$ orbital degeneracy. Its basic features (no time-reversal symmetry breaking, only partial Kight-shift drop below $T_c$, high critical fields $H_{c2}$, etc) are reminiscent to reported data in cobaltates. However, a specific comparison with (ongoing and still controversial) experiments would require that some other relevant physics (electron-phonon coupling, charge-ordering tendencies that are enhanced by orbital-polaron effects [27], phase separation, etc), may need to be included in a more realistic theory. We believe that the present work should be a proper starting point for such a theory.

To conclude, the low-energy Fermi-surface states in the underdoped cobaltates are strongly influenced by spin-orbit interaction intrinsic to the $t_{2g}$ electrons of $\text{Co}^{3+}$. This leads to nontrivial symmetry of the superexchange interactions and to a novel pseudospin-triplet paired state, qualitatively different from that in the high-$T_c$ cuprates. Rather, there might be some common physics between cobaltates and ruthenates [28] and also the recently discovered superconductors $\text{KO}_2\text{S}_2\text{O}_6$ [29], where $\text{Ru}(4d)$- and $\text{Os}(5d)$-electrons with strong spin-orbit coupling reside on nearly degenerate $t_{2g}$ levels.

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