Spin Polaron Theory for the Photoemission Spectra of Layered Cobaltates

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Recently, strong reduction of the quasiparticle peaks and pronounced incoherent structures have been observed in the photoemission spectra of layered cobaltates. Surprisingly, these many-body effects are found to increase near the band-insulator regime. We explain these unexpected observations in terms of a novel spin-polaron model for Co\textsubscript{2}O\textsubscript{2} planes, which is based on a fact of the spin-state quasidegeneracy of Co\textsuperscript{3+} ions in oxides. Scattering of the photoholes on spin-state fluctuations suppresses their coherent motion. The observed “peak-dip-hump” type line shapes are well reproduced by the theory.

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Strongly correlated behavior of electrons is a common property of transition metal oxides. This is because the bandwidth is relatively small compared to the intraionic Coulomb repulsion between the 3\textit{d} electrons. As a result, the celebrated Mott physics \cite{1} forms a basis for understanding the unique properties of oxides, such as the high-$T_c$ superconductivity and a colossal magnetoresistivity.

Recently, attention has focused on the layered cobalt oxides because they exhibit high thermoelectric power \cite{2}, i.e., the capability to transform heat energy into electricity. These compounds consist of triangular lattice Co\textsubscript{2}O\textsubscript{2} planes, separated either by Na layers as in NaCoO\textsubscript{2} \cite{3} or by BiO-BaO layers of rock-salt structure in so-called “misfit” cobaltates (see \cite{4,5}, and references therein). Besides containing the c-axis transport, the Na and BiO-BaO layers introduce also the charge carriers into the Co\textsubscript{2}O\textsubscript{2} planes, such that the valence state of Co ions is varied in a wide range from nonmagnetic band insulators to the strongly correlated Mott limit \cite{5}.

As the $t_{2g}$ shell of Co$^{3+}$ is full, this limit is naturally referred to as a band insulator \cite{6,7}, while Co$^{4+}$ $S$ = 1/2 rich compounds fall into the category of Mott systems because of unquenched spins. It has therefore been thought that layered cobaltates may provide an interesting opportunity to monitor the evolution of electronic states from a weakly correlated band-insulator regime to the strongly correlated Mott limit by hole doping of NaCoO\textsubscript{2} and misfits. Surprisingly, a completely opposite trend is found experimentally. The hallmarks of strong correlations such as magnetic order \cite{3,8}, strong magnetic field effects \cite{2}, etc., are most pronounced closer to the Co$^{3+}$ compositions, while Co$^{4+}$ $S$ = 1/2 rich compounds behave as moderately correlated metals \cite{3,9}. The best thermoelectric performance is also realized near the doped band-insulator regime \cite{4,10}; thus unusual correlations and enhanced thermopower are clearly interrelated. As direct evidence of a complex structure of doped holes, the angular resolved photoemission (ARPES) experiments \cite{5,11} observed line shapes typical for strongly correlated systems. Paradoxically again, the many-body effects in ARPES are enhanced approaching the band-insulator limit \cite{5}.

This Letter presents a theory resolving this puzzling situation in layered cobaltates. We show that holes doped into nonmagnetic band insulators NaCoO\textsubscript{2} and misfits are indeed composite objects with a broad energy-momentum distribution of their spectral functions. Besides reduced quasiparticle peaks, they display also a dispersive incoherent structure as observed \cite{5,11}. The physics behind this unexpected complexity is based on a unique aspect of Co$^{3+}$ ions, i.e., their spin-state quasidegeneracy, and on special lattice geometry of CoO\textsubscript{2} layers.

In oxides, Co$^{2+}$ is always in a high-spin 3/2 state while Co$^{4+}$ ions usually adopt a low-spin 1/2. Roughly, this selection is decided by the Hund coupling favoring high-spin values or by the $t_{2g}$-$e_g$ crystal field splitting 10$Dq$ supporting low-spin states. An intermediate case is realized for Co$^{3+}$ where the $S$ = 0, 1, 2 states compete. This leads to a distinct property Co$^{3+}$ rich oxides called “spin-state-transition” responsible for many anomalies such as spin-state changes in LaCoO\textsubscript{3} \cite{12,13}, and a spin-blockade effect in HoBaCo\textsubscript{2}O\textsubscript{4.5} \cite{14}, to mention a few manifestations of the Janus-like behavior of Co$^{3+}$.

A new situation encountered in layered cobaltates is that CoO\textsubscript{6} octahedra are edge shared. In this geometry, the charge transfer occurs along the 90$^\circ$ Co-O-Co bonds, where the largest matrix element is that between the orbitals of $t_{2g}$ and $e_g$ symmetry (see $i$ process in Fig. 1). This implies that a doped hole dynamically creates $S$ = 1 $t_{2g}$ $e_g^i$ states of Co$^{3+}$ \cite{15}. It is this point where the holes—doped into an initially nonmagnetic background—become many-body objects dressed by virtual spin excitations. Formation of spin polarons suppresses the plane-wave-like motion of holes. However, they gain in the kinetic energy by exploiting the $i$ hopping channel.

The layered structure of cobaltates results in quasi-two-dimensional electronic states as in cuprates. This should
also lower the symmetry of the $t_{2g}$ bands (threefold degenerate in the case of a cubic lattice) that accommodate doped holes. Indeed, ARPES data show a very simple Fermi surface derived from a single band of $a_{1g}$ symmetry [5,11]. This band can be described by the nearest-neighbor Hamiltonian $H_t = -i \sum_{ij \sigma} t_{ij} \tilde{f}_{i \sigma} \tilde{f}_{j \sigma}$, where the fermionic operators $\tilde{f}_i$ represent $a_{1g}$ holes. They are subject to a conventional Gutzwiller constraint (at most one hole at a given site) but this is not much relevant at small density of holes, i.e., near the band-insulator limit. Hence, holes move freely as in a semiconductor.

In contrast, the $t_{2g}$-$e_g$ hopping in Fig. 1(b) represents the many-body process as it produces the $Co^{3+} S = 1$ excitation. The model describing this process has been derived in Ref. [16] and reads as follows:

$$H_t = -\frac{t}{\sqrt{3}} \sum_{ij} [T^\dagger_{i,1,\gamma}(i) f_{j,i}^\dagger f_{i} - T^\dagger_{-i,1,\gamma}(i) f_{j,i}^\dagger f_{i}]
- T^\dagger_{0,\gamma}(i) \frac{1}{\sqrt{2}} (f_{j,i}^\dagger f_{i} - f_{j,i} f_{i}^\dagger) + \text{H.c.}].$$

(1)

Here, $T$ is the spin-triplet excitation generated by hopping of an electron from $Co^{3+}$ to the $e_g$ level of $Co^{4+}$ (described as hole motion). The process, of course, conserves the total spin. In addition, the direction $\gamma$ of the bond $(ij)$ selects the $e_g$ orbital involved in the $t$ process [see Fig. 1(c)], according to $E_g$ symmetry relations between $T_\gamma$ operators:

$$T_{\gamma} = T_{3\gamma^2 - r^2}, T_{\alpha/\beta} = -\frac{1}{2} T_{3\gamma^2 - r^2} \pm \frac{1}{2} T_{r^2 - y^2}.$$

Based on this model, we develop a theory for the photoemission experiments in cobaltates. It is evident from (1) that by creating and destroying $T$ excitations as they propagate, the holes are strongly renormalized and we deal with a spin-polaron problem. This resembles the problem of doped Mott insulators like cuprates; however, the nature of spin excitations is different here because of the nonmagnetic ground state. Instead of magnonlike propagating modes as in cuprates, fluctuations of the very spin value of $Co^{3+}$ ions are the cause of the spin-polaron physics in cobaltates [17].

For the calculation of the fermionic self-energies, we employ the self-consistent Born approximation [see Fig. 1(e)], which has extensively been used in the context of spin polarons in cuprates [21]. First, we focus on the spin-excitation spectrum. Since a direct $e_g$-$e_g$ hopping in case of 90° bonds is not allowed by symmetry, the bare $T$ spin excitation is a purely local mode, at the energy $E_T$. The coupling to the holes in (1) shifts and broadens this level. Accounting for this effect perturbatively [see Fig. 1(d)], we obtain the $T$ Green’s function $D^{\dagger}(i\omega) = i\omega - E_T - \Sigma_T(i\omega)$ with

$$\Sigma_T(i\omega) = \frac{2g^2}{3\beta} \sum_{kk'\sigma} \Gamma_k G_0(k, i\epsilon) G_0(k', i\epsilon + i\omega).$$

(2)

Here, $G_0$ is the bare electron propagator $G_0(k, i\epsilon) = (i\epsilon - \xi_k)^{-1}$ with the $a_{1g}$ dispersion on a triangular lattice $\xi_k = -2t(c_a + c_b + c_c) + \mu$, where $c_{\gamma} = \cos k_{\gamma} k_{\gamma}$ and $k_{\gamma}$ are the projections of $k$ on $a, b, c$ directions. The underlying $E_g$ symmetry of $T$ operators involved in $t$ hopping results in the factor $\Gamma_k = c_a^2 + c_b^2 + c_c^2 - c_a^2 c_b^2 - c_b c_c - c_c c_a$. We neglected a weak momentum dependence of $\Sigma_T$ for the sake of simplicity. This is justified as long as $\Sigma_T$ is small compared to the spin gap $E_T$.

Further, we approximate $\Gamma_k$ by its Brillouin-zone average $3/2$, obtaining the simple expressions for $\Sigma_T$ in terms of bare fermionic density of states $N_0(x) = \sum_k \delta(x - \xi_k)$:

$$\text{Im} \Sigma_T(E) = -\pi T^2 \int_{-E}^0 dx N_0(x) N_0(x + E),$$

(3)

$$\text{Re} \Sigma_T(E) = -\pi T^2 \int_{-\infty}^0 dx \int_{-\infty}^\infty dy \frac{N_0(x) N_0(x + y)}{y^2 - E^2}.$$ (4)

These equations determine the renormalized spin-excitation spectrum $\rho_T(E) = -\pi T^2 \text{Im} \Sigma(T)(i\omega \rightarrow E + i\delta)$ used below for calculation of the fermionic self-energy.

The self-energy diagram in Fig. 1(e) reads as

$$\Sigma(k, i\epsilon) = -\frac{2g^2}{\beta} \sum_{k',\sigma} [\Gamma_{k'} D(-i\epsilon) + \Gamma_k D(i\omega)] \times G(k', i\epsilon + i\omega),$$

(5)

where $G^{-1}(k, i\epsilon) = i\epsilon - \xi_k - \Sigma(k, i\epsilon)$. We can write...
\[ \Sigma_k(\omega) = 2\tilde{t}^2[\Phi(\omega) + \Gamma_k \Xi(\omega)], \]

\[ \Phi(\omega) = \int_0^\infty dE \rho_\perp(E) \int_0^\infty \frac{dx}{\omega - E - x + i\delta}. \tag{6} \]

\[ \Xi(\omega) = \int_0^\infty dE \rho_\perp(E) \int_{-\infty}^0 \frac{dx}{\omega + E - x + i\delta}. \tag{7} \]

The full local density of states \( N(E) = \sum_k A(k, E) \) and its \( E_g \) symmetry part \( \tilde{N}(E) = \sum_k \Gamma_k A(k, E) \) are functions of the self-energy itself, via the spectral functions \( A(k, E) = -\pi^{-1} \text{Im} G(i\epsilon \rightarrow E + i\delta) \). The above equations are thus to be solved self-consistently.

Next, we test the reliability of approximations made. To this end, we performed an exact diagonalization of our model \( H = H_1 + H_\Gamma \) on a \( \sqrt{3} \times \sqrt{3} \) hexagonal cluster [Fig. 2(d)]. We inject one hole on such a cluster and calculate its spectral function

\[ A(k, E) = -\frac{1}{\pi} \text{Im}(\text{GS} f_{k,s}(\tau - H)^{-1} f_{k,s}^\dagger |\text{GS}), \tag{8} \]

where \( \tau = E + E_{\text{GS}} + i\delta \). Since the ground state \( |\text{GS}\rangle \) contains no holes and the single hole on the cluster represents 1/7 doping, the effective doping is about 10%. Periodic boundary conditions allow us to access two nonequivalent \( k \) points [see Fig. 2(d)]. To obtain continuous profiles of \( A(k, E) \), we broaden the excited states.

![FIG. 2. Comparison of the analytical results at 10% doping (left) and from exact diagonalization (right). (a) Spectral functions and a quasiparticle weight \( Z \) obtained from Eqs. (2) and (5) with bare \( E_T = 1.2t \) (renormalized to \( E_T/t \approx 1 \) by interactions) and (b) the corresponding density of states \( N(E) \). The incoherent structure dominates \( N(E) \). A peak around \( 2t \) corresponds to the van Hove singularity smeared by interaction effects. (c) Spectral functions from exact diagonalization at \( E_T/t = 1 \). (d) The 7-site cluster in direct space (the dashed line defines the supercell) and in reciprocal space (full line is the Brillouin zone boundary). The allowed \( k = \Gamma, X \) points are indicated by • and ◦.](https://example.com/fig2)

![FIG. 3 (color online). Intensity map of the spectral density \( A(k, E) \) of the Co^{1+} holes along the \( M-\Gamma-K \) path in the Brillouin zone calculated at 30% doping and \( E_T = 2t \). As the hole energy reaches the renormalized spin-excitation energy \( E_T \), the qp peak broadens and its weight is transferred to a broad, incoherent structure. This results in a "peak-dip-hump" profile of \( A(k, E) \) seen also in Fig. 2. The top of the smoothed hump structure is indicated by triangles. The dashed line shows the bare dispersion. The Fermi surface is shown in the inset.](https://example.com/fig3)
tion of \( S = 1 \) excitations becomes very intense and a broad incoherent response develops, leading to the pronounced “peak-dip-hump” structure of \( A(k, E) \). Following the maximum of the smoothed hump structure, we observe its strong dispersion (stemming also from incoherent \( \gamma \) hopping).

Figure 3 suggests a possible determination of \( \tilde{E}_T \) from the quasiparticle damping. To address this problem, in Fig. 4 we show the energy width of the qp peak following its dispersion curve. The sharp onset of the damping at the binding energy \( -1.4t \) is clearly related to the maximum of the spin-excitation spectral function \( \Gamma(E) \). In addition, Fig. 4 shows the weight of the qp peak, which is \( k \) dependent (mainly due to the matrix element \( \Gamma_k \)).

Comparison of Figs. 3 and 4 with the data of Refs. [5,11] reveals a remarkable correspondence between theory and experiment. In particular, both the qp peak and the hump dispersions (see Figs. 2 and 3 of Ref. [5]) are well reproduced by theory, considering \( \gamma = 0.1 \) eV suggested by the band structure fit [24]. The onset energy \( \tilde{E}_T \approx 1.4t \) for the qp damping (Fig. 4) is then \( \approx 0.14 \) eV, in agreement with experiment [see Fig. 2(c) of Ref. [5]]. Physically, dilute spin polarons are expected to be pinned by disorder, thus qp peaks should be suppressed at low hole doping.

To summarize, we have presented a theory for the photoemission experiments in layered cobaltates. A strong damping of quasiparticles, their reduced spectral weights, broad and dispersive incoherent structures, and “peak-dip-hump” type line shapes all find a coherent explanation within our model. We thus conclude that unusual correlations observed near the band-insulator regime are the direct manifestation of the spin-state quasidegeneracy of Co ions, and this intrinsic feature of cobaltates should be the key for understanding their unique properties, such as the high thermopower. In particular, the spin-polaronic nature of holes should be essential for explanation of its remarkable magnetic field sensitivity [2].

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[15] \( t_\sigma^2 e^2_S/\hbar \) = 2 configuration is not accessible by hopping.
[17] In contrast to Refs. [18,19], where a static hole surrounded by \( S = 1 \) Co\(^{3+} \) ions was studied, in the present model the triplet \( S = 1 \) excitations are virtual and generated dynamically by the very motion of the hole via the \( \gamma \) process. These two pictures can merge if a hole is strongly trapped (e.g., by Na potential [20]).
[24] S. Zhou et al., Phys. Rev. Lett. 94, 206401 (2005), find the nearest-neighbor interorbital hopping \( t' = -157.8 \) meV. Projection to the \( a_{i\gamma} \)-hole subband yields [16] \( t = -2t'/3 \approx 0.1 \) eV.