The low-energy ARPES and heat capacity of Na$_{0.3}$CoO$_2$: A DMFT study

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We use the dynamical mean-field theory (DMFT) to calculate the angle resolved photoemission spectrum (ARPES) and heat capacity for Na$_{0.3}$CoO$_2$. Both the traditional Hirsch-Fye Quantum Monte-Carlo technique and the newly developed continuous time quantum Monte-Carlo technique are used to solve the DMFT impurity problem. We show that the $e'_g$ hole pockets on the Fermi surface are suppressed as the on-site coulomb repulsion is increased. A quantitative comparison with ARPES experiments and bulk heat capacity measurements indicate that the on-site coulomb repulsion is large relative to the LDA bandwidth.

The cobaltates have demonstrated a wide variety complex behavior. The Na rich region of the phase diagram displays various degrees of anomalous behavior, such as Curie-Weiss behavior near a band insulator[1], charge disproportionation[2], and non-Fermi-liquid behavior in the resistivity[3]. Alternatively, the Na poor region of the phase diagram appears to be a Fermi-liquid. The magnetic susceptibility displays Pauli behavior, the resistivity is roughly quadratic at low temperatures[1], and the system appears to be homogeneous[2]. Therefore, the Na poor region of the phase diagram seems like a natural starting point to attempt to explain the ARPES experiments and heat capacity measurements from a quantitative standpoint.

In Na$_x$CoO$_2$, the cubic component of the oxygen crystal field splits the Co d manifold into a set of 3-fold $t_{2g}$ orbitals and 2-fold $e_g$ orbitals, while the trigonal component will further split the $t_{2g}$ orbitals into $a_{1g}$ and $e'_g$. The nominal valence of Co in this system will be $4 - x$, so the Fermi-energy will fall within the $t_{2g}$ manifold. The LDA band structure displays two degenerate eigenvalues and one non-degenerate eigenvalue at the $\Gamma$-point, corresponding to the $e'_g$ and $a_{1g}$ eigenvectors. The splitting between the eigenvalues is roughly $1 \text{eV}$ with the $e'_g$ levels below the Fermi energy and the $a_{1g}$ above. Despite this distinct splitting at the $\Gamma$-point, the on-site orbital energies are nearly degenerate. Additionally, the projected density-of-states (DOS) clearly show that the $a_{1g}$ orbital character is strongest at the top and bottom of the band while the $e'_g$ is present through most of the energy range of the $t_{2g}$ bands. The Fermi surface consists of a large $a_{1g}$ pocket around the $\Gamma$-point and six small $e'_g$ satellite pockets[3].

Several experimental ARPES studies have been performed for Na$_{0.3}$CoO$_2$ [4, 5, 6, 7]. A general caricature of the LDA bands can be seen in the ARPES. The most notable difference as compared to LDA is the significant narrowing of the bands, and the suppression of the $e'_g$ pockets below the Fermi energy. Two previous studies addressed the effect of correlations on the electronic structure for $x = 0.3$, and they reached completely opposite conclusions. Zhou et al performed Gutzwiller calculations for a three-band model corresponding to the LDA $t_{2g}$ band structure[5]. Using an infinite on-site coulomb repulsion, they show that the quasi-particle bands are significantly narrowed and the $e'_g$ hole pockets are pushed beneath the Fermi surface. Although the removal of the $e'_g$ pockets agrees with the ARPES experiments, it is not clear if $U = \infty$ is an excessive assumption and therefore smaller values of the on-site coulomb repulsion must be considered. Ishida et al[6] performed DMFT calculations for the three-band $t_{2g}$ states of the cobaltates and found that electronic correlations narrow the bands and enhance the $e'_g$ hole pockets, completely opposite to what was found by Zhou et al.

Singh et al. have proposed that the inclusion of the realistic ordering of the Na destroys the $e'_g$ hole pockets, as demonstrated by LDA calculations for Na$_{0.7}$CoO$_2$[10]. Given that the pockets will inevitably be destroyed as $x \to 1$ because the chemical potential moves towards the top of the $t_{2g}$ bands, Na$_{0.7}$CoO$_2$ is an extremely liberal test case in which the pockets are barely present in the first place. Previous LDA calculations of the realistic structure which explicitly included the Na, both with and without water, had already shown that LDA predicts the survival of the pockets for Na$_{0.47}$CoO$_2$[11, 12], even when including full structural relaxations[11]. Therefore, one can safely conclude that the Na potential is not the dominant mechanism which destroys the pockets in Na$_{0.3}$CoO$_2$.

In this study, we resolve the issue of the qualitative behavior of the pockets. We calculate the ARPES spectrum and the heat capacity at a range of different $U$ in order to determine the best agreement with experiment. In particular, we focus on the presence or absence of the pockets, the linear coefficient of the heat capacity, and the average Fermi velocity measured in ARPES. The presence or absence of the pockets will have important consequences for the heat capacity given that they are the dominant contribution to the DOS at the Fermi energy, and therefore these two issues are intimately connected.

We perform DMFT calculations for the $t_{2g}$ bands of the
cobaltates, represented by the following Hamiltonian:

$$
H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_{\alpha \beta \sigma} U^{\alpha \beta}_{\sigma} n_{i\alpha \sigma} n_{i\beta \sigma} + \sum_{i \sigma} \Delta (n_{a_{1g} i \sigma} - n_{e'_{g} i \sigma})
$$

(1)

where $\alpha, \beta$ are the orbital indices (ie. $a_{1g}$ and $e'_{g}$), $i,j$ are site indices, $\sigma$ is the spin index, and $\Delta$ is the crystal-field splitting between the $a_{1g}$ and $e'_{g}$ orbitals. We use the low-energy hopping parameters $t_{ij}$ and $\Delta$ which were fit to the LDA $t_{2g}$ bands by Zhou et al \cite{13}, allowing for a direct comparison. Ishida et al did not publish their hopping parameters, but they appear to be similar given the respective bare DOS which were published \cite{9}. We assume the traditional orbital-independent double counting \cite{13} of $U(N - \frac{1}{2})$, and therefore the Hartree-Fock terms generated by DMFT will be relevant. Below we will show that $\Delta$ is a key parameter in determining the fate of the $e'_{g}$ pockets and therefore the heat capacity. Given that LDA is only an approximate technique to generate the low energy hopping parameters, we will systematically explore the effect of $\Delta$ on the results. The LDA value fit by Zhou et al is roughly $\Delta = -10 meV$, and therefore the on-site orbital energies are nearly degenerate. Alternatively, quantum chemistry calculations \cite{14} yield a value of $300meV$, so one might anticipate $-10 meV \leq \Delta \leq 300 meV$.

DMFT maps the interacting lattice problem onto an impurity problem where the non-interacting bath function is determined self-consistently \cite{13}. The effective impurity problem is solved using two different impurity solvers to ensure that the answer is robust. The traditional Hirsch-Fye quantum Monte Carlo (HFQMC) method was used (see ref \cite{13} for detailed review), in addition to the newly developed continuous time quantum Monte Carlo (CTQMC) method \cite{15, 16}. CTQMC is generally more efficient than the HFQMC and allows one to access significantly lower temperatures and larger $U$.

The $e'_{g}$ pockets are observed in the k-space direction corresponding to the real-space direction which connects nearest-neighbor Co atoms. ARPES experiments predict the $e'_{g}$ pockets to be below the Fermi energy \cite{4, 5, 6, 7}, and this is supported by the analysis of the de Haas van Alphen experiments \cite{18}. Given that two previous theoretical studies reach opposite conclusions regarding the fate of the $e'_{g}$ pockets, we explore this question in detail. When determining the Fermi surface from the Dyson equation, only the bare Hamiltonian and the self-energy at zero frequency are needed \cite{18}. Within single-site DMFT the self-energy is momentum-independent and therefore the self-energy at zero frequency acts as a renormalization of the on-site $e'_{g}$ and $a_{1g}$ energy levels. Therefore, it is useful to reverse-engineer this problem and determine what effective $e'_{g}$ and $a_{1g}$ levels are needed to destroy the pockets. This is not a-priori obvious given that the neighboring $e'_{g}$-$a_{1g}$ hopping is comparable to the $a_{1g}$-$a_{1g}$ hopping. We find that the pockets are completely insensitive to perturbations of the $a_{1g}$ on-site energy. The pockets are destroyed when the $e'_{g}$ on-site energy is shifted down by roughly 70 meV, independent of the value of the perturbation of the $a_{1g}$ level, and therefore the criterion for the destruction of the pockets is $\Sigma_{g} - \mu < -70 meV$. This is an important observation which indicates that a relatively small perturbation of the $e'_{g}$ on-site energy will destroy the pockets. DMFT calculations can now be performed to determine when this criterion is satisfied.

![FIG. 1: a.) $e'_{g}$ orbital occupation as a function of $U$. The $a_{1g}$ orbital occupation can be found from the relation $n_{a_{1g}} = 5.3 - 2n_{e'_{g}}$. HFQMC and CTQMC calculations were performed at $\beta = 40 eV^{-1}$ and $\beta = 100 eV^{-1}$, respectively. Filled points indicate that the pockets have been destroyed. b.) The self-energy of the $e'_{g}$ orbital at zero frequency minus the chemical potential for various values of the crystal field splitting $\Delta$ ($\Delta = -10 meV$) corresponds to the LDA crystal field.](image-url)
ties for Na
function. The experimentally measured heat capac-
ponds to the orbital index and
ρ that the heat capacity is 14.27 mJ
are quantitatively similar for small
The two solvers agree completely on a qualitative level,
errors within the HF method. We also plot the orbital
U indicates an enhancement of orbital polarization as U
increased, consistent with the destruction of the pockets.
This conclusion is found for both the CTQMC and
HFQMC impurity solvers.

erations enhance the pockets, and the balance of these
relations diminish the pockets while the dynamic corre-
lations enhance the pockets, and the net effect is that increasing interactions
DIMinishes the pockets. The preceding analysis is true
on-site energy is required to destroy the pockets, we be-
lieve that it is useful to probe the behavior of the self-
energy for other values of Δ as rationalized above. The
CTQMC calculations were repeated for ∆ = 50
meV and ∆ = 100meV. As anticipated, starting with a crystal
field splitting which diminishes the pockets acts coopera-
tively with interactions and causes the system to polarize
more and the pockets to be destroyed for a smaller
U (see figure 1 a and b). For ∆ = 50meV the pockets
are destroyed for U ≥ 2.0eV, while for ∆ = 100meV the
pockets are destroyed for U ≥ 1.0eV. Therefore, we con-
clude that the value of U required to destroy the pockets
depends strongly on the value of ∆.

Our findings are in qualitative agreement with Zhou
et al[8] and in qualitative disagreement with Ishida et
al[9]. It is not clear why the results of Ishida et al are
different, but it is likely the result of differences in the
bare Hamiltonian. Above we showed that the static cor-
relations diminish the pockets while the dynamic corre-
lations enhance the pockets, and the balance of these
two effects will be influenced by the bare Hamiltonian.
Regardless, our following analysis of the Fermi velocity
and heat capacity will demonstrate that the destruction
of the pockets is the only viable possibility to achieve
agreement with experiment.

Having understood the behavior of the pockets, we
now compute the linear coefficient of the heat capacity,
γ. We use Fermi-liquid theory to calculate γ from
the DOS at the Fermi energy and the quasiparticle weight
Z which is calculated in our QMC calculations. Math-
ematically, we have
\[
\gamma = \frac{2\pi^2}{3} \sum_{\alpha} \rho_{\alpha}(0)
\]
where α corresponds to the orbital index and ρ is the local spectral
function. The experimentally measured heat capacities
for Na$_3$CoO$_2$ are found to be in the range of 12-16
mJ mol$^{-1}$Co$^{-1}$K$^{-2}$[20, 21, 22, 23, 24, 25]. We begin by noting
that the heat capacity is 14.27 mJ mol$^{-1}$Co$^{-1}$K$^{-2}$ for the LDA
hoppings, which is already within the bounds of experi-
mental measurements. This may mislead one to believe
that correlations are negligible, but a more careful exam-
ination shows otherwise. The DOS at the Fermi energy
initially decreases weakly as U increases and eventually
drops in a discontinuous fashion, which signifies the de-
struction of the pockets (see figure 2). The quasiparticle
weight also decreases as U increases. Given that the lin-
ear coefficient of the heat capacity is proportional to the
ratio $\rho(\varepsilon_f)/Z$, the overall effect is not apriori obvious. The
heat capacity initially increases as U increases, then dis-
continuously drops when the pockets are destroyed, and
eventually plateaus for large $U$. Increasing $\Delta$ causes the drop in the heat capacity to occur at smaller values of $U$ and a overall lower value for the heat capacity. In order to achieve agreement with experimental measurements of the heat capacity, one needs a relatively large $U = 6eV$ when using the LDA $\Delta$, and even larger $U$ is needed for larger $\Delta$. A key point is that if the pockets are retained, the $\gamma$ becomes excessively large as $U$ increases. Given that the ARPES indicates that the bandwidth is nearly halved as compared to LDA, an appreciable $U$ must be present to narrow the LDA bands and if the pockets were still present the heat capacity would be excessive as compared to experiment. It is reasonable to expect that the heat capacity should be under-predicted when only considering the Hubbard model. There will likely be electron-phonon coupling to the local breathing mode of the octahedron, or perhaps other modes, which will induce a narrowing of the bands and therefore an enhancement of the heat capacity.

The experimentally measured Fermi velocity may also be calculated as a function of $U$ (see figure 2). Increasing the $U$ decreases the quasiparticle weight $Z$ and therefore decreases the Fermi velocity. In order to achieve velocities comparable with experiment, one needs a relatively large $U > 3eV$. This is another piece of evidence, independent of the heat capacity measurements, which indicates that the $U$ must be relatively large. Once again, if the $U$ is large then the pockets must be absent in order to get acceptable agreement with the heat capacity.

Both impurity solvers used in this study work on the imaginary axis, and therefore one must perform an analytic continuation to access real frequency quantities like the ARPES spectrum. Various approaches exist to perform the analytic continuation, but all are approximate. We expand the self-energy to first-order, which allows an exact analytic continuation, and use the resulting self-energy to construct the low energy ARPES spectrum (see figure 3). The first case corresponds to the $\Delta = -10meV$ and $U = 6eV$, the minimum to destroy the pockets for this case (see figure 3a). As shown, the pockets are too close to the Fermi energy, and the bands are excessively narrow as compared to experiment. Increasing to $U = 10eV$ will further sink the pockets, but it will also to continue to narrow the bandwidth. Alternatively, one may decrease the $U$ slightly if the $\Delta$ is increased as the pockets are suppressed at a much lower $U$. Therefore, we examine the ARPES for $\Delta = 50meV$ and $U = 4eV$, and $\Delta = 100meV$ and $U = 4eV$ (see figure 3b and 3c). Decreasing $U$ and increasing $\Delta$ increases the bandwidth and pulls the pockets down further, putting the result in better agreement with experiment. This analysis suggests that optimum $U$ should be chosen from the lower end of the range of values deduced from the analysis of the heat capacity and the velocity, and that $\Delta$ should be slightly larger than the one deduced from LDA.

In conclusion, we have examined the issue of the $e'_g$ pockets, the value of the linear coefficient of the heat capacity, and the Fermi velocity. We have demonstrated that increasing interactions destabilize the $e'_g$ pockets and pushes them beneath the Fermi energy. This is in agreement with previous calculations of Zhou et al[8] and in disagreement with previous calculations of Ishida et al[9]. Reasonable agreement can be achieved with both bulk heat capacity measurements and the Fermi velocity measured by ARPES when using an on-site coulomb repulsion which is several times the LDA bandwidth (ie. $U > 4eV$).

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