Quasiparticle Dispersion and Heat Capacity of $Na_{0.3}CoO_2$: A Dynamical Mean-Field Theory Study

C. A. Marianetti,[1] K. Haule,[1] and O. Parcollet[2]

[1]*Department of Physics and Astronomy and Center for Condensed Matter Theory, Rutgers University, Piscataway, New Jersey 08854-8019, USA*

[2]*Service de Physique Theorique, CEA/DSM/SPhT-CNRS/SPM/URA 2306 CEA/Saclay, F-91191 Gif-Sur-Yvette, France*

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We use the dynamical mean-field theory to calculate the Fermi surface and heat capacity for $Na_{0.3}CoO_2$. We resolve the conflicting outcomes of previous calculations by demonstrating that the nature of the calculated Fermi surface depends sensitively upon the bare Hamiltonian, and, in particular, the crystal-field splitting. By calculating both the Fermi surface and the heat capacity, we show that the only conclusion consistent with angle-resolved photoemission and heat capacity measurements is that the e_g' pockets are not present at the Fermi surface.

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The cobaltates have demonstrated a wide variety of complex behavior. The Na rich region of the phase diagram exhibits various signatures of non-Fermi-liquid behavior, while the Na poor region displays Fermi-liquid behavior [1,2]. Therefore, the Na poor region of the phase diagram seems like a natural starting point to explain the angle-resolved photoemission experiments (ARPES) and heat capacity measurements from a quantitative standpoint.

In Na_xCoO_2, the cubic component of the oxygen crystal field splits the Co d manifold into a set of threefold t_{2g} orbitals and twofold 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 is Co^{4-x}, so the Fermi energy will fall within the t_{2g} manifold. The Fermi surface calculated with the local density approximation (LDA) consists of a large a_{1g} pocket around the Γ point and six small e_g' satellite pockets [3].

Several experimental ARPES studies have been performed for $Na_{0.3}CoO_2$ [4–7]. 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 contradictory conclusions. Zhou *et al.* performed Gutzwiller calculations for a three-band model corresponding to the LDA t_{2g} band structure [8]. Using an infinite on site Coulomb repulsion, they show that the quasiparticle 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.* [9] performed dynamical mean-field theory (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.* [8]. Lechermann *et al.* suggested that the behavior of the pockets will be dictated by a delicate balance of the orbital filling, bandwidths, crystal-field splitting, and exchange, based on a general study of multiband systems [10]. Singh and Kasinathan have proposed that the inclusion of the realistic ordering of the Na destroys the e_g' hole pockets, as demonstrated by LDA calculations for $Na_{0.7}CoO_2$ [11]. However, previous LDA calculations for $Na_{1/3}CoO_2$ which include the realistic Na ordering demonstrate that the pockets are still present [12,13].

Experiments which indirectly probe the Fermi surface have reached varying conclusions regarding the status of the e_g' pockets. Balicas *et al.* performed both Shubnikov–de Haas experiments in addition to heat capacity measurements [14]. The authors noted that the presence or absence of the e_g' pockets will have important consequences for the heat capacity given that they are the dominant contribution to the density of states (DOS) at the Fermi energy, and the authors conclude that the pockets are not present. Alternatively, Rueff *et al.* measured the phonon dispersion via inelastic x-ray scattering and concluded that the softening of the optical modes was due to the presence of the e_g' pockets at the Fermi energy [15]. Laverock *et al.* used x-ray Compton scattering to measure the electron momentum distribution and concluded that the e_g' pockets are present at the Fermi surface [16].

In this study, we resolve the issue of the qualitative behavior of the e_g' pockets. We calculate the Fermi surface 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 e_g' pockets, the linear coefficient of the heat capacity, and the average Fermi velocity of the central a_{1g} pocket measured in ARPES. We perform DMFT calculations for the t_{2g} bands of the cobaltates, represented by the following Hamiltonian:

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

where α, β are the orbital indices (i.e., a_{1g} and e'_g), i, j are site indices, σ is the spin index, and Δ is the crystal-field splitting between the a_{1g} and e'_g orbitals. We use the low-energy hopping parameters $t_{\alpha\beta}$ and Δ which were fit to the LDA t_{2g} bands by Zhou *et al.* [8] (hereafter referred to as $H^0_k[Z]$), in addition to the parameters of Ishida *et al.* [9] and Johannes and Liebsch [17] (hereafter referred to as $H^0_k[I]$). We assume the traditional orbital-independent double counting [18], consistent with the LDA orbital-independent potential. Below we will show that Δ 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 Δ on the results. $H^0_k[Z]$ has $\Delta = -10$ meV, while $H^0_k[I]$ has $\Delta = -130$ meV. Alternatively, quantum chemistry calculations [19] yield a value of 300 meV, so one might anticipate $-130 \leq \Delta \leq 300$ meV. An on site exchange interaction may be included, but this does not have an appreciable effect when U is large as the ground state of the system is dominated by d^5 configurations which are not affected by on site exchange.

DMFT maps the interacting lattice problem onto an impurity problem where the noninteracting bath function is determined self-consistently [20]. The effective impurity problem is then solved using the continuous time quantum Monte Carlo (CTQMC) method [21,22]. When determining the Fermi surface from the Dyson equation, only the bare Hamiltonian and the self-energy at zero frequency are needed [10]. 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. We find that the pockets are completely insensitive to perturbations of the a_{1g} on site energy. The pockets are suppressed when the e'_g on site energy is decreased by roughly 70 meV for $H^0_k[Z]$ and 90 meV for $H^0_k[I]$, independent of the value of the perturbation of the a_{1g} level. Therefore the criterion for the suppression of the pockets for $H^0_k[Z]$ and $H^0_k[I]$ corresponds to $\Sigma_{e'_g} - \mu < -70$ meV and $\Sigma_{e'_g} - \mu < -90$ meV, respectively. 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.

The qualitative behavior of $\Sigma_{e'_g} - \mu$ is distinctly different for the two respective Hamiltonians. For $H^0_k[Z]$, $\Sigma_{e'_g} - \mu$ is a monotonically decreasing function of U, which indicates that the pockets are *diminished* with increasing interactions (see Fig. 1). In this case, the pockets are pushed beneath the Fermi surface for $U > 6$ eV. For $H^0_k[I]$, $\Sigma_{e'_g} - \mu$ decreases only at small U and then increases as U is increased. This indicates that the pockets are only diminished at small U, as dictated by Hartree-Fock, and are *enhanced* as U is further increased. Therefore, the fate of the e'_g pockets depends sensitively upon the bare Hamiltonian. We thus confirm that both previous studies are essentially technically correct, and coincidentally the respective bare Hamiltonians were straddling the dividing line between enhancing and diminishing the e'_g pockets as a function of increasing U. In order to better understand these results, we consider the individual behavior of both the dynamical and static portions of the self-energy. Considering the dynamical portion of the self-energy [i.e., $\Sigma_{\rm dyn}(i\omega) = \Sigma(i\omega) - \Sigma(\infty)$], we find that $\Sigma^{e'_g}_{\rm dyn}(0) > \Sigma^{a_{1g}}_{\rm dyn}(0)$, but this is countered by the fact that $\Sigma^{a_{1g}}(\infty) > \Sigma^{e'_g}(\infty)$. The static contribution of the self-energy diminishes the pockets while the dynamical part enhances the pockets, and the winner of this competition depends on the details of the bare Hamiltonian (i.e., the initial density matrix, etc.). We also plot the orbital occupations as a function of U (see Fig. 1), which track the behavior of the self-energy at zero frequency.

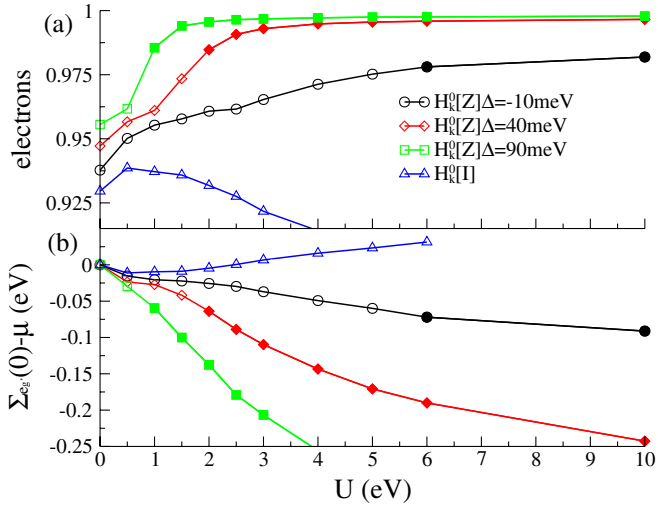

FIG. 1 (color online). (a) e'_g orbital occupation as a function of U. The a_{1g} orbital occupation can be found from the relation $n_{a_{1g}} = 5.3 - 2n_{e'_g}$. All calculations were performed at $\beta = 100$ eV^{-1}. Filled points indicate that the pockets have been suppressed. (b) The self-energy of the e'_g orbital at zero frequency minus the chemical potential for various values of the crystal-field splitting Δ.

Having established the qualitative behavior of the pockets, we continue with more quantitative analysis. Given that only a 70–90 meV downward shift of the e'_g on site energy is required to destroy the pockets, we believe that it is useful to probe the behavior of the self-energy for other values of Δ as rationalized above. The CTQMC calcula-

tions for $H_k^0[Z]$ were repeated for $\Delta = 40$ meV and $\Delta = 90$ meV As anticipated, a larger crystal-field splitting causes the system to polarize more and the pockets to be suppressed for a smaller U (see Fig. 1). Therefore, we conclude that the value of U required to destroy the pockets depends strongly on the value of Δ. This qualitative behavior also holds for $H_k^0[I]$, as increasing Δ by 50 meV for $H_k^0[I]$ causes the pockets to be *suppressed* as U is increased (not shown in the figure). In summary, we have shown that both the qualitative and quantitative behavior of the e_g' pockets as a function of U are highly sensitive to the small changes in crystal-field splitting.

Extracting a bare Hamiltonian from a density functional theory (DFT) calculation involves a degree of uncertainty, and therefore one must probe the dependence of physical observables on the critical model parameters (i.e., Δ and U). Given that the presence or absence of the e_g' pockets at the Fermi surface sensitively depends on the bare Hamiltonian, we additionally compute the heat capacity and the Fermi velocity of the central a_{1g} Fermi surface pocket. The heat capacity is very sensitive to the presence of the e_g' pockets at the Fermi surface, while the velocity of the central a_{1g} pocket is not and therefore it serves as an independent means to determine the lower bound for the value of U. Increasing U decreases the quasiparticle weight Z and therefore decreases the Fermi velocity (see Fig. 2). In order to achieve velocities consistent with experiment, one needs a relatively large $U > 3$ eV. This is in good agreement with previous estimates of U for the cobaltates.

Having put a lower bound on U, we proceed by computing 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. Mathematically, we have $\gamma = \frac{2\pi k_B^2}{3} \sum_\alpha \frac{\rho_\alpha(0)}{Z_\alpha}$, where α corresponds to the orbital index and ρ is the local spectral function [18]. The experimentally measured heat capacities for $Na_{0.3}CoO_2$ are found to be in the range of 12–16 $\frac{\text{mJ}}{(\text{mol Co})\ \text{K}^2}$ [23–28]. We begin by noting that the $U = 0$ values for the heat capacity are 14.27 and 11.4 $\frac{\text{mJ}}{(\text{mol Co})\ \text{K}^2}$ for $H_k^0[Z]$ and $H_k^0[I]$, respectively, which are both already within reasonable agreement with experimental measurements. This may mislead one to believe that correlations are negligible, but a more careful examination shows otherwise. We begin by analyzing the behavior of $H_k^0[Z]$. The DOS at the Fermi energy initially decreases weakly as U increases and eventually drops rapidly when $U = 6$ eV, which signifies the suppression of the pockets (see Fig. 2). The quasiparticle weight also decreases as U increases. Given that the linear coefficient of the heat capacity is proportional to the ratio $\frac{\rho(e_f)}{Z}$, the overall effect is not *a priori* obvious. The heat capacity initially increases as U increases, then discontinuously drops when the pockets are suppressed, and eventually plateaus for large U. Increasing Δ in $H_k^0[Z]$ causes the drop in the heat capacity to occur at smaller values of U.

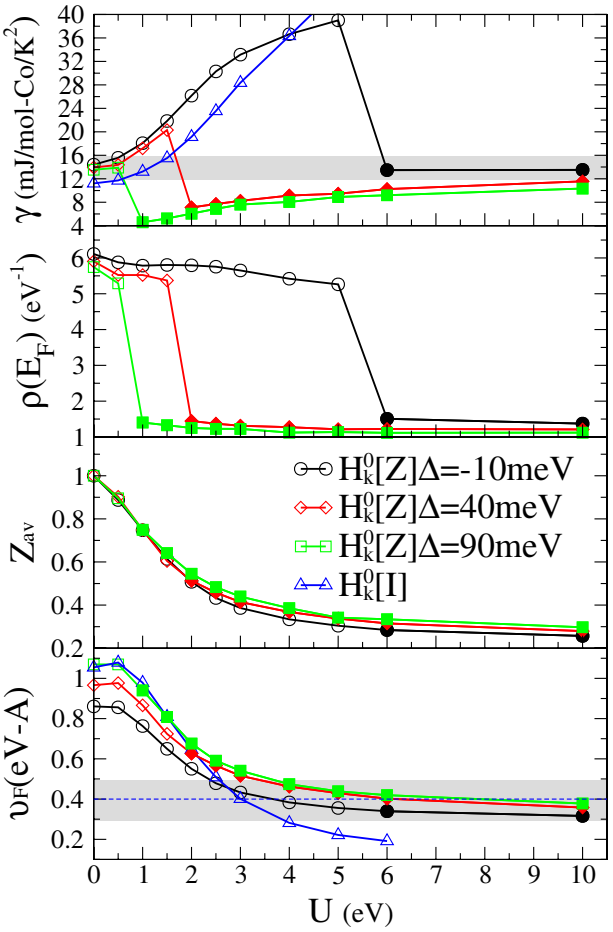

FIG. 2 (color online). The linear coefficient of the heat capacity γ, density of states at the Fermi energy $\rho(E_F)$, the quasiparticle weight Z, and the average of the absolute value of the Fermi velocity ν_F for the Γ-M and Γ-K directions are plotted. Filled points indicate that the pockets have been suppressed. The shaded region in the γ plot corresponds to the range of experimentally measured values of γ. The blue dotted line in the ν_F plot corresponds to the experimentally measured Fermi velocity, while the gray shading corresponds to the error bar [5].

The key point is that if the pockets are retained, γ becomes excessively large as U increases. Given that $U > 3$ eV, it is clear that the heat capacity is overpredicted if the pockets are present. If the pockets are absent, the heat capacity is slightly underpredicted. It is reasonable to expect that the heat capacity should be underpredicted when considering only 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. Additionally, the bare hopping parameters produced by LDA are likely too large and this reduces the calculated heat capacity. Therefore, the only conclusion consistent with the experimental heat capacity measurements is that the e_g' pockets are not present at the Fermi surface. The above analysis is directly applicable to $H_k^0[I]$. This bare Hamiltonian yields a heat capacity that is nearly

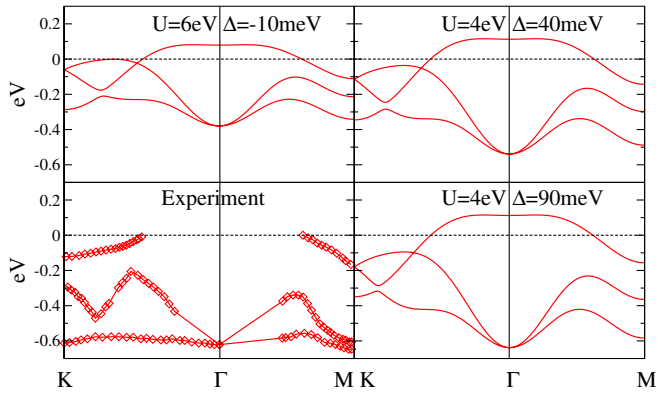

FIG. 3 (color online). The quasiparticle dispersion from the experimental measurement in Ref. [7] and our theoretical calculations. All calculations were performed at $\beta = 100\ \mathrm{eV}^{-1}$ using $H_k^0[Z]$.

a factor of 2 too large for reasonable values of U, due to the presence of the e_g' pockets. All of the above quantities saturate for large values of U, and hence comparison with higher energy experiments such as optical conductivity or inverse photoemission would be needed to put a clear upper bound on U.

The impurity solver used in this study works on the imaginary axis, and therefore one must perform an approximate analytic continuation to access real frequency quantities like the ARPES spectrum. We expand the self-energy to first order, which allows a straightforward analytic continuation, and use the resulting self-energy to construct the quasiparticle dispersion spectrum (see Fig. 3). The three sets of parameters presented indicate the qualitative trends of varying U and Δ.

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 the behavior of the e_g' pockets as a function of U is very sensitive to the details of the bare Hamiltonian, and this caused previous many body calculations to arrive at opposite conclusions as to whether the pockets are diminished [8] or enhanced [9]. Because of the fact that extracting a bare Hamiltonian from DFT calculations has a degree of uncertainty, an alternate analysis was needed. We circumvent this issue by calculating the heat capacity, which is an independent bulk measurement. Consistency with ARPES and heat capacity experiments can only be achieved if the pockets are not present at the Fermi surface. Reasonable agreement can be achieved with both bulk heat capacity measurements and the Fermi surface or velocity measured by ARPES when using an on site Coulomb repulsion which is several times the LDA bandwidth.

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