Theory of Carrier Concentration-Dependent Electronic Behavior in Layered Cobaltates

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A natural explanation for the carrier concentration-dependent electronic behavior in the layered cobaltates emerges within correlated-electron Hamiltonians with finite on-site and significant nearest neighbor hole-hole Coulomb repulsions. The nearest neighbor repulsion decreases hole double occupancy below hole density $\frac{1}{3}$, but increases the same at higher hole densities. Our conclusion is valid for both single-band and three-band extended Hubbard Hamiltonians, and sheds light on concentration dependent e'_g hole occupancy within the latter.

Layered cobaltates—anhydrous Na_xCoO_2, Li_xCoO_2 and the misfit cobaltates $[Bi_2A_2O_4]$ $[CoO_2]_m$, where A = Ba, Sr, or Ca and m is incommensurate—have attracted wide attention for their unconventional metallicity and tunability of the carrier concentration. Na_xCoO_2 consists of edge-sharing CoO_6 octahedra, with CoO_2 layers separated by Na layers. The Co ions with average charge $(4-x)+$ form a triangular lattice. Both experiments [1] and theory [2] indicate low-spin states for the Co-ions. Trigonal distortion splits the t_{2g} d orbitals into two low-lying e'_g orbitals and a higher a_{1g} orbital. Charge carriers are $S = \frac{1}{2}$ holes on the Co^{4+} sites [3]. The hole density $\rho = 1 - x$ in Na_xCoO_2 and Li_xCoO_2. Angle-resolved photoemission from Na_xCoO_2 indicate that carriers occupy the a_{1g} orbitals only [3–5], although Compton scattering finds small x-dependent e'_g contribution [6].

The electronic and magnetic behavior of these materials exhibit a peculiar carrier concentration dependence. The temperature-dependent magnetic susceptibility $\chi(T)$ in Na_xCoO_2 was early on characterized as "Pauli paramagnetic" for $x < 0.5$ and "Curie-Weiss" for $x > 0.5$ [7]. The Curie-Weiss behavior reflects strong Coulomb repulsion between the holes [1,3,4,7,8]. Strong correlation at large x is supported by observations of charge-ordering (CO) [9,10], Na-ion ordering [11], spin-density wave and intra-layer ferromagnetic correlations [12]. Qualitatively different behavior for the small x region is also agreed upon. Recent experimental work suggests that (a) $\chi(T)$ here is weakly antiferromagnetic rather than Pauli paramagnetic, and (b) the crossover between strong and weak correlations occurs at $x \sim 0.63 - 0.65$ rather than $x = 0.5$ [10].

Understanding the x dependence of the electronic and magnetic behavior of Na_xCoO_2 continues to be a challenge. It has been suggested that while the a_{1g}-only description is valid for large x, holes occupy both a_{1g} and e'_g orbitals at small x [13]. Quantum chemical configuration interaction calculations [14] find larger $a_{1g} - e'_g$ separation than local-density approximation (LDA) calculations

[2], and many-body approaches that take Coulomb hole-hole repulsion into account [15–17] do not find the e'_g pockets on the Fermi surface predicted within LDA calculations. x dependence has also been ascribed to differences in the potential due to Na layers [11,18]. Experimentally, Li_xCoO_2 [19] and Bi "misfit" cobaltates [20] do not exhibit ion ordering but, nevertheless, exhibit very similar carrier concentration dependence [19,20], suggesting that this dependence is intrinsic to the CoO_2 layers.

In the present Letter we show that a simple and natural explanation of the carrier concentration dependence emerges within a_{1g} only as well as multiband extended Hubbard models. Our discussions below involve ρ which is well defined for all systems, instead of x. Following [16] we write the three-band Hamiltonian as

$$H = -\sum_{\langle ij\rangle\alpha\beta\sigma} t_{\alpha\beta}c^\dagger_{i\alpha\sigma}c_{j\beta\sigma} + \sum_i \Delta(n_{ie'_g} - n_{ia_{1g}})$$
$$+ \frac{1}{2}\sum_{i\alpha\beta\sigma\sigma'} U^{\sigma\sigma'}_{\alpha\beta}n_{i\alpha\sigma}n_{i\beta\sigma'} + V\sum_{\langle ij\rangle\alpha\beta} n_{i\alpha}n_{j\beta}. \quad (1)$$

Here α and β refer to the a_{1g} and e'_g orbitals, $c^\dagger_{i\alpha\sigma}$ creates a hole of spin σ on orbital α on site i, $n_{i\alpha\sigma} = c^\dagger_{i\alpha\sigma}c_{i\alpha\sigma}$ and $n_{i\alpha} = \sum_\sigma n_{i\alpha\sigma}$. $t_{\alpha\beta}$ is the nearest neighbor (NN) hopping, Δ the trigonal splitting, $U \equiv U^{\sigma,-\sigma}_{\alpha\alpha}$ and $U' \equiv U^{\sigma\sigma'}_{\alpha\beta}$ are the on-site intra- and interorbital Coulomb interactions, and V is the NN Coulomb interaction. As in [16], we have ignored the Hund's rule coupling based on the very small hole occupation of e'_g orbitals (see below). As both photoemission experiments [3–5] and many-body theories [14,15,17] find the negligible role of e'_g orbitals, we discuss the one-band limit of Eq. (1) first. We show that the V term is essential within the one-band model for understanding the ρ dependence of the susceptibility. We then show that the same effect not only persists in the full three-band

model, but influences the ρ dependence of the e'_g orbital occupation as well.

Single-band limit.—Terms containing U' and Δ are irrelevant and U, V, and $t_{\alpha\alpha}$ refer to a_{1g} orbitals only. We write $t_{\alpha\alpha} = t$ and express U and V in units of t. For hole carriers $t > 0$ [3]. Existing a_{1g}-only theories largely assume $U \gg t$ [21] or $V = 0$ [15,17,18,21,22]. The few studies that have investigated the effects of finite V on triangular lattices are either for particular $\rho = 0.5$ [23] or $\frac{2}{3}$ [24], or use approximate approaches [25] that do not capture the ρ dependence seen experimentally. We consider here realistic finite U and V. We do not assume that U and V are ρ dependent. Rather, we show that ρ-dependent correlations emerge as solutions to Eq. (1).

Two different observations give the appropriate parameter range. (i) At $\rho = 1$ Eq. (1) can be replaced by a $V = 0$ Hubbard Hamiltonian with an effective on-site repulsion $U_{\mathrm{eff}} = U - V$. Within the $V = 0$ Hubbard model for the triangular lattice, transition to the Mott-Hubbard insulator occurs for $U_{\mathrm{eff}} > U_c$, where $U_c \simeq 5 - 10$. [26]. Experimentally, $\rho = 1$ CoO$_2$ is a poor metal [8], indicating that $U - V \leq 5 - 10$ for cobaltates. (ii) For $V > \frac{1}{3}U$, $\rho = \frac{2}{3}$ would be charge ordered with all sites doubly occupied (Co^{5+}) and vacant (Co^{3+}), as shown in Fig. 1(d). The absence of such CO indicates $V < \frac{1}{3}U$. Taking (i) and (ii) together, we conclude that the likely parameter regime is $6 < U < 14$, $1 < V < 4$. Our estimate of V/U is close to that of Choy *et al.* [23]. Our estimate of U/t is slightly smaller [13,17].

We now argue that for realistic U and V there occur three distinct hole density regions. (i) $\rho \leq \frac{1}{3}$, where correlation effects are strongest; (ii) intermediate $\frac{1}{3} < \rho \leq \frac{2}{3}$, where correlation effects become weaker with increasing density, and can be quite weak at the highest ρ; and (iii) $\rho > \frac{2}{3}$,

where correlation effects increase again slowly. We classify configurations by the number of double occupancies N_d. Figure 1(a) shows the $\sqrt{3} \times \sqrt{3}$ $N_d = 0$ charge-ordered configuration that should dominate the ground state of $\rho = \frac{1}{3}$. For fixed U, V creates an energy barrier to holes approaching each other. The energy cost of creating a double occupancy is thus greater than U for $\rho \leq \frac{1}{3}$, which should exhibit strongly correlated behavior. This situation changes as ρ increases, as seen in Fig. 1(b), where we have added a single hole to the charge-ordered configuration of $\rho = \frac{1}{3}$. The particular hop indicated in the figure that creates a double occupancy costs only $U - 3$ V. There are only three of these, but the number of low energy hops increases rapidly with further increase in ρ, increasing $\langle N_d \rangle$. In Fig. 1(c) we show the two extreme charge-ordered configurations for $\rho = \frac{2}{3}$, one with $N_d = 0$ [Fig. 1(c)], the other with $N_d = N_{\mathrm{max}} = \frac{1}{3}$ N. The configurations are degenerate at $U = 3$ V. There is thus strong mixing of $N_d = 0$ and $N_d > 0$ configurations for ρ close to $\frac{2}{3}$, even for $V < \frac{1}{3}U$. Adding double occupancies to the configuration in Fig. 1(d) is prohibitively expensive in energy, which implies that for $\rho > \frac{2}{3}$ the competition of $N_d = 0$ is no longer with $N_d = N_{\mathrm{max}}$ but still with $N_d = \frac{1}{3}$ N. We expect correlations to slowly increase again in this region.

We have performed exact numerical calculations to confirm the above conjectures. As a measure of correlations we have chosen the normalized probability of double occupancy $g(\rho)$ in the ground state,

$$g(\rho) = \frac{\langle n_{i,\uparrow} n_{i,\downarrow} \rangle}{\langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle} \qquad (2)$$

$g(\rho) = 1$ and 0 for $U = 0$ and $U \rightarrow \infty$, respectively, for all ρ, and has intermediate values in between. $g(\rho)$ is thus a measure of $U_{\mathrm{eff}}(\rho)$: small $g(\rho)$ implies enhanced Curie-Weiss type $\chi(T)$ while moderate to large $g(\rho)$ implies weak antiferromagnetic spin-spin correlations [27]. Our proposed mechanism suggests that $g(\rho)$ is small (large) for small (large) hole density, provided V is significant. We have calculated g for the six triangular lattice clusters in Fig. 2, using periodic boundary condition. For clusters
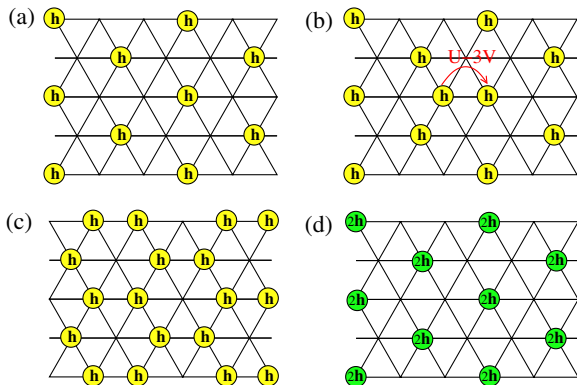

FIG. 1 (color online). Dominant ground state configurations for (a) $\rho = \frac{1}{3}$ and (b) one hole added to $\rho = \frac{1}{3}$. Circles labeled "h" ("2h") are singly (doubly) occupied sites, with vacancies occupying the vertices of the triangular lattice. The NN hop indicated by the arrow in (b) costs $U - 3$ V. Dominant configurations for $\rho = \frac{2}{3}$, with (c) $N_d = 0$, and (d) $N_d = \frac{1}{3}$ N.
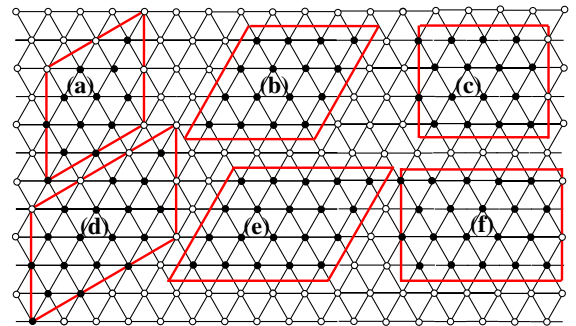

FIG. 2 (color online). Clusters investigated numerically: (a) $N = 12$; (b) and (c) $N = 16$; (d) $N = 18$; (e) and (f) $N = 20$.
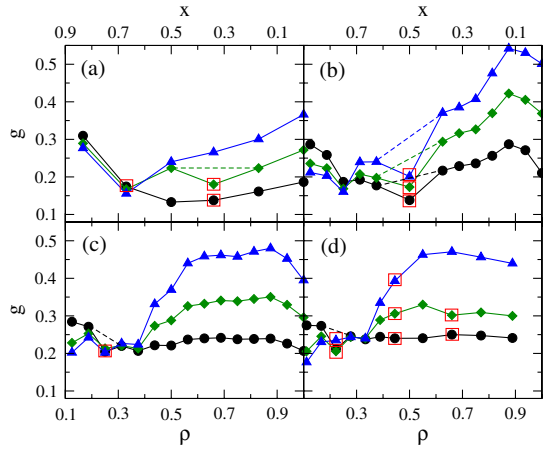
FIG. 3 (color online). Normalized probability of double occupancy of sites by holes versus hole density for $U = 10$, $V = 0$ (circles), 2 (diamonds), and 3 (triangles) on clusters with (a) $N = 12$, (b) and (c) $N = 16$, corresponding to Figs. 2(b) and 2(c), respectively, and (d) $N = 18$. Points within squares indicate $S > S_{\min}$ (see text).

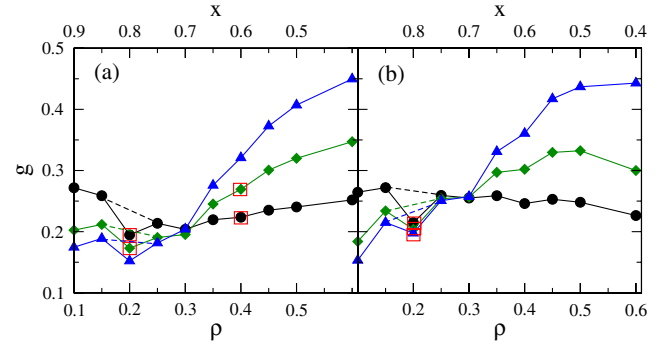

FIG. 4 (color online). Same as Fig. 3 for $N = 20$, for $U = 10$ and $V = 0$ (circles), 2 (diamonds), and 3 (triangles); (a) and (b) correspond to lattices Figs. 2(e) and 2(f), respectively.

(a)–(c) the number of holes N_h covers the complete range $\rho \leq 1$. Computer memory constraints restrict us to $\rho \leq 0.88$ for cluster (d) and $\rho \leq 0.6$ for clusters (e) and (f), respectively. Our calculations are for all realistic U and $V \leq \frac{1}{3}U$. As the results are qualitatively the same in all cases, we report our results for $U = 10$ only.

In Fig. 3 we show our results for clusters (a)–(d) for $U = 10$ and $V = 0$, 2, and 3: Our data points include both even and odd N_h, and except for $N_h \geq 14$ in Fig. 3(d) we have determined the total spin S in the ground state in each case. With few exceptions, $S = S_{\min} = 0$ ($\frac{1}{2}$) for even (odd) N_h. $S > S_{\min}$ is a finite-size effect, as for different clusters this occurs at different densities. The g values for the $S > S_{\min}$ points were calculated correctly in accordance with Eq. (2). The dips in g for higher S are expected. In every case we have included dashed straight lines connecting the neighboring points on both sides. The g for $S = S_{\min}$ at these points is likely bounded by the computed points and the dashed lines. In all four cases, $g(\rho)$ is nearly independent of ρ for $V = 0$, but exhibits the ρ dependence predicted for $V \neq 0$. The ρ dependence is weakest for $N = 12$. In all other cases there occurs a distinct strongly correlated low density region ($\rho \leq 0.4$), where V suppresses g and a relatively weakly correlated intermediate density region ($0.4 \leq \rho \leq 0.8$), where V enhances g. The predicted decrease in $g(\rho)$ for larger ρ is also visible in Figs. 3(b) and 3(c).

Figure 4 shows plots of $g(\rho)$ for the 20-site clusters of Figs. 2(e) and 2(f). As in Fig. 3 we have retained the points with $S > S_{\min}$. Distinct density regions (i) and (ii), with opposite effects of V are again clearly visible. The boundary between strongly and weakly correlated regions is $\rho \approx 0.30$, in agreement with recent experiments [10]. Calculated charge-charge correlations $\langle n_i n_j \rangle$ (not shown)

indicate that while near $\rho = \frac{1}{3}$ ($N_h = 6$ and 7) there is a tendency to CO there is no such tendency at $\rho = 0.5$ ($N_h = 10$). The qualitative agreement between our results for six different clusters, along with steeper ρ dependence with increasing N, strongly suggest that our results will persist in the thermodynamic limit.

Three-band model,—ρ-dependent g is a consequence of the competition between U and V at large ρ [27] and is unrelated to dimensionality or frustration. Since exact three-band calculations are not possible for the clusters of Fig. 2, we have performed three-band calculations for a one-dimensional (1D) periodic cluster with eight sites, each with one "a_{1g}" and two "e'_g" (hereafter a, e_1, and e_2, respectively) orbitals. The only differences between 1D and the triangular lattice are (i) the Wigner crystal occurs at $\rho = \frac{1}{2}$ in 1D instead of $\rho = \frac{1}{3}$, and (ii) the maximum in $g(\rho)$ is expected near $\rho = \frac{3}{4}$ [27] rather than $\frac{2}{3}$. We retain the same U and V and take $t_{\alpha\alpha} = t$, interorbital hopping $t_{\alpha\beta} = 0.1 - 0.3t$ ($\alpha \neq \beta$), $\Delta = 3|t|$ [14], and $U' = 0.6U$ [17]. We use periodic (antiperiodic) boundary conditions for $N_h = 4n + 2$ ($4n$) [28].

In Fig. 5(a), we have plotted $g_a(\rho)$, the normalized probability of double occupancy of the a orbitals by holes, within the three-band model [$g_e(\rho)$ varies by less than 15% over the entire range of ρ]. The carrier density ρ here is the ratio of the total number of holes and the number of a-orbitals, in agreement with the definition of ρ in Na_xCoO_2. The $g_a(\rho)$ behavior is nearly identical to that of $g(\rho)$ in Figs. 3 and 4. Interestingly, $g_a(\rho)$ behavior is the same for small and large $t_{e,a}$, in spite of moderate hole population $n(e)$ in the e orbitals in the latter case. Calculations for smaller Δ (not shown) indicate similar weak dependence of $g_a(\rho)$ on Δ.

In Fig. 5(b) we plot $r(e)$, the fraction of holes that occupy the e orbitals, assuming $t_{\alpha\beta} = 0.3t$, for (a) noninteracting, (b) U, $U' \neq 0$ but $V = 0$, and (c) $V > 0$ cases. Comparing the noninteracting and the $V = 0$ plots, it is clear that nonzero U and U' decrease the e'_g occupation because of correlation-induced band
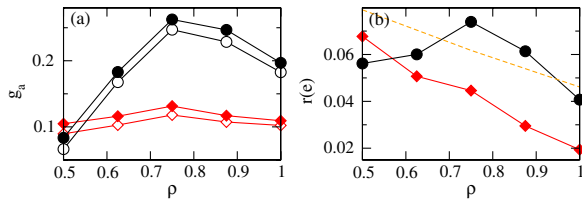
FIG. 5 (color online). (a) Normalized probability of double
occupancy of the a orbitals by holes in the 1D 3-band model for
$N = 8$, $\Delta = 3$. (b) The fraction of holes occupying e orbitals. In
both, unfilled (filled) symbols are for interorbital hopping $0.1t$
($0.3t$). Diamonds (circles) are for $V = 0$ ($V = 3$). In (b), the
dashed line shows the noninteracting ($U = U' = V = 0$) result.
For all other points $U = 10$ and $U' = 6$.

narrowing [15,17]. The $V > 0$ plot is far more interesting:
$r(e)$ shows a peak at the same ρ where $g_a(\rho)$ has a
maximum. This shows that correlation effects due to V
play a more complex role in the multiband picture: in the
large-ρ region V reduces U_{eff} [Fig. 5(a)] for the same
reason as in the single-band picture. This reduces the
extent of band narrowing at precisely these ρ, and leads
to an increase in $r(e)$ even for ρ-independent Δ. Existing
discussions of e'_g hole occupancy have largely focused on
the Fermi surface [3–6]. Our work shows that there can
indeed occur weak e'_g hole occupation, especially for ρ
close to $\frac{2}{3}$. The e'_g occupation estimated by Compton
scattering shows a ρ dependence (see Table I in [6]) that
is very similar to our results for $V > 0$ in Fig. 5(b), viz.,
increasing e'_g occupancy with increasing ρ. This result
cannot be explained with $V = 0$, as seen in Fig. 5(b).
Our calculations show that ρ-dependent $\chi(T)$ and e'_g oc-
cupation are manifestations of the same many-body effect.

Summary.—Strongly correlated behavior for small hole
densities and relatively weakly correlated behavior for
larger hole densities are both expected for nonzero NN
Coulomb interaction. To the best of our knowledge there
exists no other satisfactory theoretical explanation for the
observed weakly correlated behavior nearer to the Mott-
Hubbard semiconducting hole density and strongly corre-
lated behavior farther away from this limit. The strong
tendency to CO at ρ exactly $\frac{1}{3}$ and the absence of this
tendency at $\rho = \frac{2}{3}$ are both understood. The potential due
to Na ions, ignored in our work, will strengthen the CO
even for incommensurate fillings with $\rho \leq \frac{1}{3}$ [11]. We do
not find CO at $\rho = 0.5$, although it is moderately corre-
lated. Observed CO here [7] is likely driven by the coop-
erative effects of V and the Na-ion potential. Conversely,
the absence of Na-ion ordering for weakly correlated
$x < 0.5$ in Na_xCoO_2 further suggests that the CO and
Na-ion ordering are synergistic effects.

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