# DISPROPORTIONATION AND SPIN ORDERING TENDENCIES IN $\mathbf{Na_xCoO_2}$ AT $x = \frac{1}{3}$

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**Abstract** The strength and effect of Coulomb correlations in the (superconducting when hydrated) $x \approx$1/3 regime of Na$_x$CoO$_2$ have been evaluated using the correlated band theory LDA+U method. Our results, neglecting quantum fluctuations, are: (1) there is a critical $U_c$ = 3 eV, above which charge ordering occurs at $x$=1/3, (2) in this charge-ordered state, antiferromagnetic coupling is favored over ferromagnetic, while below $U_c$, ferromagnetism is favored; and (3) carrier conduction behavior should be very asymmetric for dopings away from $x$=1/3. For $x < \frac{1}{3}$, correlated hopping of parallel spin pairs is favored, suggesting a triplet superconducting phase.

## 1. Introduction

Since the discovery of high temperature superconductivity in cuprates, there has been intense interest in transition metal oxides with strongly layered, (quasi) two-dimensional (2D) crystal structures and electronic properties. For several years now alkali-metal intercalated layered cobaltates, particularly Na$_x$CoO$_2$ (NxCO) with $x \sim 0.50 - 0.75$, have been pursued for their thermoelectric properties.[1] Li$_x$CoO$_2$ is of course of great interest and importance due to its battery applications. The recent discovery[2] and confirmation[3–5] of superconductivity in this system, for $x \approx 0.3$ when intercalated with H$_2$O, has heightened interest in the NxCO system.

The crystal structure[6–8] is based on a 2D CoO$_2$ layer in which edge-sharing CoO$_6$ octahedra lead to a triangular lattice of Co ions. Na donates its electron to the CoO$_2$ layer, hence $x$ controls the doping level of the layer: $x$=0 corresponds to Co$^{4+}$, S=$\frac{1}{2}$ low spin ions with one minority $t_{2g}$ hole, and $x = 1$ corresponds to non-magnetic Co$^{3+}$. Nearly all reports of non-stoichiometric materials quote values of $x$ in the 0.3 - 0.75 range, and the materials seem generally to show metallic conductivity. Reports of the magnetic behavior are of particular interest to us. For $x$ in the 0.5 - 0.75 range, the susceptibility $\chi(T)$ is Curie-Weiss-like (C-W) with reported moment of the order of magnitude 1 $\mu_B$ per Co$^{4+}$[2, 3] which indicates the presence of correlated electron behavior on the Co ions. Magnetic ordering at 22 K with very small ordered moment has been reported for $x$=0.75[9] and Wang *et al.* measured field dependence [4] that indicated the spin entropy of the magnetic Co system is responsible for the unusual thermoelectric behavior. Thus for $x \geq 0.5$ magnetic Co ions and magnetic ordering give evidence of correlated electron behavior.

However, for $H_2O$ intercalated samples with $x$ ≈0.3, (*i.e.* the superconducting phase) C-W behavior of $\chi$ vanishes. [3, 5, 10, 11]. It is extremely curious that the appearance of superconductivity correlates with the disappearance of Co moments in the samples. From a single-band strongly interacting viewpoint, the $x = 0$ system corresponds to the half-filled triangular lattice that has been studied extensively for local singlet (resonating valence bond) behavior.[12] The $x \approx 0.3$ region of superconductivity in NxCO is however well away from the half-filled system, and the behavior in such systems is expected to vary strongly with doping level.

There is now a serious need to understand the electronic structure of the normal state of the unhydrated material, and its dependence on the doping level $x$. The electronic structure of the $x$=1/2 ordered compound in the local density approximation (LDA) has been described by Singh.[13] Within LDA all Co ions are identical ("Co$^{3.5+}$"), the Co $t_{2g}$ states are crystal-field split (by 2.5 eV) from the $e_g$ states, and the $t_{2g}$ bands are partially filled, consequently the system is metallic consistent with the observed conductivity. The $t_{2g}$ band complex is $W \approx$ 1.6 eV wide, and is separated from the 5 eV wide O $2p$ bands that lie just below the Co $d$ bands. Singh noted that the expected on-site Coulomb repulsion $U$=5-8 eV on Co gives $U >> W$ and correlation effects can be anticipated. A value of $U \approx$ 4 eV was assumed by Wang, Lee, and Lee [14] to justify a strongly correlated $t-J$ model treatment of this system. While it must be kept in mind that the study of this system is still in its infancy and no clear experimental data plus theoretical interpretation agreement has established the degree of correlation, we also take the viewpoint here that effects of on-site repulsion need to be assessed.

Although the experimental evidence indicates nonmagnetic Co ion in the superconducting material, most theoretical approaches[14–16] consider the strongly interacting limit where not only is $U$ important, it is large enough to prohibit double occupancy, justifying the single band $t - J$ model. Another question to address is whether the single band scenario is realistic: indeed the rhombohedral symmetry of the Co site splits the $t_{2g}$ states into $a_g$ and $e_g'$ representations, but the near-octahedral local symmetry leaves their band centers and widths very similar.

In this paper we begin to address the correlation question using the correlated band theory LDA+U method. We focus on the $x$ ≈1/3 regime where superconductivity emerges. We find that $U \geq U_c = 3$ eV leads to charge ordering at $x$=1/3 accompanied by antiferromagnetic (AFM) spin order; of course, the fluctuations neglected in the LDA+U method, the availability of three distinct sublattices for ordering, and the tendency of the Na ions to order[8] (which can mask other forms of ordering at the same wavevector), can account for the lack of ordering (or of its observation).

## 2. Method of Calculation

Two all-electron full-potential electronic methods have been used. The full-potential linearized augmented-plane-waves (FLAPW) as implemented in Wien2k code [17] and its LDA+U [18] extension were used. Valence and conduction $s, p$, and $d$ states were treated using the APW+lo scheme [19], while the standard LAPW expansion was used for higher $l$'s. Local orbitals were added to describe Co $3d$ and O $2s$ and $2p$ states. The basis size was determined by $R_{mt}K_{max} = 7.0$. In addition, the full-potential nonorthogonal local-orbital minimum-basis scheme (FPLO) of Koepernik and Eschrig[20] was also used extensively. Valence orbitals included Na $2s2p3s3p3d$, Co $3s3p4s4p3d$, and O $2s2p3s3p3d$. The spatial extension of the basis orbitals, controlled by a confining potential [20] $(r/r_0)^4$, was optimized for the paramagnetic band structure and held fixed for the magnetic calculations. The Brillouin zone was sampled with regular mesh containing 50 irreducible k-points. Both popular forms[21] of the LDA+U functional have been used to assess possible sensitivity to the choice of functional, but in these studies the differences were small. We do not consider interlayer coupling in the work presented here, which allows us to use a single layer cell in the calculations.

## 3. Results of Self-Consistent Calculations

*LDA electronic structure at* $x = \frac{1}{3}$. The crystal field splitting of 2.5 eV puts the (unoccupied) $e_g$ states (1 eV wide) well out of consideration. The trigonal symmetry of the Co site splits the $t_{2g}$ states into one of $a_g$ symmetry and a doubly degenerate $e_g'$ pair. The $a_g$ band is 1.5 eV wide (corresponding to $t = 0.17$ eV in a single band picture) while the $e_g'$ states have nearly the same band center but are only 1.3 eV wide; hence they lie *within* the $a_g$ band. As might be anticipated from the local octahedral environment, there is mixing of the $a_g$ and $e_g'$ bands throughout most of the zone, and the $a_g$ DOS does not resemble that of an isolated band in a hexagonal lattice. For the paramagnetic

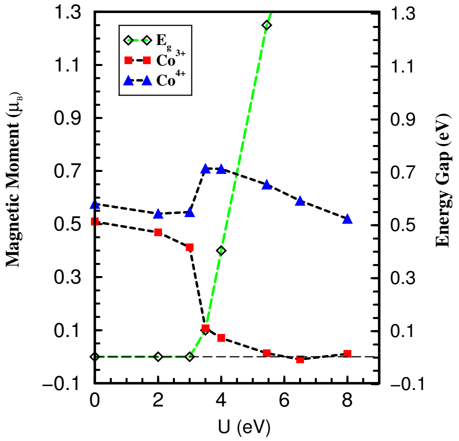

*Figure 1.* Effect of the intraatomic repulsion $U$ on the magnetic moment of the Co1 and Co2 ions for ferromagnetic order. The LDA+U method in the FPLO code was used. Disproportionation to formal charge states $Co^{3+}$ and $Co^{4+}$ states occurs above $U_c$ = 3 eV.

case $x = \frac{1}{3}$ corresponds to $\frac{8}{9}$ filling of the $t_{2g}$ band complex, resulting in hole doping into the $e_g'$ states as well as in the $a_g$ states.

Singh found that ferromagnetic (FM) phases seemed to be energetically favored for all noninteger $x$ [13]. No ferromagnetism is seen in this system, so NxCO becomes another member in small but growing list of compounds[22] whose tendency toward FM is *overestimated* by LDA because they are near a magnetic quantum critical point. We confirm these FM tendencies within LDA for $x$=1/3, obtaining a half metallic FM state with a moment of $\frac{2}{3}\mu_B$/Co that is distributed almost evenly on the three Co ions, which occupy two crystallographically distinct sites because of the Na position. The exchange splitting of the $t_{2g}$ states is 1.5 eV, and the Fermi level ($E_F$) lies within the metallic minority bands and just above the top of the fully occupied majority bands. The FM energy gain is about 45 meV/Co. With the majority bands filled, the filling of the minority $t_{2g}$ bands becomes $\frac{2}{3}$, leading to larger $e_g'$ hole occupation than for the paramagnetic phase. We conclude that, in opposition to much of the theoretical speculation so far, $x = \frac{1}{3}$ is necessarily a multiband ($a_g$ + $e_g'$) system. Our attempts using LDA to obtain self-consistent charge-ordered states, or AFM spin ordering, always converged to the FM or nonmagnetic solution.

*LDA+U Magnetic Structure and energies* First the behavior of the LDA+U results versus $U$ were studied (on-site exchange was kept fixed at 1 eV). The dependence of the magnetic moment on $U$ (obtained from the FPLO code) for FM ordering is shown in Fig. 1. Recall that the ordered array of Na ions in our cell gives two crystallographically inequivalent Co sites. For $U < U_c \approx$

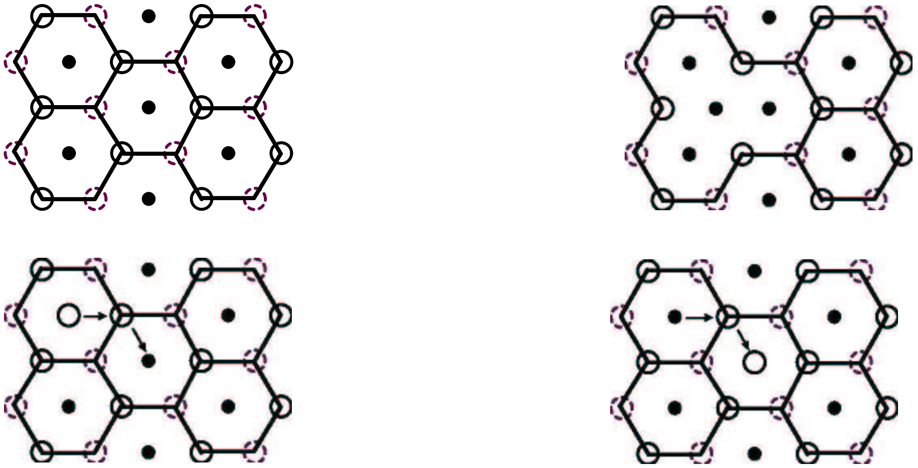

*Figure 2.* <Upper left> The charge ordered triangular Co lattice → honeycomb lattice, with antiferromagnetic spin order designated by solid circles ($\uparrow$), dashed circles ($\downarrow$), and filled circles (Co$^{3+}S = 0$ sites). Lines denote nn magnetic couplings. <Upper right> addition of a $\uparrow$ electron converts a Co$^{4+}S = \frac{1}{2}$ site to a nonmagnetic site. Hopping of a neighboring hole to this site costs 4J in energy. The lower two panels illustrate the correlated pair hopping process after a $\uparrow$ hole is added to the system: hopping of the hole to a neighboring site, followed by refilling of the site by the added hole, results in an identical (but translated) state.

3 eV, the moments are nearly equal and similar to LDA values (which is the $U \rightarrow 0$ limit). Above $U_c$, charge ordering accompanied by a metal-insulator (Mott) transition occurs by disproportionation into nonmagnetic Co$^{3+}$ and two $S = \frac{1}{2}$ Co$^{4+}$ ions. Nonmagnetic Co$^{3+}$ states lie at the bottom of the 1 eV wide gap, with the occupied Co$^{4+}$ $e_g'$ states 1-2 eV lower. After adding the on-site correlation to LSDA results, the hole on the Co$^{4+}$ ion occupies the $a_g$ orbital. A possibility that we have not attempted would be to obtain a solution in which the hole occupies an $e_g'$ orbital, in which case one should then investigate orbital ordering in addition to charge- and spin-ordering.

Reasonable estimates for cobaltates put $U$ at 5 eV or above, so we now concentrate on results for $U$=5.4 eV, which we expect is near the lower end of reasonable values. For this value of $U$ both FM and AFM spin-ordered solutions are readily obtained, with AFM energy 1.2 mRy/Co lower than for FM order. In terms of nn coupling on the charge-ordered honeycomb lattice, the FM - AFM energy difference corresponds to $J$ = 11 meV. Referring to the paramagnetic bandwidth identified above, the corresponding superexchange constant would be $4t^2/U \sim 20$ meV.

*Discussion and Comparison with Experiment* These calculations establish that at $x$=1/3, there is a strong tendency to charge-order, and that there is a nn $J$ of antiferromagnetic sign; hence we consider as reference the $\sqrt{3}\times\sqrt{3}$ charge-ordered AFM state shown in Fig. 2. Considering the charge-ordering energies as dominant over the magnetic energies, the fundamental problem at $x = \frac{1}{3}$ becomes the spin behavior of the half-filled honeycomb lattice. Spin correlations and quantum fluctuations on the honeycomb lattice have been considered by Moessner *et al.*[23] based on the quantum dimer model, where singlet-pairing regimes indeed are found in which the rms magnetization on a site is strongly reduced. Such pairing would strongly suppress the Curie-Weiss susceptibility.

The foregoing discussion neglects (among other aspects) the metallic nature of NxCO. Now we consider "doping" away from $x$=1/3. Addition of an electron (of, say, spin up) converts a $\mathrm{Co}^{4+} \downarrow$ to a $\mathrm{Co}^{3+}$, that is, it destroys a spin down hole which also was a potential carrier (if charge order were lost). This frees up a site for hopping of a neighboring hole, but the energy cost of doing so is $4J$ (loss of two favorable $J$ and gain of two unfavorable $J$) and thus is strongly inhibited. Now we turn to the removal of an $\uparrow$ electron (addition of a hole) corresponding to superconducting region $x < \frac{1}{3}$, which has quite a different effect. This type of doping converts an inert $\mathrm{Co}^{3+}$ to a $\mathrm{Co}^{4+}$ that is surrounded by six $\mathrm{Co}^{4+}$ sites with alternating spins. Single particle hopping is disallowed (strictly speaking, it costs $U$); however, correlated *parallel-spin pair hopping* as shown in Fig. 2 returns the system to an equivalent state and therefore requires no net energy. This process suggests a tendency toward triplet pairing superconductivity in this regime, although our results are too preliminary to permit serious conclusions. Although some progress on such processes might be made analytically within a single band model, the multiband nature of NxCO turns even the relatively simple Hubbard model on a triangular or honeycomb lattice into a formidable numerical problem.

## 4. Summary and Acknowledgments

Now we summarize. We have used the LDA+U method to evaluate the effects of Hubbard-like interactions in NxCO, and find charge disproportionation and a Mott insulating state at $x = \frac{1}{3}$ when fluctuations are neglected. Nearest neighbor coupling $J \approx 11$ meV provides AFM correlations. Indications based on this "mean field" AFM charge-ordered state are for very different behavior for electron or for hole doping relative to $x = \frac{1}{3}$; hole doping from this point tends to favor parallel-spin pair-hopping and thus possible triplet superconductivity. Fluctuation effects may however be substantial.

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