Charge- and Spin-Ordering Tendencies in Na_xCoO_2 at $x = \frac{1}{3}$

J. Kuneš, K.-W. Lee, and W. E. Pickett
Department of Physics, University of California, Davis CA 95616
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The strength and effect of Coulomb correlations in the (superconducting when hydrated) $x \approx 1/3$ regime of Na_xCoO_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. The lack of any observed magnetic behavior in this regime is addressed.

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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 a few years now alkali-metal intercalated layered cobaltates, particularly Na_xCoO_2 (NxCO) with $x \sim 0.50 - 0.75$, have been pursued for their thermoelectric properties.[1] The recent discovery[2] and confirmation[3, 4, 5, 6, 7, 8, 9, 10] of superconductivity in this system, for $x \approx 0.3$ when intercalated with H_2O, has heightened interest in the NxCO system.

The structure[11, 12, 13] 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 with reported moment of the order of magnitude 1 μ_B per Co^{4+} (with substantial variation between reports or samples). [2, 3, 8] This local moment 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,[14] and Wang *et al.* measured field dependence[9] 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 are evident.

However, for H_2O intercalated samples with $x \approx 0.3$, (*i.e.* the superconducting phase) Curie-Weiss behavior of χ vanishes. [3, 7, 8, 15, 16]. It is extremely curious that the appearance of superconductivity correlates with the disappearance of Co moments in the samples. In the single band, strongly interacting limit, the $x = 0$ system corresponds to the half-filled triangular lattice that has been studied extensively for local singlet (resonating valence bond) behavior.[17] Indeed, the distorted lattice $S = \frac{1}{2}$ Heisenberg systems TiOCl and TiOBr also show nearly T-independent χ that has been interpreted in terms of local singlet formation.[18] 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.

Although the primary interest has been in the superconductivity of NxCO, there is first a real 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.[19, 20] 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 $W \approx 1.5$ 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.

Notwithstanding the experimental evidence for nonmagnetic Co ion in the superconducting material, most of the theoretical discussion[21, 22] has focused on the strongly interacting limit, where U is not only important, but in fact is so large it prohibits double occupancy, as described by the single band $t-J$ model. Another feature to address is whether the single band scenario is realistic: although the rhombohedral symmetry of the Co site splits the t_{2g} states into a_g and e'_g representations, the near-octahedral symmetry makes their density of states (DOS) very similar.

In this paper we begin to address the correlation question using the correlated band theory LDA+U method. We focus on the $x \approx 1/3$ 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[13] (which can mask other forms of ordering at the same wavevector), can account for the lack

of ordering (or of its observation).

Two all-electron full-potential electronic methods have been used. The full-potential linearized augmented-plane-waves (FLAPW) as implemented in Wien2k code [23] and its LDA+U [24, 25] extension were used. The s, p, and d states were treated using the APW+lo scheme [26], 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[27] 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 [28] $(r/r_0)^4$, 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[29, 30] of the LDA+U functional have been used. We do not consider interlayer coupling here, and use a single layer cell.

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 $[(|xy> + |yz> + |zx>)/\sqrt{3}$ in the local coordinate system] and a doubly degenerate pair e'_g $[(|xy> + \alpha|yz> + \alpha^2|zx>)\sqrt{3}$ and its complex conjugate, where $\alpha = exp(2\pi i/3)]$. The a_g band is 1.6 eV wide (corresponding to $t = 0.13$ 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 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.

Analogous to the results of Singh for $x = 0.3, 0.5, 0.7$ [19, 20], we find ferromagnetic (FM) tendencies for x=1/3 within LDA. A half metallic FM result is found, with a moment of $\frac{2}{3}\mu_B$/Co that is distributed almost evenly on the three Co ions. The exchange splitting of the t_{2g} states is 1.5 eV, and the Fermi level (E_F) lies just above the top of the fully occupied majority bands (the minority bands are metallic). 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. Hence, unlike the standard assumption being made so far, (within LDA) $x = \frac{1}{3}$ is always a multiband ($a_g + e'_g$) system. 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 $U < U_c \approx 3$ eV, the moments are nearly equal and similar to LDA values (which is the $U \to 0$ 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. The "hole" on the Co^{4+} ion occupies the a_g orbital. A possibility that we have not attempted would be to locate the hole in the e'_g orbital and investigate orbital ordering in addition to charge- and spin-ordering. The previous application of the LDA+U method to NxCO did not allow the possibility of charge ordering.[31]

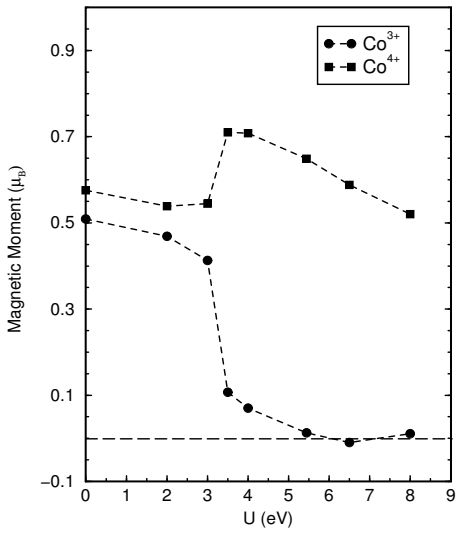

FIG. 1: Effect of the intraatomic repulsion U on the magnetic moment of the Co1 and Co2 ions for ferromagnetic order. The LDA+U method in the FPLO code was used. Disproportionation to formal charge states Co^{3+} and Co^{4+} states occurs above $U_c = 3$ eV.

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 $4t^2/U = 12$ meV, a remarkably consistent value perhaps reflecting that this "Mott insulating" charge-ordered solution fits well within a single band picture.

Discussion. These calculations establish that at x=1/3, there is a strong tendency to charge-order, and

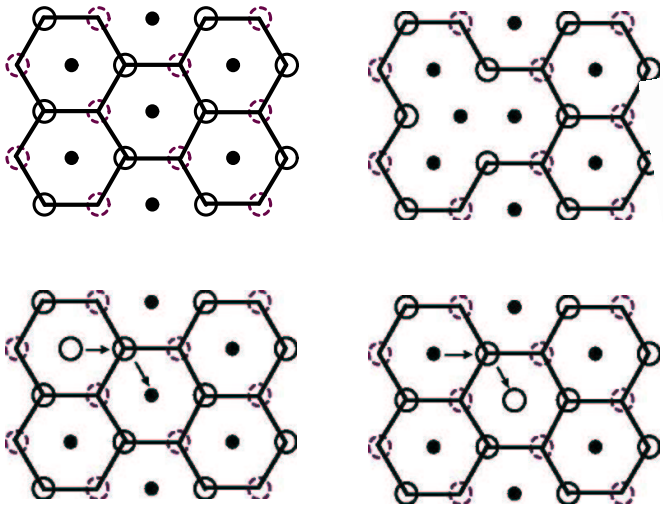

FIG. 2: Upper left: The charge ordered triangular Co lattice → honeycomb lattice, with antiferromagnetic spin order designated by solid circles (↑), dashed circles (↓), and filled circles (Co^{3+} $S=0$ sites). Lines denote nn magnetic couplings. Upper right: addition of a ↑ electron converts a Co^{4+} $S=\frac{1}{2}$ 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 ↑ 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 state (translated by a superlattice constant).

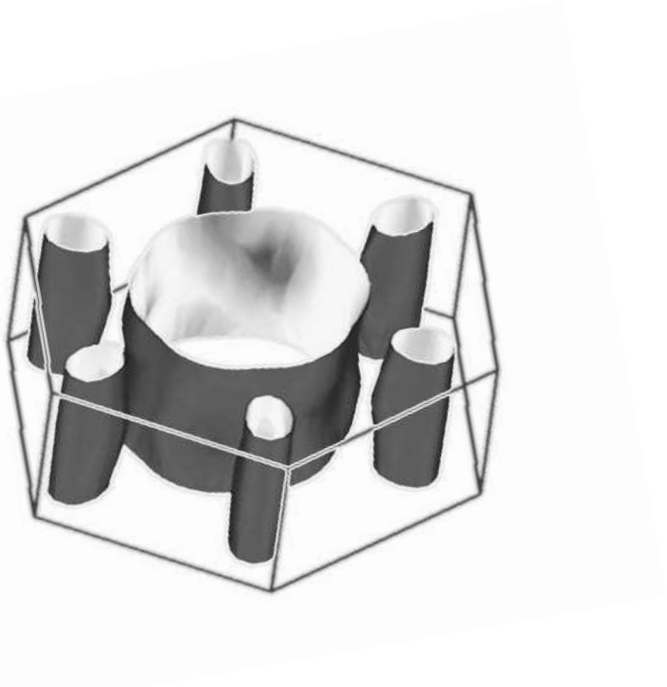

FIG. 3: Fermi surface for (virtual crystal) NxCO, x=0.30, in the two dimensional Brillouin zone. The large cylinder contains a_g holes, whereas the six small cylinders contain holes that are primarily e'_g-like.

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. This charge- and spin-ordered state can be distributed over the three Co atoms in the unit cell in six distinct ways corresponding to putting the Co^{3+} ion on each of the sites and having $S_z=\pm\frac{1}{2}$ on the Co^{4+} sites, giving basis states (in an S_z representation) $|1>=|0+->, |2>=|0-+>, |3>=|+0->, |4>=|-0+>, |5>=|+-0>, |6>=|-+0>$ [here $|lmn>$ gives the S_z component of atoms a,b,c in the cell]. A general reference state can then be written as an equal amplitude linear combination $|\psi>\propto\sum_{j=1}^{6}e^{i\beta_j}|j>$, where $\{\beta_j\}$ are arbitrary phases. The z component of the moment $<\psi|2\mu_B S_z|\psi>$ vanishes in such a state, being the mean of spin projections of each of the basis states, but $\vec{S}^2\neq 0$. Accounting for the lack of any free moments (as is observed) requires local singlet formation. Moreover, in 2D spin-half systems, large quantum fluctuation effects must be accounted for.

Pursuit of a fluctuating but correlated singlet phase that is metallic (with superconducting ground state) is a goal that is beyond the intentions of this paper, but some guidelines may be drawn. 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, and then how that is altered by doping. Spin correlations and quantum fluctuations on the honeycomb lattice have been considered by Moessner *et al.*[32] based on the quantum dimer model, and such considerations may be relevant to NxCo.[33]

The foregoing discussion neglects (among other aspects) the metallic nature of NxCO. Now we consider doping away from the x=1/3 honeycomb AFM. Addition of an electron (of, say, spin ↑) converts a Co^{4+} ↓ to a 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 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 Co^{3+} to a Co^{4+} that is surrounded by six 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, and can be repeated indefinitely. Antiparallel-spin pair hopping leaves a trail of disrupted bonds. This triplet-pair hopping process suggests a tendency toward triplet pairing superconductivity in this regime, mediated not by FM spin fluctuations[20] but rather by the underlying charge-ordering tendencies and AFM correlations. Progress on the understanding of such processes be made within a single band model, but the full multiband nature of NxCO may turn even the relatively simple Hubbard model on a triangular or honeycomb lattice into a formidable numerical problem.

Fermiology. Finally we return to the basic character-

istic – the metallic normal state. Considering the instability toward FM both at small U and at more realistic values, this material might be considered as an example of what has been called a "correlation-induced paramagnet."[34] More likely, perhaps, is that it is a fluctuation-induced paramagnet. Whatever the underlying reason, a page can be taken from the high T_c cuprate chapter of materials physics that, in spite of considerable correlation effects, in the metallic phase the paramagnetic Fermi surface will emerge.

In Fig. 3 we show the x=0.33 LDA Fermi surface, which is similar to the $x = 0.5$ one shown by Singh[19]. A large Γ-centered hole cylinder shows some flattening perpendicular to the Γ-K direction, this cylinder holds 0.43 a_g holes/Co. In addition, there are six additional, primarily e'_g in character, hole cylinders lying along the Γ-K directions, containing 0.04 holes in each of the six small cylinders. The total is the 0.67 holes necessary to account for the $x = 0.33$ electron count. This FS geometry leads to several important phase space features. There are the nesting wavevectors that translate one of the small cylinders into another, giving three distinct intercylinder nesting vectors. If these cylinders were circular, these vectors would represent strong nesting vectors for charge- or spin-density waves, and in addition the susceptibility for $Q \leq 2k_F$ scattering processes is constant in two dimensions.[35] The actual cylinders have an eccentricity of 1.25, weakening these nesting features somewhat. There are in addition the processes with $Q \leq 2K_F$ of the large cylinder.

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 $J = 11$ 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 as suggested on the basis of NMR data,[6] but of a new type driven by a combination of charge-ordering and AFM tendencies. The $x = \frac{1}{3}$ Fermi surface has been presented and discussed, assuming strong 2D fluctuations restore the paramagnetic metallic state (as is observed). State character at the Fermi surface indicates that multiband effects are likely to be important to the complete understanding of the behavior of NxCO.

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