

Disproportionation and Critical Interaction Strength in Na_xCoO_2 : Concentration Dependence

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We present results of studies of charge disproportionation (CD) and spin differentiation in Na_xCoO_2 using the correlated band theory approach (local-density approximation+Hubbard U:LDA+U). The simultaneous CD and gap opening can be followed through a first order charge disproportionation transition. By comparison with experiments, we propose a value of the Coulomb repulsion strength $U(x)$ that has significant dependence on the carrier concentration x , for which we obtain a phase diagram. The connection between the Co-O bond-length and effects of on-site correlation is also reported.

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Since the discovery of superconductivity with $T_c \sim 4$ K in water-intercalated Na_xCoO_2 (NxCO) by Takada et al. in the early of 2003,[1] several hundred papers have been published. The system shows several similarities to high T_c superconducting cuprates: layered transition metal oxide; vicinity of (presumed) Mott insulator CoO_2 ; variation with carrier concentration x ; a “superconducting dome.” However, it also has differences from cuprates: electron-doped system from Mott insulator phase, actually nonmagnetic metallic sister $x = 0$ phase, triangular lattice which can be frustrated, different superconducting dome shape, and low T_c .

In addition to its interesting properties in view of superconductivity, its normal state has a rich phase diagram depending on carrier concentration x . [2] For $x < 0.5$ the Pauli-like susceptibility has been observed, while for $x > 0.5$ the susceptibility shows local moment (Curie-Weiss) behavior. For $0.75 \leq x \leq 0.85$, NxCO shows antiferromagnetic (AFM) alignment of ferromagnetically ordered CoO_6 layers. [3] Specifically at $x=0.5$, the system has been observed to undergo a charge disproportionation ($2\text{Co}^{3.5+} \rightarrow \text{Co}^{3+} + \text{Co}^{4+}$) and metal-insulator transition at 50 K, while the rest of the phase diagram is metallic. [2]

We have focused on normal state electronic and magnetic structure of NxCO , with specific interest in ordering near the ground state, and characterizing the strength and consequences of correlation effects. In transition metal oxides in general, the mechanism of charge ordering or charge disproportionation (CD) is an important issue, and our work provides new inroads in the understanding of the mechanisms of disproportionation.

Our calculations were based on the supercell approach, [4, 5] using the full-potential local-orbital method (FPLO). [6] Both popular schemes for LDA+U functional were monitored. (The intra-atomic exchange integral $J=1$ eV was left unchanged.) Both have the same Hubbard-like density-

density interaction, but differ in just how to subtract out “double counting” of the pair interaction. One way, the so-called Fully Localized Limit (or Atomic Limit), [7] is an atomic-like treatment and is appropriate for large on-site Coulomb repulsion U , *e.g.* strong localization of the correlated orbital. Another is often called the Around Mean Field [8] and is more appropriate when U is not so strong. In this sodium cobaltate, our calculations have shown similar results from both schemes.

Within the local density approximation (LDA), all Co magnetic moments are nearly equivalent, that is, there are only $\text{Co}^{(4-x)+}$ ions. The distorted CoO_6 edge-sharing and the layered structures make t_{2g} manifold split into $a_g + e'_g$. Upon introducing U , both magnetic moments decrease linearly at small U . (So far, there is no agreement on the best value of U . Our value is specifically determined to allow the modeling of NxCO with LDA+U calculations.) At a critical value U_c , the moments change discontinuously due to a first-order transition: the state with similar magnetic moments no long is a solution, and the new state shows changes in moments just as expected from charge disproportionation $\text{Co}^{(4-x)+} \rightarrow x\text{Co}^{3+} + (1-x)\text{Co}^{4+}$. This change occurs simultaneously with metal-insulator transition associated with the Mott transition of the a_g orbital. Before CD, the a_g band has a similar band center and width as the doubly degenerate e'_g band.

One example of this CD is shown in Fig. 1 for $x = 0.5$, note that it is possible to follow hysteresis within the region $3.2 \leq U \leq 3.6$ eV and outside this range only one of the states, CD or undisproportionated (UD), is obtained. The two solutions can be observed in another way, using fixed spin moment (FSM) calculations within LDA+U in the critical region (bottom panel of Fig. 1). In this method, the energy is calculated versus a constrained value of the total moment, and the energy versus total magnetic moment plot becomes two curves, in which one state

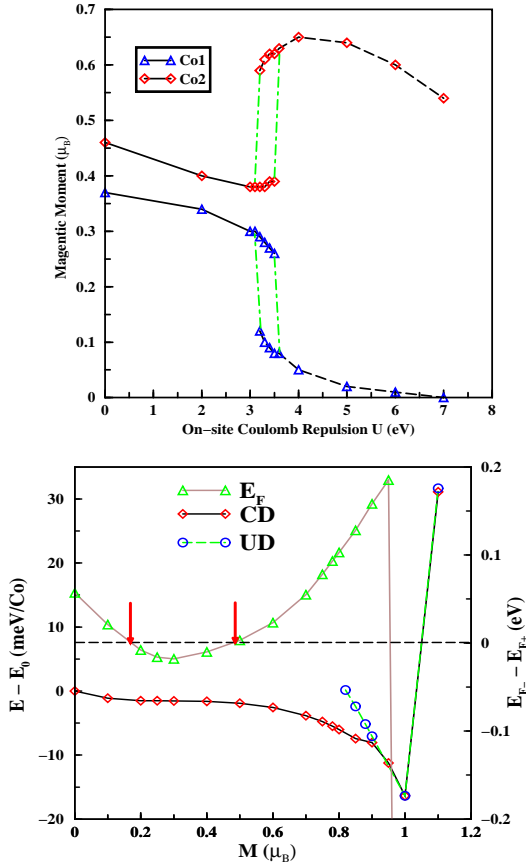


FIG. 1: Upper panel: Effect of the on-site Coulomb repulsion U on the magnetic moments for ferromagnetic ordering in $\text{Na}_{0.5}\text{CoO}_2$. The change shows a first-order transition (and accompanying hysteresis) in the critical region (3.2 eV to 3.6 eV). Metal-insulator transition simultaneously occurs with CD ($\text{Co1} \rightarrow \text{Co}^{3+}$, $\text{Co2} \rightarrow \text{Co}^{4+}$) due to nature of the first-order transition. Dashed and solid lines indicate the CD and UD states, respectively. Bottom panel: Fixed spin moment calculation of energy vs. total magnetic moment M (in $\mu_B/2\text{Co}$) at $U=3.3$ eV in $\text{Na}_{0.5}\text{CoO}_2$. The left and right sides of the y-axis denote the total energy difference and difference between minority and majority Fermi energy (effective applied field), respectively. The arrows mark zeroes of the Fermi energy difference, which correspond to extrema of the energy.

or the other is reached depending on starting point. Compared with LDA FSM results by Singh,[9] our LDA+ U FSM shows two differences that are worthy of note. First, at $M = 0\mu_B$, this system is antiferromagnetic (AFM) with Co magnetic moment $0.34\mu_B$; Singh started from a nonmagnetic state at $M=0$ and kept all Co ions identical. Secondly, at small M , the energy vs. total moment plot is nearly flat, but having two extrema [stable at $M = 0.16\mu_B$ and unstable at $M = 0.5\mu_B$]. Due to the miniscule energy

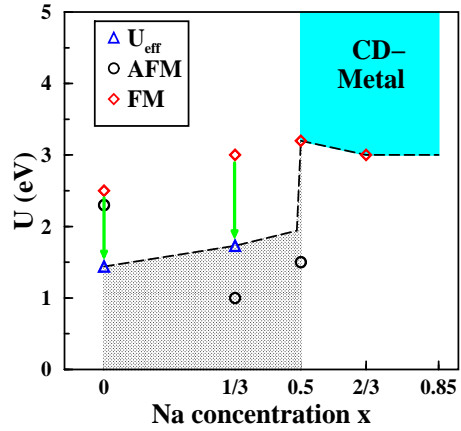


FIG. 2: Effect of Na concentration x on the critical on-site Coulomb repulsion U_c for CD. Allowing antiferromagnetic ordering, U_c drops largely by about 2 eV for $x > 0$, while the change is negligible for $x = 0$. The arrows denote drop of the effect on-site Coulomb repulsion U^{eff} due to three-band nature for $x < 0.5$ (see text). Considering ferromagnetic ordering, comparison with experiments suggests a change of U with sharp jump at $x = 0.5$, depicted by the shaded region. The data are from Ref. [4, 5, 10].

barrier, this small net moment minimum will not be accessible experimentally.

As shown in Fig. 2 and described in the caption, the critical value U_c for disproportionation depends on the carrier concentration x and the type of magnetic order. In the lower half of the range $x \leq 0.5$, U_c increases linearly for ferromagnetic (FM) ordering. However, allowing AFM ordering, $U_c(x)$ shows somewhat complicated behavior. While U_c for both FM and AFM is almost identical at $x = 0$, the value for presumed AFM order decreases sharply for $x \neq 0$. From Fig. 2, U_c for AFM is smaller by 2 eV than that of FM for $x=1/3$ and $x=1/2$. (note $U_c \sim 1$ eV for AFM at $x=1/3$). [The supercells we used do not allow for combined disproportionation and AFM ordering for $x = 2/3$.]

Furthermore, comparison with experiments suggests that $U(x)$ is significantly dependent on the carrier concentration x . First, no observation of CD nor any significant correlation effects at all for $x < 0.5$ indicates that $U(x < 0.5)$ is less than U_c . However, the study of Gunnarsson and coworkers shows that in a N -multiband system the effective Coulomb repulsion becomes $U^{eff} = U/\sqrt{N}$. [11] Below U_c , the a_g band is only distinguishable from the t_{2g} manifold (in energy) by lying slightly higher, and hosting most of the $1-x$ holes. As a result the system at $x < 0.5$ maintains multiband (three-band) behavior, resulting in $U_c^{eff} = U_c/\sqrt{3} \sim 1.4$ eV and 1.7 eV for $x = 0$ and $x = 1/3$, respectively. Since only a

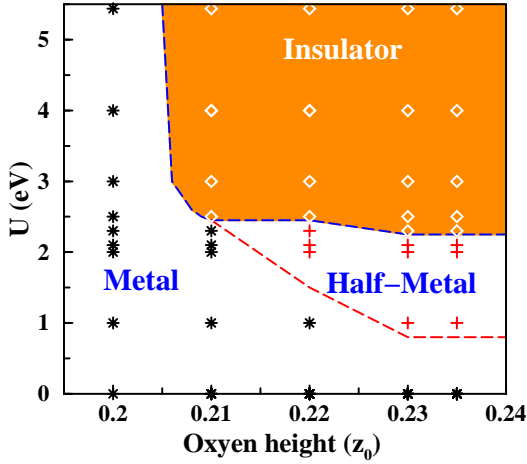


FIG. 3: Phase diagram depending on oxygen height (z_0) and U for ferromagnetic ordering at $x = 0$. (Energetically, $z_0 = 0.235$ is favored.) Lattice constant $c = 4.2509$ Å is used. The symbols describe metallic (*), half-metallic (+), and insulating (diamond) states. The data are from Ref. [5].

tiny band gap (~ 15 meV) is observed at $x = 0.5$, [12] $U(x = 0.5)$ must be near the minimum value for CD, i.e. $3.5 - 4$ eV. For $x > 0.5$, the observed Curie-Weiss susceptibility indicates $(1-x)\text{Co}^{4+}$ and $x\text{Co}^{3+}$ ions, so that the charge is disproportionated even though the system is a good metal. [13] Thus, $U(x > 0.5)$ is above 3 eV, perhaps over 4 eV. We will discuss this $x=0.5$ state elsewhere. It remains for further research to decide how accurately LDA+U should be for the band gap, or whether dynamics of the correlations are important.

Another issue which is drawing attention in these cobaltates is whether the change of O height (i.e., Co-O bond-length) is important as the carrier concentration x increases. Johannes et al. have calculated the oxygen height z_0 by energy minimization, and concluded that the change has little effect in the range $0.3 \leq x \leq 0.75$. [14] However, their cal-

culations, and therefore conclusions, are confined to the local density approximation results and predictions. We have carried out a study at $x=0$ to address whether correlation effects described by the LDA+U method are affected by the oxygen height. Figure 3 shows phase diagram in the relevant portion of the $U - z_0$ plane in the relevant range of U and allowing FM ordering of the system.

For $z_0 \geq 0.21$, the system undergoes a metal-insulator transition, implying CD, as U is increased. The critical value U_c depends little on O height. In fact, ΔU_c is only 0.1 eV between $z_0 = 0.22$ and $z_0 = 0.23$, which is the same variation of O height as measured between $x = 0.3$ and $x = 0.7$. This result suggests that the critical value U_c for CD is little affected by O height in this system. In addition, it is worthwhile to note that a metal to half-metal transition occurs even for very small U before the transition to insulator (for example, at $U=1$ eV for $z_0 = 0.23$).

Note however that for a height $x_0=0.20$, no CD is obtained for U up to 5.5 eV, much different from the behavior for $z_0 \geq 0.21$. So while this bondlength lies outside the accessible range, it does show that there is a regime where correlation effects depend very strongly on the Co-O bond length, and that the system is not so far from that regime. Finally, we note that the transitions with varying U discussed here should be of special interest for high pressure research because, for a system near U_c , varying U will be analogous to applying pressure to change U/W ratio (W is the correlated orbital's bandwidth).

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