Disproportionation, Metal-Insulator Transition, and Critical Interaction Strength in $Na_{1/2}CoO_2$

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Charge disproportionation (CD) and spin differentiation in $Na_{1/2}CoO_2$ are studied using the correlated band local-density approximation + Hubbard U (LDA+U) approach. The simultaneous CD and gap opening seen previously is followed in detail through a first-order charge disproportionation transition $2Co^{3.5+} \rightarrow Co^{3+} + Co^{4+}$. Disproportionation in the Co a_g orbital results in half of the ions (Co^{3+}) becoming electronically and magnetically dead, transforming the quarter-filled a_g system into a half-filled subsystem that subsequently undergoes the observed charge ordering or metal-insulator transition. Comparing with data in the $x \approx 0.3$ regime suggests the system has moved into the multiband regime where the effective Coulomb repulsion $U \rightarrow U_{\text{eff}} = U/\sqrt{3}$ strongly lessens correlation effects.

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The discovery by Takada and coworkers of superconductivity [1] in $Na_{0.3}CoO_2 \cdot 1.3H_2O$ near 5 K has led to extensive studies of the rich variation of properties in the Na_xCoO_2 system ($0.2 \leq x \leq 1$). It has been pointed out [2–4] that the formal charge of the Co ions that occupy a triangular lattice, whose simple average is $4 - x$, changes at $x \simeq 0.5$: for $x > 0.5$ the observed Curie-Weiss (CW) susceptibility indicates $(1 - x)$ Co^{4+} ions with spin $S = \frac{1}{2}$ and x Co^{3+} with $S = 0$, while for $x < 0.5$ the susceptibility is Pauli-like and all Co ions are identical ("$Co^{(4-x)+}$"). At $x = 0.5$ there is charge ordering (CO) as observed by electron diffraction, [3,5,6] probably accompanied by antiferromagnetic (AFM) spin ordering. While the rest of the phase diagram is metallic, this $x = 0.5$ phase undergoes a CO+ metal-insulator transition (MIT) at 50 K [3,7].

The mechanism(s) underlying CO has been a central question in numerous transition metal oxides, especially the cuprates and manganates. The CO question is beginning to be addressed in these cobaltates, from the mechanism of ordering at commensurate concentrations [2,4,8] to the effects of fluctuations when the concentration varies from a commensurate fraction [2,9]. Preceding the question of CO however must come the more basic one of charge disproportionation (CD) of a lattice of identical $Co^{(3+x)+}$ ions for $x < 0.5$ to disproportionated Co^{3+}/Co^{4+} ions with their distinct charges and spins. CD is a signature of intraatomic correlation and is closely associated with local moment formation, but it also has a collective nature to it (every ion disproportionates). Moment formation has been studied primarily in single-band models in conjunction with the correlation-driven MIT, [10] but CD in multiband systems is a substantially more involved question and is relatively unstudied.

Recently some of the present authors obtained a CD-MIT [4] in a study of Na_xCoO_2 ($x = 1/3$, also $x = 2/3$) using the LDA + U (local-density approximation + Hubbard U) method. For no apparent reason, the CD-CO transition appeared *simultaneously* with the MIT (band gap opening) as the interaction strength U was varied in the 3–4 eV range. One of the central questions in these cobaltates is the relevance of its multiband nature. The single-band Hubbard model undergoes a MIT only at half filling. The orbital degeneracy of open $3d$ shells has stimulated studies into the possibility of orbital-selective metal-insulator transitions, [11,12] but there has been no investigation yet into an entirely new possibility: CD into filled and therefore dead ions, followed by MIT within the resulting system. In Na_xCoO_2 the threefold t_{2g} manifold lacks $x/6$ carriers per Co of being filled; structure-induced broken symmetry $t_{2g} \rightarrow a_g + e_g'$ raises additional issues, but the band centers remain the same in this system. Local-density approximation (LDA) calculations indicate both a_g and e_g' Fermi surfaces already at $x = \frac{3}{4}$, and the presence of e_g' Fermi surfaces has become a central component of several models of the superconducting phase [13].

A question we address is that of correlation versus band-filling effects as they relate to the mechanism of CD-CO-MIT transitions in a multiband system, with Na_xCoO_2 as the example. There have been a few pioneering applications of correlated band theories to model disproportionation [2,4,14]. We study more thoroughly the $x = \frac{1}{2}$ case, which has become more compelling since a CO-MIT was observed [3]. The variable in our study will be U, but in a small parameter range such as near the critical value U_c, varying U will be analogous to applying pressure to change the U/W ratio; hence predictions are open to verification by pressure experiments. Comparison with observations suggest $U_c \approx 3.5$ eV, with multiband effects reducing the effective $U \rightarrow U_{\text{eff}} \approx U_c/\sqrt{3}$ for $x < 0.5$, and reduction of carrier density for $x > 0.5$ progressively increasing correlations in that regime.

Our calculations, based on the underlying hexagonal structure (space group $P6_322$, $a = 2.84$ Å, $c = 10.81$ Å, [15]) were done with a two Co supercell (space group $P2/m$) allowing two ions Co1 and Co2 to be realized in the cell. The O height was taken as $z_0 = 0.168(c/2) = 0.908$ Å as relaxed by LDA calculation by Singh [16]. The calculations were carried out with the full-potential nonorthogonal local-orbital minimum-basis scheme [17] and both popular schemes [18,19] for LDA + U functional with the main results being common to each. Since Na_xCoO_2 is a metal (except at $x = \frac{1}{2}$ which we address), the results quoted in this Letter are those from the so-called "around mean field" scheme [18] appropriate for relatively small U. The Brillouin zone was sampled with 128 (306 for LDA + U calculations) k points in the irreducible wedge. Orbitals for the basis set contained $3s3p4s4p3d$ for Co, and $2s2p3s3p3d$ for O and Na, and provide excellent basis flexibility. Almost identical results were obtained with the WIEN2K code [20]. The doubled unit cell allows for CD into Co^{3+} and Co^{4+}, but with only one magnetic ion there is no issue of spin order (except simple alignment). Hence we work throughout with a ferromagnetic (FM) doubled cell. In the local spin density approximation a FM state is favored slightly over the nonmagnetic state, with a total moment of 1 μ_B as noted first by Singh [16]. Because the Na ions are ordered above the CO transition, [21] the Co ions have somewhat different moments because the symmetry is already broken by the Na ordering.

The effect of the on site Coulomb repulsion U on the magnetic moments is displayed in Fig. 1. Although unconstrained, the total cell moment remains at 1 μ_B: half metallic in the metallic phase, insulating in the CD phase. Both Co magnetic moments decrease slowly (-0.025 μ_B/eV) with increasing U, due to some majority charge transfer Co → O. At $U = U_{c2} = 3.6$ eV, the solution changes character *discontinuously*, with resulting moments providing the clear identification $\text{Co1} \rightarrow Co^{3+}$, $\text{Co2} \rightarrow Co^{4+}$. By $U = 4.5$ eV the large moment achieves its maximum and the small moment is negligible. For larger U the Co^{4+} moment tends to decrease. Upon decreasing U the moments vary continuously down to $U = U_{c1} = 3.2$ eV, below which the solution jumps back to the initial undisproportionated state. There is a 0.4 eV hysteresis in this CD transition centered at $U_c = 3.4$ eV. The first-order nature is consistent with no symmetry having been broken in our choice of simulation cell, and also accounts for the *simultaneous* CD and gap opening observed previously [4]: the regime of accelerating disproportionation includes the opening of the gap, but this region is inaccessible because of its higher energy than either the undisproportionated or CD states. This first-order transition is analogous to low-spin ↔ high-spin transitions mapped out using fixed spin moment calculations [22], but generalizing to a two dimensional space of Co1 and Co2 moments μ_1, μ_2, respectively, as considered first by Moruzzi, Marcus, and Kübler [23].

The disproportionation does not show up as strongly in $Co^{4+} \rightarrow Co^{3+}$ charge transfer as in the spin redistribution. As U increases from zero, a small amount of charge from both Co ions transfers (0.04–0.05e/eV) onto the O ions (this shift is smaller if using the "fully localized limit" LDA + U functional [19]). At the transition, as shown in Fig. 2, the $\text{Co1} \rightarrow Co^{3+}$ charge is continuous at the transition, while the $\text{Co2} \rightarrow Co^{4+}$ charge jumps by ~0.1 electron. The discontinuities in the majority and minority charges separately are also pictured in Fig. 2.

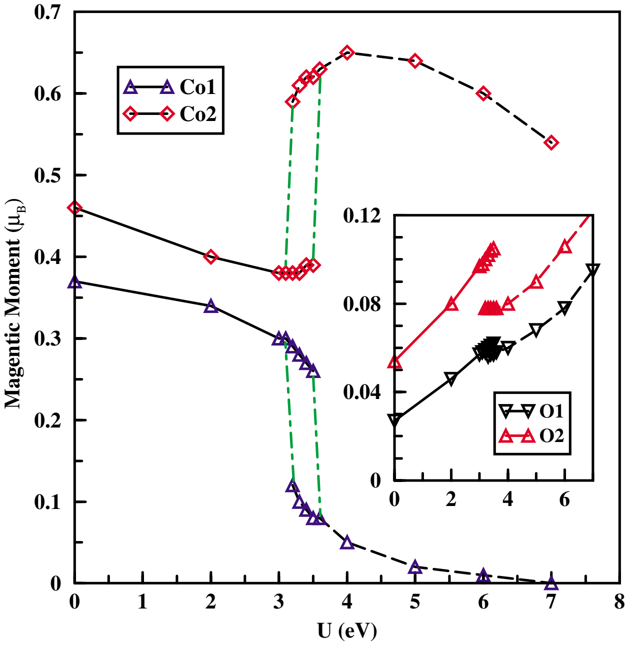

FIG. 1 (color online). Effect of U on the magnetic moments for Na_xCoO_2. The jump reflects a first-order transition (and accompanying hysteresis) in the critical region (3.2–3.6 eV). Gap opening (metal-insulator transition) simultaneously occurs with CD due to the first-order nature. Dashed and solid lines represent the CD and the undisproportionated state, respectively. Inset: Change of the magnetic moments for the O ions: O1 (with $2n$ site symmetry) is shared by two Co1 and one Co2, while O2 (with $2m$ site symmetry) is shared by one Co1 and two Co2.

The picture of the charge rearrangement at the transition becomes clearer when the a_g occupation is monitored, as shown in Fig. 3. At the CD transition, much of the *minority* a_g charge on Co1 ($\rightarrow Co^{3+}$) transfers to the *majority* on Co2 (becoming Co^{4+}). The *total charge* difference is only a fraction of the change in minority a_g charge, because it is compensated rather strongly by a rehybridization with the O ions and back polarization of the other $3d$ (e_g' and e_g) states, reminiscent of what was seen for variation of the cation (Na or Li) content . A large change in spin is achieved without a large change in total charge because of the multiband nature of the system at and near the Fermi level.

The energy $E(U)$ is presented in Fig. 4. The total energy is essentially continuous at the transition (equal at the midpoint $U = 3.4$ eV). As CD occurs, the (Kohn-Sham all-electron) kinetic energy jumps sharply by 0.74 eV/Co

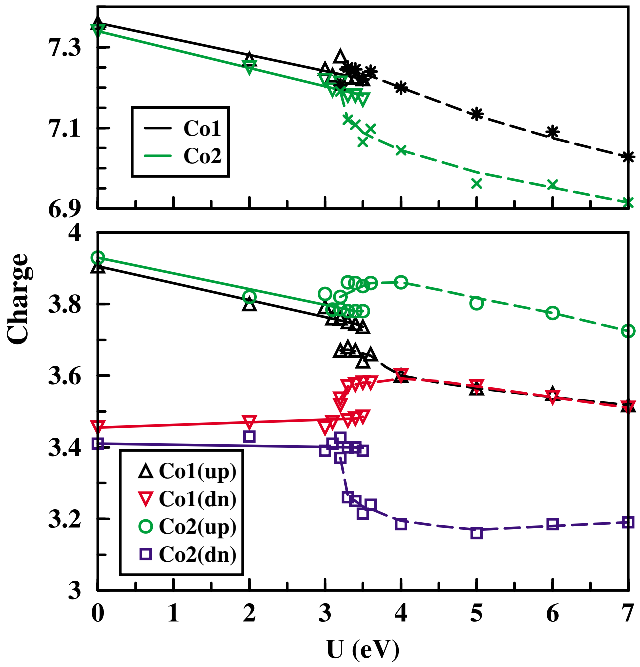

FIG. 2 (color online). Change with U of d charge for the two Co ions. Upper panel: change of total $3d$ charge (the charge is transferred to O ions). Lower panel: changes of the majority and minority separately.

while other contributions decrease (in eV/Co): 0.46 for the (electron + nuclear) potential energy, 0.09 for the LDA exchange-correlation, and 0.18 for the LDA + U correlation energy. The LDA + U correction is modest but essential to the transition, and only becomes large enough to tip the balance at $U = U_c$.

Now we discuss the relation of our study to data for $\mathrm{Na}_{1/2}\mathrm{CoO}_2$ and draw further inferences from our results. Whereas previous LDA + U studies [25] of the $\mathrm{Na}_x\mathrm{CoO}_2$ system did not obtain disproportionation, we have shown that reducing constraints allows, and leads to, disproportionation. Na orders in this system above the MIT [3] so our Na-ordered cell is realistic in that respect. The observed cell is twice as large as we have allowed, so it has not been possible to study AFM ordering in our cell. In $x = \frac{1}{2}$ samples, Co^{3+} and Co^{4+} ions are disproportionated already at high temperature (CW susceptibility) but charge/spin *disordered* until the transition; (poor) conduction changes abruptly to insulating behavior when CO occurs at 50 K. In our ($T = 0$) simulation, Co1 and Co2 are undisproportionated for $U < U_c = 3.4$ eV, whereas for $U > U_c$ the ions disproportionate. Since the gap is tiny ($\sim$15 meV from infrared conductivity data [7]) we conclude that U is near its minimum value for CD, i.e., $U \approx 3.5$–4 eV. Within LDA + U, the MIT is orbital selective, [11,12] however this result is no doubt affected by the larger a_g bandwidth compared to that of the e_g' orbitals.

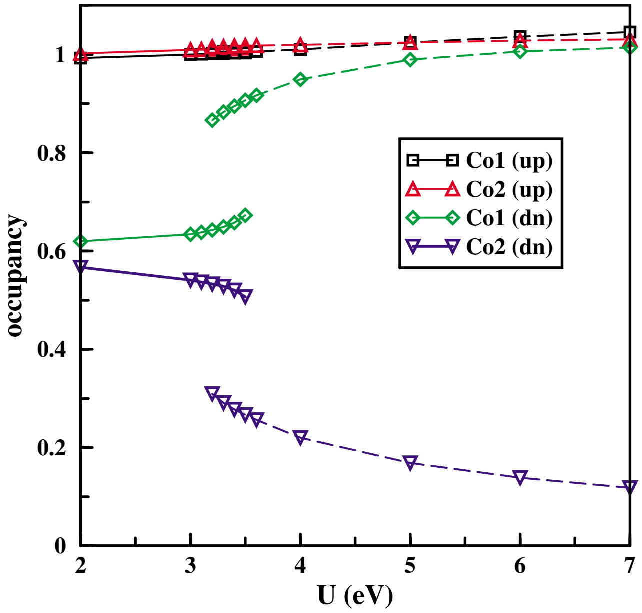

FIG. 3 (color online). Change of the occupancy n_{a_g} of the a_g state versus U, which reveals the strong a_g charge disproportionation at the transition. Majority orbitals of both Co ions are fully occupied regardless of U. At $U = U_c$, the occupancy of the minority decreases for Co2 and increases for Co1 by $0.23e$.

From susceptibility, heat capacity, and resistivity data, and confirmed by the large field-dependent thermopower [26], a large Kadowaki-Woods ratio [27], and many reports of magnetic ordering, the $x = 0.6$–0.8 phases clearly are highly correlated. This trend could result from an increase in the value of U (for example, fewer carriers lead to less screening) or the increase in signatures of correlation could arise from enhanced effects due to lower carrier density. While the $\mathrm{Na}_x\mathrm{CoO}_2$ system is $1 - x$ hole-doped from a band (not Mott) insulator, nevertheless this doping leads to $(1 - x)$ $S = 1/2$ ions due to the CD.

On the other hand, in the superconducting phase $x \approx 0.3$ the resistivity is lower and the mass enhancement over the band value is very small [2,4], so this phase is rather weakly correlated. We propose that this change of behavior is not due to a strong decrease in the value of U (as from additional screening, say) but rather because of a single-band-to-multiband crossover. Studies of the multiband Hubbard model [28] indicate the occurrence of the MIT is governed no longer by U/W, but by an effective $U_{\mathrm{eff}} = U/\sqrt{N}$ where N is the degeneracy ($N = 3$ here). Such a strong decrease in the effective repulsion could readily account for the observed drastic decrease in correlation effects.

Finally we note another important implication of our results. LDA + U conventional wisdom states that the "precise value of U is not very important", and indeed this is often checked explicitly and found to be true. Our discovery of the possibility of a CD transition in the

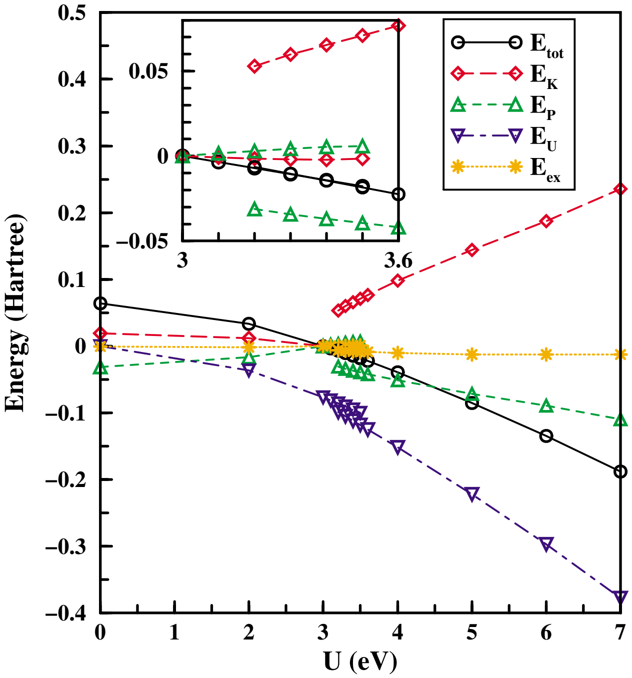

FIG. 4 (color online). Change in energy $E(U)$ per doubled supercell versus U, relative to E ($U = 3$ eV), showing the various contributions discussed in the text. Values shown are energy differences with respect to the value at $U = 3$ eV, except the LDA + U energy E_U whose actual value is plotted. Inset: Blowup of the critical region.

LDA + U method versus the strength of U reveals that care be exercised, because releasing constraints by allowing symmetry breaking to occur may lead to regimes where the precise value of U is crucial.

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