Disproportionation Transition at Critical Interaction Strength: 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 theory approach. The simultaneous CD and gap opening seen previously is followed through a first order charge disproportionation transition 2Co$^{3+}$ + Co$^{4+}$, whose ionic identities are connected more closely to spin (S=0, S=1/2) than to real charge. Disproportionation in the Co $a_g$ orbital is compensated by opposing charge rearrangement in other 3$d$ orbitals. At the transition large and opposing discontinuities in the (all-electron) kinetic and potential energies are slightly more than balanced by a gain in correlation energy. The CD state is compared to characteristics of the observed charge-ordered insulating phase in Na$_{1/2}$CoO$_2$, suggesting the Coulomb repulsion value $U$ is concentration-dependent, with $U(x = 1/2) \approx 3.5$ eV.

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The discovery by Takada and coworkers of superconductivity$^1$ in Na$_{0.5}$CoO$_2$ at 1.3 K near 5 K has led to extensive studies of the rich variation of properties in the Na$_x$CoO$_2$ system ($0.2 < x < 1$). It has been pointed out$^2$ that the formal charge of the Co ions that occupy a triangular lattice, whose simple average is $4 - x$, changes at $x \approx 0.5$: for $x > 0.5$ the observed Curie-Weiss (C-W) susceptibility indicates $(1 - x)$ Co$^{3+}$ ions with spin $S = \frac{1}{2}$ and $x$ Co$^{3+}$ ions with $S = 0$, while for $x < 0.5$ the susceptibility is Pauli-like and all Co ions are identical ("Co$^{(4-x)+}$"). In a narrow region around $x = 0.5$ there is charge ordering (CO) as observed by electron diffraction,$^3$ probably accompanied by antiferromagnetic 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 as verified by resistivity$^4$ and optical conductivity.$^5$ $^8$

The mechanism of charge ordering has been a central question in many classes of 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$^2$ to the effects of fluctuations when the concentration varies from a commensurate fraction.$^2$ $^{10}$ Preceding the question of CO however must come the more basic one of disproportionation of a lattice of identical Co$^{3+}$ 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.$^{11}$ but CD in multiband systems (as Na$_{0.5}$CoO$_2$ almost certainly is) 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$_x$CoO$_2$ ($x = 1/3$, also $x = 2/3$) using the correlated band theory method LDA+U (local density approximation plus Hubbard U). 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. Another feature that was not clarified is that this CD involved rather little actual redistribution of charge but at $x = \frac{1}{4}$ showed up dramatically in the magnetic moment as the metamorphism $3$Co$^{3+}$ $\rightarrow$ Co$^{3+}$+2Co$^{4+}$. One of the central questions in these cobaltates is the relevance of its multiband nature, a complicating aspect that has stimulated studies into the possibility of orbital-selective metal-insulator transitions.$^{12}$ $^{13}$ In Na$_x$CoO$_2$ the threefold $t_{2g}$ manifold is partially filled, with broken symmetry $t_{2g} \rightarrow a_g + e_g$ arising from the CoO$_2$ layered structure. LDA calculations indicate both $a_g$ and $e'_g$ Fermi surfaces already at $x = \frac{1}{3}$, and the presence of $e''_g$ Fermi surfaces has become a central component of several models of the superconducting phase.$^{14}$

Another important question is that of correlation effects and especially the mechanism of CD/CO/MIT transitions. There have been a few pioneering applications of correlated band theories to model disproportionation.$^2$ $^4$ $^{15}$ In this paper we study more thoroughly the $x = \frac{1}{4}$ case, which has become more compelling since a CO/MIT was observed.$^1$ 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 direct experimental comparison. In addition, the CD/CO that is observed as $x \rightarrow 0.5$ sug-
were done with a two Co supercell with space group $P6_3/m$ allowing two ions Co1 and Co2 to be realized in the cell. The O height was taken as $z_0 = 0.168(a/2) = 0.908 \, \text{Å}$ as relaxed by LDA calculation by Singh. The calculations were carried out with the full-potential nonorthogonal local-orbital minimum-basis scheme (FPLO) and both popular schemes for LDA+U functional with the main results being common to each. Since $\text{Na}_x\text{CoO}_2$ is a good metal (except at $x = \frac{1}{2}$ which we address), the results quoted in this paper are those from the so-called “around mean field” scheme 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 $2s2p3s3p3d$ for Co, O, and Na provide excellent basis flexibility.

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 (by a small energy) over the nonmagnetic state, with a total moment of 1 $\mu_B$ as noted first by Singh. Because the Na ions are ordered above the CO transition, the Na site is nonsymmetric with respect to the Co sites, and 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. We follow behavior with $U$ continuously by using the solution from one value of $U$ as the starting point for the case with incrementally increased/decreased $U$. Although unconstrained, the total cell moment remains at 1 $\mu_B$: half metallic in the metallic phase, insulating in the CD phase. Both Co magnetic moments decrease slowly (-0.025 $\mu_B$/eV) with increasing $U$, probably due to some charge transfer Co $\rightarrow$ O. At $U = U_{c2} = 3.6$ eV, the solution changes character discontinuously, with the small and large moments providing the clear identification Co1$\rightarrow$Co$^{3+}$, Co2$\rightarrow$Co$^{4+}$. By $U = 4.5$ eV the large moment obtains a 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. Hence we find a 0.4 eV hysteresis in this CD transition centered at $U_{c2} = 3.4$ 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:\textsuperscript{3} 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,\textsuperscript{22} but generalizing to a two dimensional space of Co1 and Co2 moments $\mu_1, \mu_2$ respectively as considered first by Moruzzi, Marcus and K"ubler.\textsuperscript{23}

Although Co1 and Co2 become quite different above $U_c$, the disproportionation does not show up as strongly in Co$^{3+}$ ↔ Co$^{4+}$ charge transfer as in the spin rearrangement. As $U$ increases from zero, a small amount of charge from both Co ions transfers (0.04-0.05 e/Co) onto the O ions (this shift is smaller if using the “fully localized limit” LDA+U functional\textsuperscript{21}). At the transition, as shown in Fig. 2 the Co1$\rightarrow$Co$^{3+}$ charge is continuous at the transition, while the Co2$\rightarrow$Co$^{4+}$ charge jumps by $\sim$0.1 electron. The discontinuities in the majority and minority charges separately are also pictured in Fig. 2.

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 and back polarization of the other 3$d$ ($e_g$ and $e_g$) states, reminiscent of what was seen for variation of the Na content.\textsuperscript{24} A large change in spin is achieved without large change in total charge because of the multiband nature of the system at and near the Fermi level.

The energy $E(U)$ is shown in Fig. 4. In the critical region, the undisproportionated state is favored marginally (only 8 meV/Co), a difference so small that the total energy is essentially continuous at the transition. As CD occurs, the (Kohn-Sham) kinetic energy jumps sharply by 0.74 eV/Co while other contributions decrease: (in eV/Co) 0.46 for the (electron+nuclear) potential energy, 0.09 for the LDA exchange, and 0.18 for the LDA+U correlation energy ($\propto U$). 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 Na$_1$/2CoO$_2$. Na orders in this system above the MIT\textsuperscript{22} so our Na-ordered cell is realistic in that respect. The observed cell is twice as large as we have allowed, so it is not possible to study AFM ordering in our cell. In $x = \frac{1}{2}$ samples, Co$^{3+}$ and Co$^{4+}$ ions are disproportionated (C-W susceptibility) but charge/spin disordered above the transition; conduction is poor and abruptly becomes insulating when CO occurs. In our ($T=0$) simulation, Co1 and Co2 are undisproportionated with a half metallic spectrum for $U < U_c$, whereas for $U > U_c$ the ions dis-

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**FIG. 3:** 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 0.23 $e$.

**FIG. 4:** 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. Insert: Blowup of the critical region.
proportionate. Within LDA+U, the MIT is orbital-selective. While the distinction between our results and cobaltate behavior are evident, the question of CD is quite separate from that of CO: experimentally, the C-W susceptibility indicates CD in the sample at high temperature, but the simultaneous MIT/CD occurs only at 50 K.

From the infrared conductivity Hwang et al. have reported a very small 10 meV gap in their insulating Na sample at high temperature, but the simultaneous C-W susceptibility indicates CD in the system is very close to (only slightly larger than) $U_c$, i.e. $U(x = \frac{1}{2}) \approx 3.5 - 4$ eV. From susceptibility, heat capacity, and resistivity data the $x = 0.7 - 0.8$ phases are clearly more correlated ($U > 4$ eV), confirmed by the very large field-dependent thermopower, an extremely large Kadowaki-Woods ratio, and many reports of magnetic ordering. 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 so this phase is at most weakly correlated with $U(x \approx 0.3) < 3$ eV.

Whereas previous LDA+U studies of the NaCoO$_2$ system did not obtain disproportionation, we have shown that reducing constraints allows, and leads to, disproportionation. In opposition to LDA+U conventional wisdom (“precise value of $U$ is not very important”), results for Na$_x$CoO$_2$ are very sensitive to the value of $U$ around the critical value $U_c = 3.4$ eV. We view Na$_x$CoO$_2$ in terms of a concentration dependent $U(x)$, which may be in part a guise for a single band → three band crossover around $x = \frac{1}{2}$ as discussed earlier. In such cases studies of the multiband Hubbard model suggest $U_{\text{eff}}$ for the single band regime ($x$ close to unity) becomes $U_{\text{eff}} = U_c/\sqrt{3}$ for the three band regime ($x < \frac{1}{2}$), in which case $U$ for the superconducting phase could be even smaller than our estimate above.

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[1] K. Takada et al., Nature 422, 53 (2003).
[2] J. Kuneš, K.-W. Lee, and W. E. Pickett, in Proc. NATO Advanced Research Workshop on New Challenges in Superconductivity, NATO Science Series II (Kluwer, 2004) in press.
[3] M. L. Foo et al., Phys. Rev. Lett. 92, 247001 (2004).
[4] K.-W. Lee, J. Kuneš, and W. E. Pickett, Phys. Rev. B 70, 045104 (2004).
[5] H. W. Zandbergen et al., Phys. Rev. B 70, 024101 (2004).
[6] Q. Hwang et al., J. Phys.: Condens. Matter 16, 5803 (2004).
[7] J. Hwang, J. Yang, T. Timusk, and F. C. Chou, cond-mat/0405200.
[8] N. L. Wang et al., cond-mat/0405218.
[9] O. I. Motrunich and P. A. Lee, Phys. Rev. B 69, 214516 (2004).
[10] G. Baskaran, cond-mat/0306569.
[11] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[12] A. Liebsch, Phys. Rev. Lett. 91, 226401 (2003).
[13] A. Koga, N. Kawakami, T. M. Rice, and M. Sigrist, Phys. Rev. Lett. 92, 216402 (2004).
[14] K. Kuroki, Y. Tanaka, and R. Arita, Phys. Rev. Lett. 93, 077001 (2004); M. D. Johannes, I. I. Mazin, D. J. Singh, and D. A. Papaconstantopoulos, Phys. Rev. Lett. (in press) cond-mat/0403135; M. Mochizuki, Y. Yanase, and M. Ogata, cond-mat/0407094.
[15] V. I. Anisimov et al., Phys. Rev. B 54, 4387 (1996); S. Yamamoto and T. Fujiwara, J. Phys. Soc. Japan 71, 1226 (2002); Z. Szotek et al., Phys. Rev. B 68, 054415 (2003). Some of the results of Ref. [4] have been reproduced by Z. Li et al., cond-mat/0403727.
[16] Von M. Jansen and F. Hoppe, Z. Anorg. Allg. Chem. 408, 104 (1974).
[17] D. J. Singh, Phys. Rev. B 61, 13397 (2000).
[18] K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
[19] V. I. Anisimov et al., Phys. Rev. B 48, 16929 (1993).
[20] M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B 49, 14211 (1994).
[21] Q. Huang, M. L. Foo et al., cond-mat/0406570.
[22] K. Schwarz and P. Mohn, J. Phys. F 14, L129 (1984); G. L. Krasko, Phys. Rev. B 36, 8565 (1987).
[23] V. L. Moruzzi, P. M. Marcus, and J. Küberl, Phys. Rev. B 39, 6957 (1989).
[24] C. A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. 92, 196405 (2004).
[25] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 70, 054415 (2003). Some of the results of Ref. [4] have been reproduced by Z. Li et al., cond-mat/0403727.
[26] V. L. Moruzzi, P. M. Marcus, and J. Küberl, Phys. Rev. B 39, 6957 (1989).
[27] C. A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. 92, 196405 (2004).
[28] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 70, 054415 (2003). Some of the results of Ref. [4] have been reproduced by Z. Li et al., cond-mat/0403727.