Na_xCoO_2 in the $x \to 0$ regime: Coupling of structure and correlation effects

K.-W. Lee and W. E. Pickett
Department of Physics, University of California, Davis, California 95616, USA
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The study of the strength of correlations in Na_xCoO_2 is extended to the $x=0$ end of the phase diagram, where Mott insulating behavior has been widely anticipated. The inclusion of correlation as modeled by the LDA +U approach leads to a Mott transition in the a_g subband if $U \geqslant U_c = 2.5$ eV. Thus, U smaller than U_c is required to model the metallic, nonmagnetic CoO_2 compound reported by Tarascon and co-workers. The orbital-selective Mott transition of the a_g state, which is essentially degenerate with the e_g' states, occurs because of the slightly wider bandwidth of the a_g bands. The metal-insulator transition is found to be strongly coupled to the Co—O bond length, due to associated changes in the t_{2g} bandwidth, but the largest effects occur only at a reduced oxygen height that lies below the equilibrium position.

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I. INTRODUCTION

The unusual, correlated electron behavior of the Na_xCoO_2 (NxCO) system that has been confirmed in the $x \approx 0.6-0.8$ range[1] attracted the initial interest in this layered transition metal oxide system. The discovery that the hydration of $x \approx 0.3$ samples results in superconductivity[2,3] with $T_c = 4.5$ K has suggested analogies to the high-temperature superconducting cuprates—a quasi-two-dimensional transition metal oxide displaying superconductivity only within a certain doping range—and greatly heightened the excitement in this system. While several workers have already embarked on modeling the superconducting mechanism and symmetry,[4–8] there remains a much more fundamental issue: just how strong are correlation effects where superconductivity is observed? It is now recognized[9] that normal state properties do not show signs of correlated behavior around $x \sim 0.3$. However, correlation effects are easily evident in the $x \approx 0.6-0.8$ range: magnetic fluctuations are observed, the high-temperature susceptibility reflects local moments, the linear specific heat coefficient is strongly enhanced above the band value, and magnetic ordering occurs in the high end of this range. None of this behavior is observed for $x \approx 0.3$: susceptibility and NMR data show there are no magnetic ions, and the linear specific heat coefficient is not enhanced over the band value.

Signs of correlation effects are particularly evident at $x = 0.5$, where a metal-insulator transition (MIT) occurs[10] around 50 K, and strong signs of charge disproportionation $2Co^{3.5+} \to Co^{3+} + Co^{4+}$ are seen followed by ordering of the Co^{4+} spins. The possibilities of such behavior for $x \approx 0.3$ have been discussed[11,12] because strong on-site repulsion, geometrical effects, and commensurability all should conspire to encourage ordering at $x = 1/3$. Nevertheless, there has been no experimental indication of any such tendencies,[13] with the most direct conclusion being that correlation effects seem really minor in this regime. One suggestion[9,14] is that the multiband character of the $x = 1/3$ region considerably reduces the effect of the on-site Coulomb repulsion compared to strongly correlated phenomena observed in the $x \approx 2/3$ region.

Several new evaluations of the cobalt oxidation state in hydrated NxCO lend a new urgency to the issue of the degree of correlation in the system. Takada and collaborators, who discovered the superconductivity originally,[2] subsequently revealed that in their hydrated materials the formal valence of Co was +3.4 rather than the +3.65 that would be inferred from the $x = 0.35$ concentration of Na.[15] They identified the oxonium ion (also called hydronium) H_3O^+, one product of the hydration product, as being an additional dopant of the CoO_2 layer. Corroborating conclusions have been reached by Milne *et al.*[16] and Karppinen *et al.*:[17] their superconducting materials have a mean Co charge state close to +3.42 rather than the +3.65–3.7 that would be the case if only Na doping were responsible. Chen *et al.*[18] report that they can obtain the charge-ordered $Co^{+3.5}$ phase via doping with a combination of Na^+ and H_3O^+. The implication of these reports is that superconductivity occurs in the strongly correlated regime "x" > 0.5 rather than in the weakly correlated half of the phase diagram.

There have been few theoretical studies of the $x = 0$ limit (CoO_2), because this limit is extremely difficult to reach experimentally, and there is very limited data. Most of the models[19–21] of correlated-electron behavior in this system implicitly (or explicitly) assume that the Co on-site Coulomb repulsion U is strong enough that the $x = 0$ phase will be a Mott insulator. The electronic structure studies so far have taken this viewpoint as well,[22,23] by applying LDA+U correlated band theory with a large enough Hubbard repulsion strength U to model the presumed insulating phase. The most direct way for this to happen is for the e_g' states somehow to remain occupied and out of the picture, and for Mott physics to occur within the a_g band alone, resulting in Mott insulating behavior. (The layered structure and the distorted CoO_6 edge-sharing structure result in the symmetry lifting $t_{2g} \to a_g + e_g'$.) On the face of it, there are two impediments to this scenario: (1) what breaks the balance between the a_g and e_g' orbitals, both of which contain a substantial fraction of holes when x is small?; and (2) since the existing experimental information indicates that CoO_2 is a nonmagnetic metal rather than a correlated insulator, is CoO_2 close to a Mott insulating phase or not?

In this paper we present an investigation of the $x=0$ compound CoO_2, using the correlated band theory (LDA+U) approach, but accounting also for the experimental information that is available. Conventional band theory in the local density approximation (LDA) gives a half-metallic (or nearly so) ferromagnetic ground state for the CoO_2 layer throughout the NxCO system; this is not the correct picture for $x<0.75$, where there is no magnetic order (except exactly at $x=0.5$). This lack of magnetic order makes NxCO for $x<2/3$ a candidate for a fluctuation-induced paramagnet.[24] The appropriate value of U for this system is not well established, but seems to be significantly x dependent,[9,14] so we will vary its value within realistic limits to ascertain its effect, and attempt to be consistent with the available data.

II. EXPERIMENTAL INFORMATION

Whereas it had been thought previously that CoO_2 was too unstable to synthesize, Amatucci, Tarascon, and Klein[25] found that use of a dry plastic battery technology could be used to produce CoO_2 powders reproducibly by deintercalation of Li from Li_xCoO_2. This end compound was found to have a single CoO_2 layer hexagonal cell with $a=2.82$ Å, $c=4.29$ Å. The oxygen height in the octahedrally coordinated CoO_6 arrangement was not established, but the compound is metallic and nonmagnetic.[26] The metallicity perhaps explains why no Jahn-Teller distortion is seen for this nominally d^5 ion: the metallic behavior indicates that the Co^{4+} and O^{2-} formal valences cannot be taken as seriously as if it were an insulator.

Subsequent work by Tarascon *et al.*[27] on the $Li_xNi_{1-y}Co_yO_2$ system, and higher resolution data, reproduced the CoO_2 material. The lattice constants were slightly smaller, $a=2.80$ Å, $c=4.25$ Å, and the oxygen position was weakly constrained by the data to the range $0.17<z_0<0.23$. This structure of CoO_2 results in neighboring layers of charged "O^{2-}" ions that have been thought to be the cause of the instability of CoO_2 (and certainly would seem to contribute). The possibility of O—O bonding across the van der Waals gap in CoO_2 has been discussed,[27] and is consistent with the observed metallic character.

III. CRYSTAL STRUCTURE AND METHOD OF CALCULATION

All reports[27–30] of CoO_2 indicate the familiar edge-sharing octahedron structure (space group $P\bar{3}m1$, No. 164). We used the experimental lattice constants $a=2.8048$ Å, and $c=4.2509$ Å,[27] and optimized the oxygen height within LDA. The resulting value is $z_0c=0.235c=0.999$ Å, i.e., 95 deg Co—O—Co bond angle and 1.90 Å Co—O bond length (compare $z_0c\simeq 0.269c=1.14$ Å, 90 deg and 1.98 Å for undistorted octahedra). In both ferromagnetic (FM) and paramagnetic (PM) cases, the same relaxed value was found, so the value is insensitive to magnetic order. Venkatraman and Manthiram[29] reported $z_0c=0.257c$, but for nonstoichiometric $CoO_{1.72}$ samples. Our calculated value is 9% larger than the relaxed value ($z_0c=0.908$ Å, 98 deg) at $x=0.5$ by Singh,[31] indicating a large effect of the Na^+ ions or the c lattice parameter, or perhaps as important, the added electronic charge. When the lattice constants are fixed for all x, the relaxed O height z_0 increases nearly monotonically for $x\geqslant 0.3$.[22,32] The optimized z_0c at $x=0$ by Zhang *et al.*[22] is smaller by 0.1 Å than ours, because they used an artificially large c lattice constant (50% larger than the experimental one) to remove interlayer interactions. The difference illustrates that the interlayer interaction (i.e., the effect of a c lattice constant) is significantly coupled to the O height.

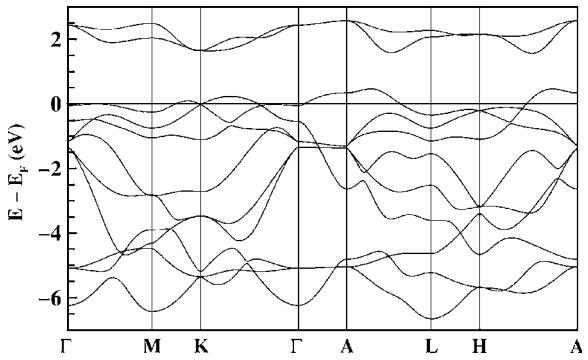

FIG. 1. LDA paramagnetic band structure of CoO_2. The e_g bands lie above 1.5 eV, and the t_{2g} bands in the range of −1 to 0.5 eV (but have strong hybridization with O $2p$ bands which are mainly below −1 eV).

The calculations reported here were carried out with two all-electron full-potential electronic methods, full-potential local-orbital method (FPLO)[33] and Wien2k,[34] with physically equivalent results. Both popular schemes[35,36] for the LDA+U functional were compared. (The intra-atomic exchange integral $J=1$ eV was left unchanged.) As found in previous studies,[9,11,14] this cobaltate system seems to lie in an intermediate regime, where the two forms[35,36] of the LDA+U functional give similar results; the difference in the double-counting corrections is small when the spin polarization is small. The Brillouin zone was sampled with 162 (545 for the fixed spin moment calculations) k points in the irreducible wedge and the basis sets were $3s3p4s4p3d$ for Co and $2s2p3s3p3d$ for O. The full-potential linearized augmented-plane waves (FLAPW), as implemented in WIEN2k code[34]

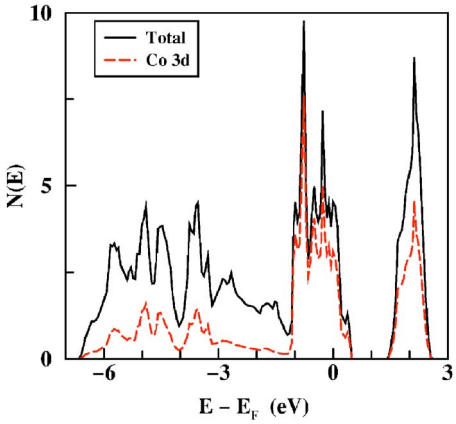

FIG. 2. (Color online) LDA paramagnetic DOS of CoO_2. The crystal field splitting of $t_{2g}-e_g$ is 2.5 eV, and the bandwidth of the t_{2g} manifold is 1.5 eV.

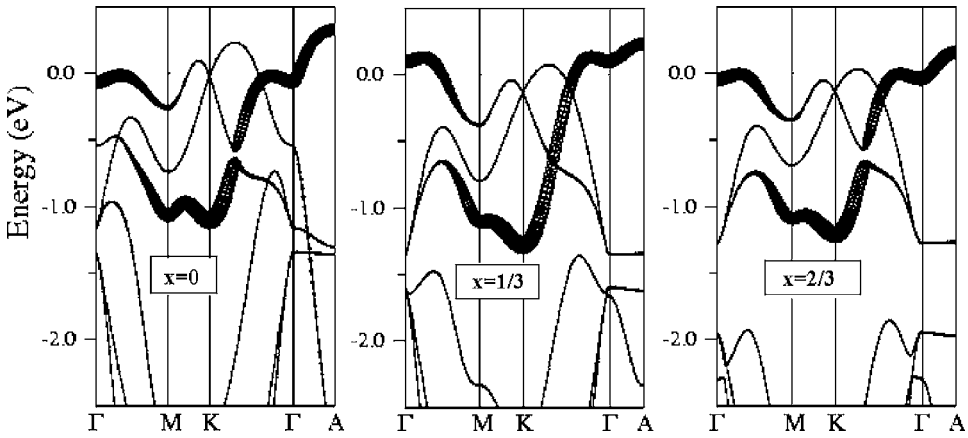

FIG. 3. LDA paramagnetic blowup band structures near t_{2g} manifold at $x=0$, 1/3, and 2/3 (in the virtual crystal approximation at $x=1/3$ and 2/3). As x increases, the e_g' cylindrical Fermi surfaces are shrunk and the band separation (near −1.5 eV) along the Γ-A between t_{2g} and O $2p$ becomes larger. The Fermi energy is at zero. The thickened lines emphasize the bands with strong a_g character. Lattice constants $a=2.8048$ Å, $c=4.2509$ Å and the oxygen height $z_0=0.235$ (0.999 Å) are used at $x=0$, while $a=2.84$ Å, $c=5.405$ Å, and $z_0=168$ (0.908 Å) at $x=1/3$ and 2/3.

was also used with the basis size determined by $R_{mt}K_{max}=7.0$ and APW sphere radii (2.0 for Na and Co, 1.5 for O). The calculations at $x=1/3$ and 2/3 were done with the virtual crystal approximation (Na nuclear charge $Z=10+x$) under the same conditions as the previous calculations by the present authors.[14]

IV. NONMAGNETIC $x=0$: CoO_2

This case corresponds most closely to nonmagnetic metallic CoO_2, as reported by Tarascon and co-workers.[25,27] The magnetic instability within LDA (incorrect, but generic for NxCO) will be discussed below. The LDA PM full band plot for CoO_2 is given in Fig. 1, with the corresponding density of states (DOS) given in Fig. 2. The result is metallic, containing one hole per Co in the t_{2g} bands. The $t_{2g}-e_g$ crystal-field splitting is 2.5 eV, the same amount as $x=1/3$, 1/2, and 2/3.[11,14,31] The t_{2g} manifold is in the range of −1 to 0.5 eV relative to the Fermi energy E_F, but is hybridized with O $2p$ bands, which are mainly below −1 eV, as can be seen by the Co $3d$ character in the O $2p$ band region, and *vice versa*.

It is instructive to compare this $x=0$ limit with the $x>0$ results already published.[9,11,14,22–24,31,32] The variation with x is provided for comparison in the enlarged band structures around the t_{2g} manifold at $x=0$, 1/3, and 2/3 given in Fig. 3. Although the Co—O bond length at $x=0$ is 2.5% larger than the $x=1/3$ and 2/3 values, suggesting less Co—O coupling; in fact, the d-p mixing is strongest at $x=0$. The reason is that the decrease in mixing due to t_{pd} is compensated by the decreasing in the $\varepsilon_{t_{2g}}-\varepsilon_p$ energy separation. The dispersion of the a_g band along the Γ-A line is much larger for $x=0$, so that quasi-two-dimensionality is reduced as the Na content x decreases (hole doping increases). In addition, the band separation near −1.5 eV along the Γ-A line between t_{2g} and O $2p$ becomes larger. The e_g' cylindrical Fermi surfaces containing holes become smaller as x increases, and have disappeared at $x=2/3$, consistent with previous reports.[32,37] These changes contribute to the suggested three-band to one-band crossover near $x\sim 0.5$.[9,14]

V. MAGNETIC TENDENCIES

As for all $0<x<1$, a FM state is favored energetically within LDA at $x=0$ over a PM state. The energy difference, 18 meV/Co, is quite small, considering the moment is near 1 μ_B. For comparison, the energy gain due to a simple Stoner instability, $Im^2/4$ with $I\approx 0.7$–0.8 eV, would give a much larger value approaching 150 meV. The disagreement with experiments, which report no magnetism,[25–27] will be addressed in the next section.

Figure 4 shows the ferromagnetic DOS at the relaxed height $z_0=0.235$, compared with $z_0=0.20$. Increasing the oxygen height in this range (which relaxes the energy) reveals three trends: (1) narrowing of the unoccupied e_g bands and the mostly occupied t_{2g} bands, (2) a shift of the occupied

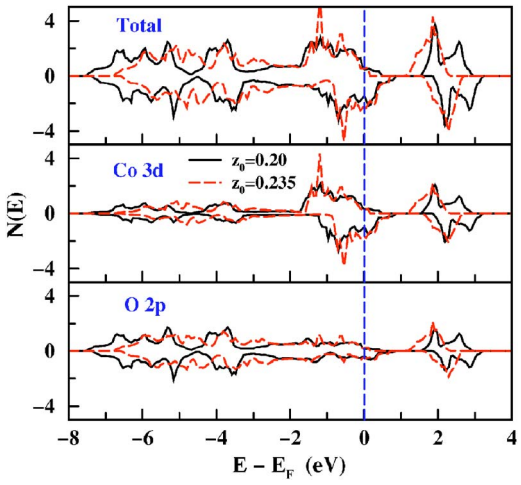

FIG. 4. (Color online) Effect of the oxygen height z_0 on the LDA ferromagnetic DOS at $x=0$. As the Co—O bondlength increases, the $t_{2g}-e_g$ crystal-field splitting decreases, but the mixing of Co $3d$ and O $2p$ remains strong. Note that it is not half-metallic, in contrast to the case of $0<x<1$, within LDA. The vertical dashed line indicates the Fermi energy.

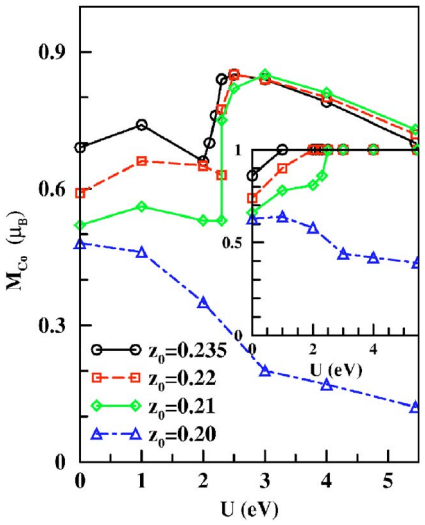

FIG. 5. (Color online) Effect of the on-site Coulomb repulsion U and the change of Co—O bond length z_0 on magnetic moment in the FM state at $x=0$. At $z_0 \leqslant 0.20$, the system is always metallic, regardless of U. (So it shows a different behavior from $z_0 \geqslant 0.21$.) At $z_0 \geqslant 0.21$, there is a first-order transition (metal to insulator) at $U_c=2.5$ eV. Although the $z_0=0.235$ case shows a little smooth transition, the sloop at U_c is still very steep. The inset is a change of the total magnetic moment with respect to U.

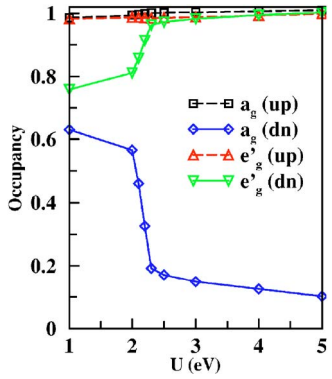

FIG. 6. (Color online) Change of the occupancies of the a_g and e_g' states versus the on-site Coulomb repulsion U in the FM state at the optimized O height, which shows an important role of the a_g band. The occupancy of the a_g minority orbital decreases by $0.27e$ at $U_c=2-2.5$ eV, while both the majority orbitals are fully occupied regardless of U.

O $2p$ bands toward E_F, and (3) a reduction of the crystal-field splitting. In addition, as the Co—O bond length, i.e., the O height z_0, increases, electrons transfer from O $2p$ to Co $3d$ at the rate $\Delta Q_d/\Delta z_0 \approx 1$. The charge transfer is primarily into the a_g majority band, because the e_g' majority manifold is nearly fully occupied already at $z_0=0.20$. At the relaxed $z_0=0.235$, the system is almost half-metallic. As a related effect, the magnetic moment also increases as the O height increases.

A change of the magnetic moment with the on-site Coulomb repulsion strength U is displayed in Fig. 5 for four values of the oxygen height. At $z_0=0.20$, the magnetic moment decreases rapidly above $U=1$ eV, since the system is still metallic, regardless of U. But at $z_0 \geqslant 0.21$, the magnetic moments jump sharply around $U_c=2-2.5$ eV, with the jump occurring simultaneously with the gap opening. This first-order transition was obtained also at $x=1/3$, $1/2$, and $2/3$.[9,11,14] For $z_0 \geqslant 0.21$, the amount of jump in the Co magnetic moment is decreased with increasing the O height. As a result, $z_0=0.235$ case shows a slightly smoothed transition, but the slope at U_c is still very steep. This difference suggests that O height plays an important role in the metal-insulator transition. For $U \approx U_c$, the oxygen modes may acquire anomalous behavior due to coupling to the Co charge state.

The effect of the on-site Coulomb repulsion U on the occupancy of the a_g and e_g' states in Fig. 6 reflects the dominating role of the a_g minority band for the MIT, as it becomes the upper Hubbard band. While the majority orbitals of the a_g and e_g' states are fully occupied regardless of U, the occupancies of the minority orbitals show a remarkable change at $U_c=2-2.5$ eV. In particular, the occupancy of the a_g minority orbital decreases by $0.27e$ at U_c, leading to the Mott transition. The transfer of a_g spectral weight from $U=1$ eV to $U=2.5$ eV shown in Fig. 7 vividly exposes the Mott character of the transition. At $U_c=2.5$ eV, the minority a_g band is completely unoccupied while the majority band lies much deeper, mixing strongly with the O $2p$ bands and becoming spread over a 5 eV range.

In contrast to our previous findings for $x=1/2$,[9] we have not been able to trace any hysteresis. A hysteretic region indicates that the two states are nearly degenerate, so the lack of hysteresis indicates that the difference in energy slopes dE/dU of the two states differs much more than for $x>0$ case.

One other feature can be noted: the peak at $U=1$ eV in Fig. 5 results from a transition from metal to half-metal. The inset of Fig. 5, showing a change of the total magnetic moment with respect to U, shows the metal→half-metal transition clearly since the total magnetic moment must be 1 μ_B for a half-metal or an insulator. It is not completely clear why no Mott/disproportionation transition occurs at $z_0=0.20$. However, it may be due to the increased hybridization between Co a_g states and O p_z states. Even within LDA, the width of the a_g bands at $z_0=0.20$ is about 25% larger than at $z_0=0.235$. The increased hybridization will make the a_g-derived Wannier orbital less localized and therefore less susceptible to correlation effects.

Antiferromagnetic tendency. We used a two-Co supercell with the optimized O height to study antiferromagnetism (AFM) (although FM is always favored energetically over AFM). The effect of the on-site Coulomb repulsion U on the magnetic moments is shown in Fig. 8. In the region below U_c, the Co magnetic moment decreases rapidly as U is increased, being only 60% of LDA at $U=2$ eV, a trend that is strongly related to the Co→O charge transfer. As for the FM case, there is a first-order MIT at $U_c=2.3$ eV, with the change of magnetic moment (to 0.72 μ_B) being even more dramatic than for the FM case.

VI. FIXED SPIN MOMENT STUDY

As noted in the Introduction, CoO_2 is reported to be metallic and nonmagnetic. Both LDA and LDA+U calculations

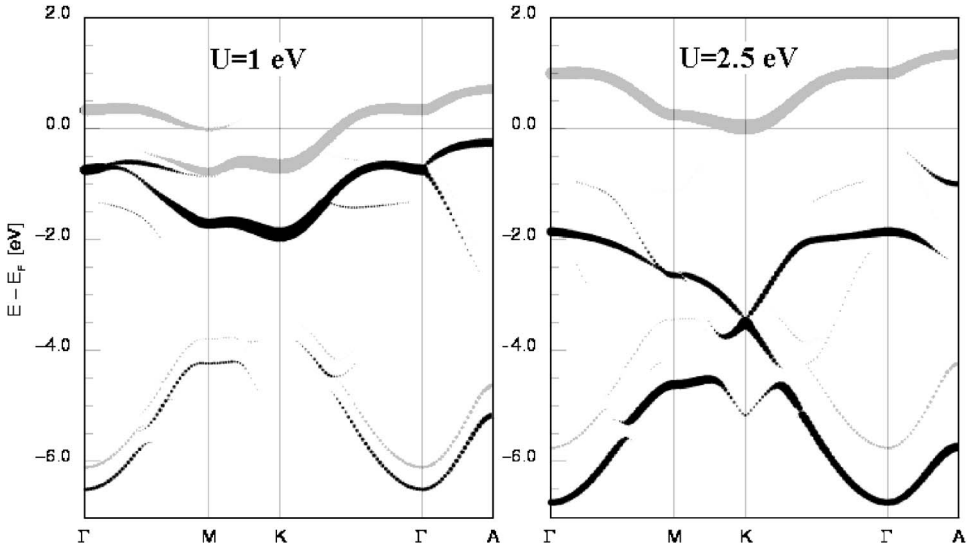

FIG. 7. Change of the a_g states versus the on-site Coulomb repulsion U in the FM state at the optimized O height, illustrating the Mott transition within the a_g band. The gray lines indicate the minority character of the a_g band, while the black lines denote the majority character. The $U=0$ (LDA) result is indistinguishable from the $U=1$ eV result shown here.

show energetically favored ferromagnetic solutions, as happens throughout the NxCO system.[11,14,31] Fixed spin moment (FSM)[38] calculations help to establish the extent of the contradiction. Figure 9 shows the variation of total energy with the total magnetic moment on a per formula unit basis. The behavior is similar to the FSM results of Singh at $x=0.3$, 0.5, and 0.7.[24] In particular, the sharp energy increase above $M=1.0\ \mu_B$ is due to the crystal-field induced gap between the t_{2_g} and e_g manifolds.[24] However, the energy change versus magnetic moment shows a slightly different behavior from Singh's $x>0$ results. It has a minimum at $M=0.86\ \mu_B$ (the value from the self-consistent calculation, close to but not quite half-metallic) before increasing, followed by the sharp jump in energy at $M=1\ \mu_B$, which occurs upon filling the majority bands.

We have evaluated the Stoner (exchange interaction) I from these FSM calculations.[39] This method properly accounts for the small contribution from the oxygen sites. The enhanced susceptibility is given by

$$\chi = \chi_0/[1 - N(E_F)I], \tag{1}$$

where the bare susceptibility is given by $\chi_0=2\mu_B^2 N(E_F)$ and $N(E_F)$ is the single-spin density of states at the Fermi level. At small M, the energy difference is $E(M)-E(0)=(1/2)\chi^{-1}M^2$. Since $N(E_F)$ for FM is 1.36 states/eV spin, $I=0.89$ eV, $[IN(E_F)=1.2]$ comparable with the value obtained from the exchange splitting.

This prediction of a FM ground state occurs throughout the Na_xCoO_2 system (except perhaps right at $x=1/2$). For $x \geq 0.75$ the CoO_2 layers are FM (and stacked with alternating spin direction), but for $x<0.75$ no FM is observed. There are now several metals where enhanced paramagnets are predicted by local or semilocal density theory to be FM, but it is somewhat peculiar that this state of affairs persists to $x=0$ and a moment of nearly 1 μ_B. It might be that the Moriya

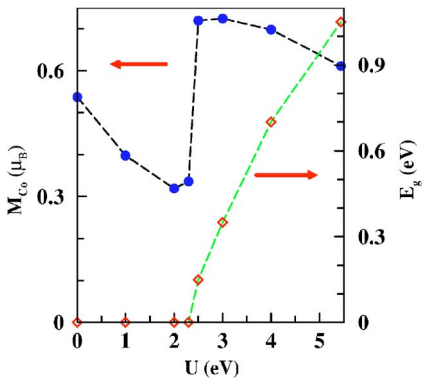

FIG. 8. (Color online) Effect of the on-site Coulomb repulsion U on the magnetic moment in the AFM state at $x=0$. There is a first-order transition (metal to insulator) at $U_c=2.3$ eV. The left axis indicates a Co magnetic moment, while the right axis gives the energy gap.

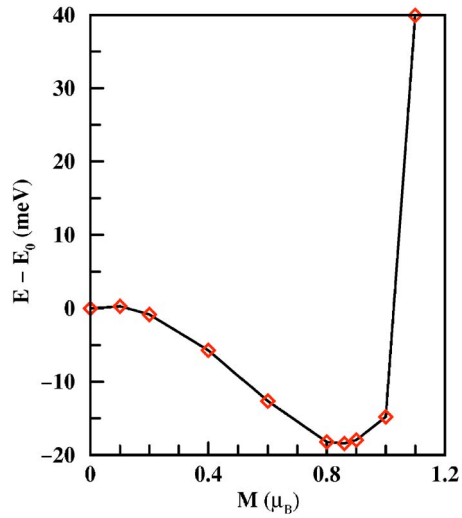

FIG. 9. (Color online) LDA fixed spin moment calculation at $x=0$. Note that a minimum occurs at $M=0.86\ \mu_B$ before a sharp jump at $M=1\ \mu_B$. M is the total magnetic moment per formula unit in μ_B.

theory for the correction of the susceptibility of weak ferromagnets, as implemented, for example, by Larson *et al.*,[43] or perhaps dynamical effects such as are contained within dynamical mean field theory[40] will be necessary to correct the prediction. These questions give important directions for further work.

VII. DISCUSSION AND SUMMARY

In this paper we have explored the electronic structure and magnetic tendencies of Na_xCoO_2, and specifically addressed the limits on correlation that the experimentally reported nonmagnetic metallic phase at $x=0$ imposes. Taken in conjunction with results in the literature, our study of the electronic structure and consequences of including correlation effects in the band structure of CoO_2 extends the studies of NxCO across the entire $0 \leqslant x \leqslant 1$ regime. Within this system, increasing the Na concentration x leads to three main effects. First, the O $2p$ manifold moves downward from the t_{2g} complex. This shift can be due to a change in the Madelung potential, and possibly also to rehybridization of Co $3d$ and O $2p$.[21] Second, the width of the t_{2_g} manifold shows some minor change with increasing x, becoming a little narrower. This can be interpreted as the active $3d$ states becoming, in effect, more localized. Such a trend is consistent with our earlier suggestion that the on-site Coulomb repulsion U increases appreciably with x.[14] Third, the band separation (between Co t_{2_g} and O $2p$) around -1.5 eV becomes obvious and increases as x increases. This trend reflects the fact that mixing between Co $3d$ and O $2p$ states becomes weaker as x increases. Figure 4 reveals that a change of the Co—O bond length at $x=0$ hardly affects the separation, implying that the separation is induced by increasing electrons (or decreasing holes) as x increases.

The observation by Tarascon and co-workers that CoO_2 is metallic and nonmagnetic provides us with our main conclusion: the effective Coulomb repulsion strength U must be less than $U_c=2.3$ eV. Above that value, a Mott-type transition occurs to a magnetic insulating phase. This critical value is lower than what has been obtained by the same methods for $x>0$, and supports the notion (and evidence) that the value of U varies through the NxCO system, by at least a factor of 2.

This value of U_c, in fact, is an upper limit; if the system were given more flexibility (i.e., if we allowed antiferromagnetic ordering by choosing a supercell) some ordering might occur for even smaller U. The (unobserved) insulating phase we find for $U>U_c$ corresponds to Mott transition of the a_g orbital. It is degenerate with the e_g' orbitals, however, its bandwidth is slightly wider. As a result, allowing FM order even within LDA already breaks the a_g-e_g' degeneracy by populating the a_g orbital with most of the holes (see Fig. 7). Thus, it is the symmetry breaking arising from the slightly larger a_g bandwidth that results in the Mott transition of the a_g states for $U>U_c$. This choice is a type of orbital-selective Mott transition, which is more commonly discussed at half-filling of the multiband system[41,42] and thereby leaves metallic bands. Alternatives to a Mott transition of the a_g state are possible, with a Mott transition within the e_g' orbitals coupled with orbital ordering and accompanying symmetry-lowering distortion being one. The (slightly) smaller bandwidth of the e_g' orbitals would be a factor that would favor this possibility.

This Na_xCoO_2 system lies on the $U<U_c$ side of the Mott/disproportionation transition everywhere, except at $x=1/2$, where (assisted by commensurability) it becomes a very small gap magnetic insulator. We take this small gap to indicate that $U \approx U_c$ (but slightly larger) at $x=1/2$, in which case the critical point can be accessed by a small variation of the system. An immediate prediction is that pressure, which reduces the lattice constant and thereby increases the bandwidth W, will reduce the U/W ratio, and result in an insulator-to-metal transition. Due to the small gap, the required pressure may be modest.

Finally, we remind that recent evidence[15–18] suggests the oxidation state of Co for the superconducting materials is representative of an effective doping level $x_{eff}=0.55-0.60$. If true, this puts superconductivity in a more interesting part of the phase diagram, where superconductivity would arise from electron doping of the $x=0.5$ disproportionated, charge-ordered, and spin-ordered magnetic insulator.

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