Charge and Spin Ordering in Insulating $Na_{0.5}CoO_2$: Effects of Correlation and Symmetry

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Ab initio band theory including correlations due to intra-atomic repulsion is applied to study charge disproportionation and charge- and spin-ordering in insulating $Na_{0.5}CoO_2$. Various ordering patterns (zigzag and two striped) for four-Co supercells are analyzed before focusing on the observed "out-of-phase stripe" pattern of antiferromagnetic Co^{4+} spins along charge-ordered stripes. This pattern relieves frustration and shows distinct analogies with the cuprate layers: a bipartite lattice of antialigned spins, with axes at 90° angles. Substantial distinctions with cuprates are also discussed, including the tiny gap of a new variant of "charge transfer" type within the Co 3*d* system.

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The Na_xCoO_2 system, which forms the basis for a quasi-two-dimensional transition metal oxide superconductor (T_c = 4.5 K) when hydrated,[1] shows a wide variety of unexplained behaviors in the accessible range $0 < x \leq 1$. Counterintuitively (considering it is a 2D transition metal oxide) it shows *uncorrelated* behavior in the normal state for $x < 0.5$[2] (superconductivity arises when $x \approx 0.3$ samples are hydrated). Then, rather unexpectedly for a hole-doped band insulator, it displays correlated behavior for $x > 0.5$ including an enhanced linear specific heat coefficient and local moments (Curie-Weiss susceptibility). Both of these regimes are metallic. Precisely at x=0.5, however, it evolves through Na ion ordering, charge ordering, and magnetic ordering transitions to attain a ground state that is insulating[3] with a very small gap (few tens of meV).

Much of the interest in this system lies in the triangular arrangement of the Co ions, and the expectation that the system should be addressable in terms of nonmagnetic Co^{3+} and spin-half Co^{4+} ions. Ordering phenomena, whether charge, spin, or orbital, acquires a different character on a triangular lattice[4, 5, 6] than on the heavily studied square lattice of the cuprate superconductors. The system becomes magnetically ordered at $x \geq 0.75$ (antialigned stacking of ferromagnetic layers[7]). The insulating state was discovered by Foo *et al.*, who presented electron diffraction data indicating robust Na ion ordering (in an orthorhombic four-Co supercell[8, 9] whose cell shape is shown in Fig. 1. The Na ordering persisted to above room temperature, and it was suggested that Na ordering would be coupled to charge (hole) ordering. The zigzag Na order they inferred, involving equally the two distinct types of Na sites, was confirmed by Yang *et al.*[10], and calculations by Zhang *et al.* indicated this ordering arises because it minimizes the Coulomb interactions between the Na^+ ions.[11]

As the temperature is lowered, a kink in the in-plane susceptibility χ_{ab} at T_{c1}=88 K signals antiferromagnetic (AFM) ordering of some Co spins.[3, 12, 13] Infrared reflectivity studies[14, 15, 16] detect a gap of ∼15 meV opening below T_{c2} = 52 K, where Foo *et al.* observed[3] the onset of insulating behavior in the resistivity $\rho(T)$. T_{c2} has been called the charge-ordering temperature but there is also additional magnetic rearrangement, signaled by a kink in χ_c.[12, 13] At T_{c3}=27 K Gašparović *et al.* observed an additional kink in χ_{ab} with no signature in $\rho(T)$; this is the temperature where Foo *et al.* had observed structure in $\rho(T)$ reflecting more insulating behavior.[3] Unlike the upper two transitions, there is no entropy change[8] at T_{c3}. The interpretation of this onset of insulating behavior was suspected to be charge ordering,[3, 15] inviting neutron diffraction. The two studies reported to date[12, 13] confirm (1) two types of Co ions (*i.e.* charge disproportionation), one consistent with spin half but with a reduced ordered moment (0.25-0.34 μ_B), the other spin being much smaller, and (2) AFM ordering below T_{c1}=88 K of one of the types shown in Fig. 1(b) or (c), with that of Fig. 1(b) providing the best fit.

First principles local density approximation (LDA) calculations by Singh at x=0.5 predict[17] ferromagnetic (FM) Co layers to be much more stable than a simple AFM arrangement, and treating the Na ions explicitly does not change this conclusion.[18] A crucial development occurred with the discovery that, by using the correlated LDA+U method, explicit charge disproportionation occurs[2] above a critical value U_{cr}. Subsequent ordering of the holes then can relieve the frustration on the triangular lattice, whereupon it was found that AFM order became favored over FM at x=0.5.[19]

The questions of type(s) of order, mechanism of ordering, and character of the insulating state have begun to be clarified by the data discussed above. A quantitative understanding of the behavior is likely to require accounting for: the multiband t_{2g} system

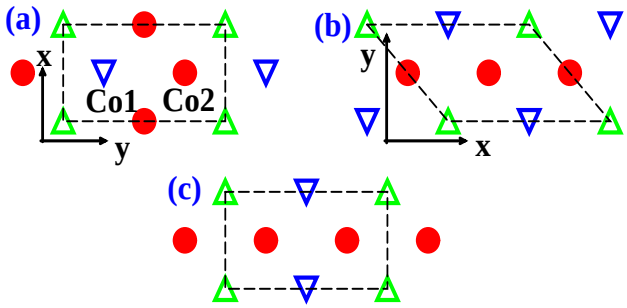

FIG. 1: (color online)Charge and spin ordering of (a)zigzag (ZZ) and (b) stripe (OP-ST) patterns suggested by Gašparović *et al.* and (c) in-phase stripe simplification of Yokoi *et al.* in the Co layer. In the OP-ST model (b) the Co2 ions lies at a site of in-plane inversion symmetry and is neighbored symmetrically by ↑ and ↓ spins. Triangle and filled circle denote magnetic (Co1) and nonmagnetic (Co2) cobalts, respectively, and the direction of the triangles indicates spin orientation. In the calculations, Na lies above Co2.

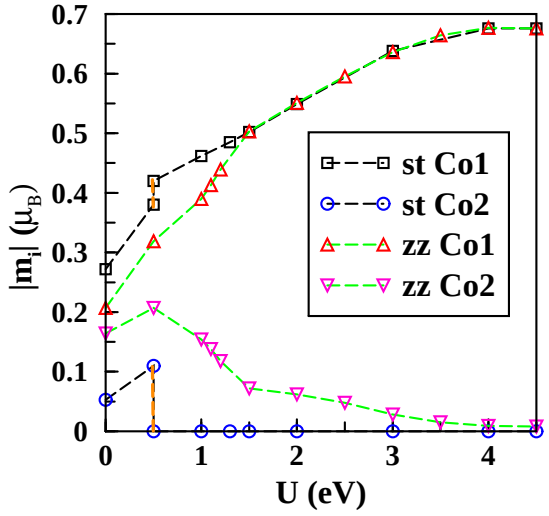

FIG. 2: (color online)Effect of U on magnitude of the Co local magnetic moments m_i in the stripe and zigzag patterns of AFM $Na_{0.5}CoO_2$. At U_c=1.5 eV, charge disproportionation Co1→Co^{4+} (S=1/2) and Co2→Co^{3+} (S=0), occurs with gap opening.

with symmetry broken down to $a_g + e'_g$; the triangular, non-bipartite lattice that frustrates AFM ordering and provides several nearly degenerate possibilities for charge order[11, 20, 21]; correlation effects strong enough to drive charge disproportionation but small enough to leave a tiny charge gap.

We have addressed these questions using the same methods[22] as for our previous studies on this system,[2, 19] with attention to Brillouin zone sampling (up to 312 k-points in the irreducible zone). Specifically, we utilize the disproportionated states provided by the LDA+U approach to address, for the three superlattice symmetries shown in Fig. 1, the energetics, the relative orientations and magnitudes of the magnetic moments, and characteristics of the electronic structure in the insulating phase. These Co orderings correspond to (a) zigzag (ZZ), (b) out-of-phase stripe (OP-ST), and (c) in-phase stripe (IP-ST). It must be noted that the Na ion zigzag phase is not the same as this Co zigzag; the Na zigzag involves one site on top of Co and another site not on top of any Co that is "less zigzag" than this Co ZZ order. For the calculations presented here, we have not addressed specifically the question of the interaction between Co charge and Na, which has been addressed to some extent by Li *et al.*[18] Consistent with the neglect of the layer stacking that results in two CoO_2 layers per cell, we have instead dealt with Na sites only above two of the four Co atoms, and use this placement to provide the small symmetry-breaking that leads to disproportionation. Specifically, the Na ions sit above the Co2 site (which becomes the nonmagnetic Co^{3+} site).

Our attempts to obtain an AFM state for the IP-ST model of Fig. 1(c) converged to a FM state (or nonmagnetic, if AFM symmetry was enforced).[23] Thus we will consider only the model given in Fig. 1(b) as a stripe (ST) pattern in this paper. Within LDA, FM is favored over AFM for both ZZ and ST patterns, as for all other values of x.[17] The energy difference is substantial for ZZ (300 meV/Co) but surprisingly small for ST (8 meV/Co). This favoring of FM by LDA confirms the need for including effects of correlation, as we do by applying the LDA+U method. As emphasized previously, results depend on the value of U and it is necessary to determine the appropriate value. This is rather straightforward for x=0.5: there should be disproportionation, charge- and spin-ordering (AFM) and a very small gap. We first review behavior versus the repulsion strength U. Hund's rule J=1 eV is kept fixed.

The effect of U is evident in the calculated Co moments, displayed in Fig. 2. At U=0 (*i.e.* LDA level) the effects of symmetry (determined by the Na placement) is already strong. The Co1 and Co2 moments are nearly equal for ZZ, while there is already almost negligible moment on Co2 for ST. This difference reflects the higher symmetry of the Co2 ion in the ST pattern of Fig. 1(b): it is surrounded symmetrically (in-plane inversion) by two Co1↑, two Co1↓, and two nonmagnetic Co2. Increasing U, Co1 magnetic moments in both patterns increase monotonically and become identical at and above U=1.5 eV. The low-spin Co2 magnetic moments show a much greater difference between the two patterns. For ST it be-

comes immediately (by U=0.5 eV) zero, while for ZZ there is at U=0.5 eV what might be identified as the charge disproportionation transition, but beyond this point the Co2 moment simply decreases monotonically, never becoming identically zero. From Fig. 1(a) the lack of symmetry in ZZ is clear: although surrounded by two ↑ and two ↓ Co1 spins, and two low-spin Co2 ions, there is no in-plane inversion, so a moment is allowed. While the Co1 and Co2 ions are clearly disproportionated in Fig. 2, the charge difference is only ∼0.2 e (this difference is 0.02 e smaller for ST than ZZ).

The gap opens, for both patterns, at U=U_{cr}=1.5 eV. It is noteworthy that the disproportionation had occurred already at smaller U (see Fig. 2); thus we find here a richer behavior than in our previous studies with smaller cells or different Na concentrations, where disproportionation/ordering had coincided with gap opening. Such a difference was also obtained for a similar supercell by Li *et al.*, who however found a somewhat larger value of U_{cr}.[18] This critical interaction strength coincides with a Mott-like transition in the Co1 a_g states, with upper and lower Hubbard bands separated by 2.2 eV as shown in Fig. 3. Almost independent of U, the ZZ pattern is favored over ST by the very small value of 22 meV/Co; given the fact that the Na zigzag arrangement has been simplified in our calculations, we can only say that these two patterns have no significant difference in energy.

The upper Hubbard band in the insulating state is quite flat, and in fact shows more dispersion perpendicular to the layers (200 meV) than within the layers. The band structures are pictured along directions parallel to ($\hat{x}$), and perpendicular to ($\hat{y}$), the ZZ or ST chains of Co ions in Fig. 3 for U=2 eV, a value slightly above U_{cr} to make the gaps more clearly visible. For the ZZ case, the minimum gap occurs at a corner of the zone that is not shown. The dispersions going away from the zone center of the uppermost two valence bands are entirely different for the two patterns, being positive for ST but negative for ZZ. The uppermost bands have primarily Co2 $e'_g(t_{2g})$, and not a_g, character. In spite of these differences in dispersion through the zone, the orbital-projected density of states, not shown, is extremely similar for the ZZ and ST bands shown in Fig. 3.

We focus now on the observed ST pattern. The gap occurs at the zone boundary point Y along k_y. Although Co 3d states border the gap on both sides, this is an unusual $d-d$ charge transfer gap (not the usual $p-d$ case), with unoccupied Co1 minority a_g states above, and primarily Co2 e'_g states below the gap. The stronger dispersion of the upper Hubbard band above the gap along Y-Γ compared to X-Γ

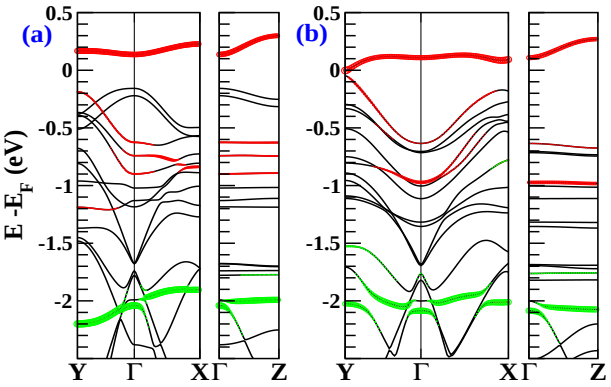

FIG. 3: (color online) View of the AFM band structures in the t_{2g} manifold at U=2 eV for (a) the zigzag (ZZ) and (b)the stripe (ST) patterns. The plot is along perpendicular (Γ-Y) and parallel (Γ-X) directions for the each chain. Z denotes the zone-boundary point along < 001 > direction. The thickened lines emphasize the bands with strong a_g character for each spin of a magnetic Co1. The energy zero lies in the gap.

can be understood as follows. Electrons excited into the upper Hubbard reside in the minority a_g states on Co1, for example, a spin ↑ electron will hop between Co1 ions with moments oriented ↓. Propagating in the $\hat{y}$ direction, it can hop through a single Co2 ion; in the $\hat{x}$ direction however, it must avoid the U cost of hopping onto an oppositely aligned Co1 ion, thus requiring hops through *two* Co2 ions before returning to another Co1 ↓ ion, and its dispersion is reduced accordingly. Valence band holes introduced into the system will occupy nonmagnetic Co2 e'_g states, while electrons will occupy minority a_g states on Co1.

Since the crystal field ($t_{2g} \rightarrow e_g$) gap is ∼2 eV, the optical transitions in the IR for the magnetically disordered metallic phase (T>T_{c1}) reflect $e'_g \rightarrow a_g$ excitations, *i.e.* transitions within the t_{2g} complex. Below the metal-insulator transition at T_{c2}, the excitations across the gap are to the upper Hubbard band, and the main weight of these transitions – the new (Co1 ↔ Co2) charge-transfer type mentioned above – is shifted up in energy by only a few tens of meV.[14, 15, 16] This small shift is consistent with the small bandwidth that we find for the upper Hubbard band.

An interesting analogy with the AFM cuprate layer arises. In this observed ST pattern Fig. 1(b), the antiferromagnetic arrangement has the bipartite, and 90°, topology of spins characteristic of the cuprate plane, except with anisotropy of (Co^{4+}-Co^{4+}) parallel and perpendicular hopping amplitudes t_x, t_y and exchange couplings J_x, J_y. Note that

exchange J_x is between near neighbors while J_y is between second Co neighbors. There are however strong distinctions to be made with cuprates. In cuprates U is 3-4 times larger, the effective metal-metal near neighbor hopping is 2-3 times greater, and the 2 eV gap typifies a robust Mott insulator. In this cobaltate system the tiny gap reflects a marginally insulating correlated state, and the low energy excitations require three d bands, versus the dominance of the single $d_{x^2-y^2}$ state in the cuprates. It also seems that magnetic coupling cannot be treated in the usual Heisenberg form, because the superexchange mechanism is not dominant and the rather flimsy moments depend strongly on the type of magnetic order. (A spin Hamiltonian might be reasonable for treatment of spin waves within a given ordered state.)

Our results suggest a specific picture of the temperature evolution at x=0.5. Noting that the FM ordered layers for $x \geq 0.75$ are consistent with itinerant character and the $0.5 < x < 0.75$ regime with fluctuation-suppressed magnetism, the magnetic ordering below T_{c1} may be more of a spin density wave (SDW) character which gaps some but not all of the Fermi surface; recall that for the ST pattern the FM-AFM energy difference is very small at small U, and that even at U=0 there is a substantial difference in moments on Co1 and Co2, that is, an SDW . Several band structure studies have pointed out nesting features in the paramagnetic Fermi surface.[2, 17, 24] The challenge that this picture must face is that the primary magnetic order is unchanged at the insulating transition T_{c2}: Gašparovic *et al.* find that the principal ordered moment grows with decreasing temperature[13] continuously through the insulating transition at T_{c2}. The additional order that results in a kink in χ_c at T_{c2} has not yet been elucidated, but our results are consistent with the prevailing picture that disproportionation arises finally at T_{c2}. The redistribution of spectral weight below T_{c2} observed in optical experiments show differences (weight shifted to 20-30 meV[16] or 70-100 meV[14]), but they seem consistent with the correlated band structure of Fig. 3 and particularly the narrowness of the unoccupied band.

It can reasonably be asked whether the ground state of this system should be considered as a correlated insulator, as outlined above, or instead as perhaps a SDW (at T_{c1}) – CDW (at T_{c2}) system. Balicas *et al.* have found that, when an applied in-plane field increases beyond 25 T the conductivity increases by a factor of two (a sort of insulator-metal transition), and observation of magnetoresistance oscillations suggest the restoration of part of the Fermi surface.[25] Certainly the insulating phase is delicate. However, the observation of a substantial ordered moment on Co1 (0.25-0.34 μ_B)[12, 13] and little or none on Co2 speaks for a charge disproportion picture (into identifiable Co^{4+} and Co^{3+} moments) and hence a correlated insulator below T_{c2}. The observed value of the Co1 moment is reduced somewhat from our calculated value of $0.5\mu_B$, as would be expected from two-dimensional fluctuations of a spin-half moment already reduced substantially by hybridization[26] with O $2p$ states.

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