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Interplay of frustration, magnetism, charge ordering, and covalency in the ionic Hubbard model for $Na_{0.5}CoO_2$

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We investigate the ionic Hubbard model on a triangular lattice at three-quarters filling. This model displays a subtle interplay between metallic and insulating phases and between charge and magnetic orders. We find crossovers among Mott, charge transfer and covalent insulators, and magnetic order with large moments that persist even when the charge transfer is weak. Our theoretical results are consistent with experiments on $A_{0.5}CoO_2$ (A=K,Na) and identify these materials as correlated covalent insulators.

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The competition between metallic and insulating states in strongly correlated materials leads to many behaviors. The Mott insulator occurs when a single band is half filled, and the effective on-site Coulomb repulsion, U, is much larger than hopping integral, t. A menagerie of strongly correlated states is found when a system is driven away from the Mott insulating state, either by doping, as in the cuprates,[1] or reducing U/t, as in the organics.[2] Geometric frustration causes yet more physics in Mott systems.[2] Therefore the observation of strongly correlated phases in the triangular lattice compounds $A_{0.5}CoO_2$, where A is K or Na, has created intense interest.[3]

A important question raised by experiments on $A_{0.5}CoO_2$ (Refs. 4–10) is: what is the origin of the insulating state? A single band Hubbard model on the triangular lattice at three-quarter filling leads to a metallic state in qualitative disagreement with observations. Previous theoretical studies have proposed a charge ordering insulating state occurs because of long-range Coulomb interactions.[11] However, the large charge ordering predicted by these theories is absent experimentally.[4,5] Weakly correlated theories[12] also predict a charge ordered insulator; furthermore, such calculations do not capture the strong electronic correlations seen experimentally (see below and, e.g., Refs. 6 and 7).

In this Rapid Communication we study the ionic Hubbard model on a triangular lattice at three-quarter filling motivated by our recent proposal[13] that it is an effective low-energy Hamiltonian for Na_xCoO_2 at values of x at which ordering of the sodium ions occurs. This Hamiltonian displays a subtle interplay between metallic and insulating phases and charge and magnetic orders. It has regimes analogous to Mott, charge transfer,[14] and covalent insulators.[15] In the parameter range relevant to $Na_{0.5}CoO_2$ we find a covalent insulator. Unlike a charge-transfer insulator, in which an alternating pattern of filled and empty sites causes a gap to open, this covalent insulator is characterized by weak charge transfer with a small gap arising from strong nonlocal bonding between the inequivalent sites. In spite of the small charge transfer in the covalent insulator regime a large magnetic moment is found. These features are consistent with a wide range of experiments of $A_{0.5}CoO_2$.[8]

The Hamiltonian for the ionic Hubbard model is

$$H = -t\sum_{\langle ij\rangle\sigma} c^{\dagger}_{i\sigma}c_{j\sigma} + U\sum_{i} n_{i\uparrow}n_{i\downarrow} + \sum_{i\sigma}\epsilon_i n_{i\sigma}, \qquad (1)$$

where $c^{(\dagger)}_{i\sigma}$ annihilates (creates) an electron with spin σ at site i, t is the hopping integral, U is the effective Coulomb repulsion between electrons on the same site, and ϵ_i is a the site energy. We specialize to the case with two sublattices, A ($\epsilon_i=\Delta/2$) and B ($\epsilon_i=-\Delta/2$), consisting of alternating rows, with different site energies on the two sublattices (c.f., Fig. 15 of Ref. 13). This is the lattice relevant to $A_{0.5}CoO_2$ where the difference in site energies results from the ordering of the A-atoms.[4,13,16,17] On a half-filled square lattice the ionic Hubbard model displays a crossover between Mott and band insulating states.[18,19] Marianetti and Kotliar[20] also studied the Hamiltonians proposed in Ref. 13 for x=0.3 and 0.7. Otherwise, this model has not been studied away from half-filling[21] and/or on geometrically frustrated lattices, except for the case of one dimension.[22]

Two limits of model (1) at 3/4 filling may be easily understood. For noninteracting electrons, U=0, a metallic state occurs for all Δ as at least one-band crosses the Fermi energy. In the atomic limit t=0, and $U>\Delta$ one expects a charge-transfer insulator with a charge gap of about Δ, whereas for $U<\Delta$ a Mott insulator with charge gap of U occurs. However, realistic parametrization of A_xCoO_2 materials imply $U\gg\Delta$ and $\Delta\sim|t|$ (Ref. 23); we will show below that in this parameter regime the model shows very different behavior from either of the limits discussed above. This interesting regime needs to be analyzed using nonperturbative and/or numerical techniques. Thus, we have performed the Lanczos diagonalization calculations on 18 site clusters with periodic boundary conditions.

In Fig. 1 we plot the charge transfer, n_B-n_A as a function of $\Delta/|t|$ for several values of U. We also plot n_B-n_A in two analytically tractable limits: the noninteracting limit, U=0 (Ref. 24); and the strong-coupling limit $U\gg\Delta\gg|t|$.[25] Several interesting effects can be observed in this calculation. First, the sign of t strongly affects the degree of charge transfer on the triangular lattice. Second, charge transfer depends only weakly on U. Third, regardless of the sign of t or the magnitude of U, the charge transfer increases rather slowly as Δ increases.

The charge gap, i.e., the difference in the chemical

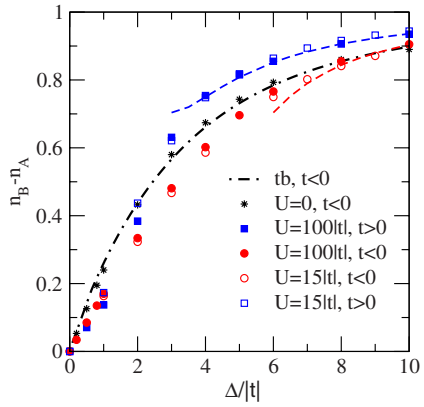

FIG. 1. (Color online) Variation in the charge transfer with Δ for different Coulomb repulsion energies. The Lanczos results on an 18-site cluster for: $U/|t|=0$ (stars), 15 (open symbols), and 100 (filled symbols) are shown. The $U=0$ results are in excellent agreement with the infinite lattice tight-binding (tb) result (dashed-dotted line) (Ref. 24). Strong-coupling results (dashed lines) are also shown for comparison.

potentials for electrons and holes, is $\Delta_c \equiv E_0(N+1)+E_0(N-1)-2E_0(N)$, where $E_0(N)$ is the ground-state energy for N electrons. We plot the variation in Δ_c with Δ for various values of U in Fig. 2. Δ_c vanishes for $U=0$, however finite-size effects mean that we cannot accurately calculate Δ_c for small Δ. $\Delta_c=\Delta$ for $t=0$ and $U \gg \Delta$; this result is reminiscent of a charge-transfer insulator.[14] Both perturbative[26] and numerical results show that the charge gap depends on the sign of t due to the different magnetic and electronic properties arising from the geometrical frustration of the triangular lattice. In contrast, on a square lattice, Δ_c, does not depend on the sign of t.

In the limit, $\Delta \gg U \gg |t|$, the A and B sublattices are well separated in energy; the B sites are doubly occupied (i.e., the

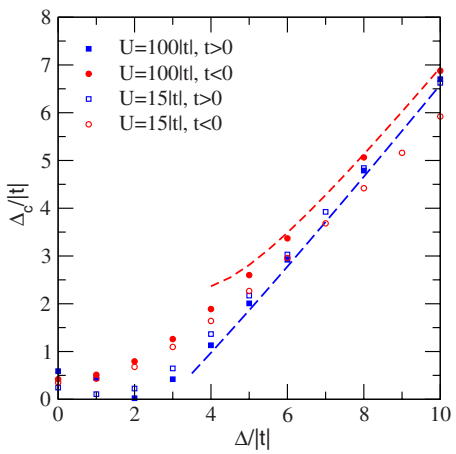

FIG. 2. (Color online) Variation in the charge gap, Δ_c, with Δ for $U/|t|=15$ and 100 (the charge gap is zero for $U=0$). The tendency toward an insulating state is greater for $t<0$ than for $t>0$. Dashed lines show the strong-coupling limit: $U \gg \Delta \gg t$. Note that although strong correlations are essential for creation of the charge gap they are not required for the charge transfer, cf. Fig. 1. Note that, for $U \gg \Delta$ with U large, the charge gap is robust against the value of U.

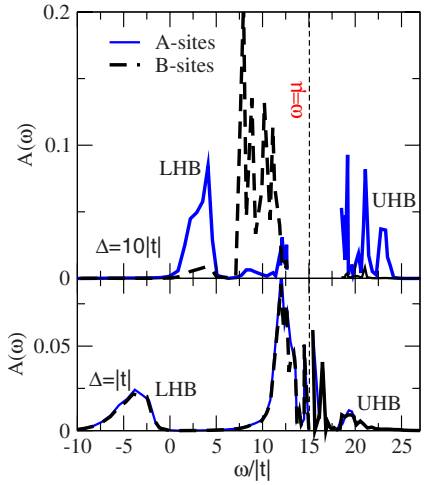

FIG. 3. (Color online) Evolution from a charge-transfer insulator to a covalent insulator. The energy dependence of the spectral density, $A(\omega)$, is shown for two different parameter regimes of the model with $t<0$ and $U=15|t|$. The spectral density in the upper panel ($\Delta=10|t|$) is that characteristic of a charge-transfer insulator (Ref. 15) there is a single weakly correlated band largely associated with the B sites and lying between lower Hubbard band (LHB) and upper Hubbard band (UHB) (separated by $\sim U$) that are largely associated with the A sites and $\Delta_c \sim \Delta$. In contrast, the lower panel ($\Delta=|t|$) shows a spectral density characteristic of a covalent insulator (Ref. 15): there are only small difference between A and B sites, the separation of the LHB and UHB is $>U$ and $\Delta_c \sim |t|$.

B sublattice is a band insulator) and the A sublattice is half filled and hence becomes a Mott insulator. If there were no hybridization between that chains, one would find a metallic state for any finite charge transfer from the B sites to the A sites (self doping) even for $U \gg |t|$ as the A chains are now electron-doped Mott insulators and the B chains are hole-doped band insulators. However, Fig. 2 shows that the insulating regime of the model extends far beyond the well understood $n_B-n_A=1$ regime. This is because the real space interpretation is incorrect as hybridization between A and B chains is substantial. For $|t| \sim \Delta \ll U$ the system can remain insulating with a small gap $[\mathcal{O}(t)]$. This state is analogous to a covalent insulator.[15]

One expects that for $\Delta=0$ the ground state is metallic as there the system is 3/4 filled. However, a small but finite $\Delta=0^+$ leads to a strongly nested Fermi surface for $t>0$, whereas for $t<0$ the Fermi surface rather featureless. Thus, rather different behaviors might be expected for different signs of t even at weak coupling. At large U our exact diagonalization results suggest that a gap may be present even for a small value of Δ/t. However finite-size effects, inherent to the method, mean that it is not possible to resolve whether a gap opens at $\Delta=0$ or at some finite value of Δ.

To test this covalent insulator interpretation in the $\Delta \sim |t|$ and large U regime we have also calculated the spectral density, $A(\omega)$, cf. Fig. 3. There are three distinct contributions to the $A(\omega)$: at low energies there is a lower Hubbard band (LHB); just below the chemical potential ($\omega=\mu$) is a weakly correlated band; and just above $\omega=\mu$ is the upper Hubbard band (UHB). Furthermore, the large energy separation, much

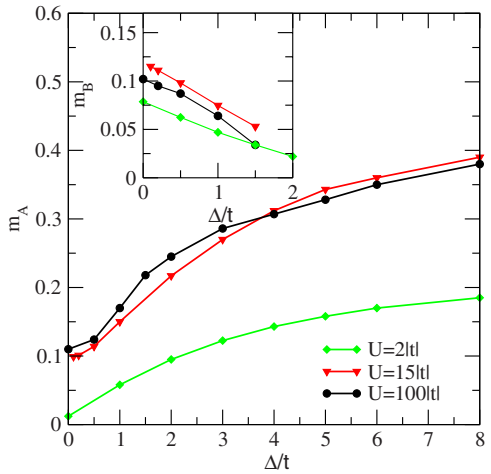

FIG. 4. (Color online) The magnetic moment as a function of Δ for $t<0$ and various U. The magnetic moment on the A sites, m_A, (main panel) is strongly enhanced when $U \gg |t|$. The inset shows the moment on the B sublattice. m_B is much smaller, reduced by Δ, and only weakly dependent on U. These results demonstrate that, for large U and $\Delta \gtrsim |t|$, the electrons on the A sublattice are much more strongly correlated than those on the B sublattice despite the small charge transfer (see Fig. 1).

larger than the expected $U=15|t|$, between the lower and upper Hubbard bands is due to an upward (downward) shift of the upper (lower) Hubbard bands due to the strong hybridization. In contrast, in the strong-coupling limit $A(\omega)$ has a much larger gap, $\mathcal{O}(\Delta)$, between the contributions from the weakly correlated band and the upper Hubbard band.

The magnetic moment associated with the possible antiferromagnetism, $m_\nu=(3\langle S_i^z S_j^z\rangle)^{1/2}$, where $\nu=A$ or B and $S_i^z=\frac{1}{2}(n_{i\uparrow}-n_{i\downarrow})$, is evaluated between two next-nearest neighbors on the ν sublattice at the center of cluster (to reduce finite-size effects[27]). Figure 4 shows that m_A increases with Δ and is substantially enhanced by U, whereas m_B is always small. This is in marked contrast to a spin-density wave, as predicted by Hartree-Fock calculations where the magnetic moment is far smaller than that experimentally observed.[28]

We now turn to discuss the consequences of our results for understanding experiments; for simplicity and concreteness we focus on Na_xCoO_2. The $x=0.5$ materials have remarkably different properties from those on other values of x.[6,7] Above 51 K the intralayer resistivity of $Na_{0.5}CoO_2$ is weakly temperature dependent with values of a few mΩ cm (Ref. 6) characteristic of a bad metal.[13] Below 51 K the resistivity increases, consistent with a small gap opening ($\sim$10 meV).[6] Thus a (bad) metal-insulator transition occurs at 51 K. The insulating state of $Na_{0.5}CoO_2$ has a number of counterintuitive properties, not the least of which is the absence of strong charge ordering. NMR observes no charge ordering up to a resolution of $n_B-n_A<0.4$,[5,9] while neutron crystallography suggest $n_B-n_A\simeq 0.12$.[4] Thus the insulating state is not the simple charge-transfer-like state predicted by Eq. (1) in the strong-coupling limit. $Na_{0.5}CoO_2$ develops a commensurate magnetic order below 88 K.[5,8] A large magnetic moment [$m=0.26(2)\mu_B$ per magnetic Co ion] is observed in spite of the weak charge order [note that classically $m<(n_B-n_A)\mu_B/2$]. Above 100 K the optical conductivity[7] shows no evidence of a Drude peak, consistent with a bad metal. In the insulating phase spectral weight is lost below $\sim$10 meV, consistent with the gap seen in the dc conductivity and a peak emerges at $\sim$20 meV, which is too sharp and too low energy to correspond to a Hubbard band.[7] Angular resolved photoemission spectra (ARPES) shows that the highest-energy occupied states are $\sim$10 meV below the Fermi energy.[10] No equivalent insulating state is seen in the misfit cobaltates,[5] which supports the contention that Na ordering is vital for understanding the insulating state.

In order to compare our results with experiments on $Na_{0.5}CoO_2$ we need to restrict ourselves to the relevant parameter values: $t<0$ and $|t|\sim\Delta\ll U$.[23] This corresponds with the regime of the three-quarter filled ionic Hubbard model that is both the most interesting and the most difficult to study via exact diagonalization because of the deleterious finite-size effects. Nevertheless we propose that in $Na_{0.5}CoO_2$ the insulating state is analogous to a covalent insulator. This explains a wide range of experiments. The peak observed at $\omega\sim 30$ meV in the optical conductivity[7] is interpreted as the transfer of an electron from the weakly correlated band to form a doublon in the strongly correlated band. The weak charge transfer ($n_B-n_A=0.1-0.3$; cf. Fig. 1) is caused by the strong hybridization between the A and B sublattices and is consistent with the value extracted from crystallographic experiments [0.12 (Ref. 4)] and the bounds from NMR [$<$0.4 (Ref. 5)]. The large moment [$(0.1-0.2)\mu_B$; cf. Fig. 4] is comparable to the moment found by neutron scattering [$0.26\mu_B$ (Ref. 8)] and results from the electrons in the strongly correlated band, i.e., the single-spin hybridized between the A and B sublattices. Finite-size effects mean that we cannot accurately calculate the charge gap in this regime. However, we propose that the experimental system corresponds to a parameter range where the gap is small, $\Delta_c<\mathcal{O}(|t|)$, consistent with the gap, $\sim$7–10 meV,[6,10] seen experimentally in ARPES and resistivity. This is consistent with the expectation that $\Delta_c\to 0$ as $\Delta/|t|\to 0$. Accurately calculating Δ_c for small $\Delta/|t|$ and large U, and hence further testing our hypothesis, therefore remains an important theoretical challenge.

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[23] Atomistic calculations give $t=-(0.08-0.14)$ eV, $U=2.5-2.8$ eV, and $\Delta=0.03-0.16$ eV (Refs. 16 and 29). Further, CoO_2, which is described by model (1) at half filling with $\Delta=0$, is a strongly correlated metal rather than a Mott insulator.[30] This suggests $U/|t| \lesssim 12-15$, the critical value for a Mott insulator on the triangular lattice (Refs. 13 and 31).
[24] The tight-binding band structure of model (1) consists of two bands due to hybridization between *A* and *B* sites. At 3/4 filling, for $t>0$ and any non-zero Δ, the lower band is filled and the upper band is half filled, while for $t<0$ the lower band is filled for $|\Delta| \gtrsim 0.64t$.
[25] In the strong-coupling limit we find, from degenerate perturbation theory that, for either sign of t, $n_B-n_A=1-8(t/\Delta)^2+16(t/\Delta)^3+\mathcal{O}[(t/\Delta)^4]$. For $t=0$ the ground state of model (1) is a charge ordered insulator consisting of rows of doubly occupied *B* sites alternating with rows of singly occupied *A* sites. In the strong-coupling limit, $U \gg \Delta \gg |t|$, virtual hopping processes lead to magnetic interactions between electrons in *A* sites. Equation (1) reduces to a Heisenberg model on an rectangular lattice: $H=J\Sigma_{\{ij\}}[\mathbf{S}_i\cdot\mathbf{S}_j-\frac{1}{4}]+J_\perp\Sigma_{[ij]}[\mathbf{S}_i\cdot\mathbf{S}_j-\frac{1}{4}]$, where $J=\frac{4t^2}{U}-\frac{8t^3}{\Delta^2}$ and $J_\perp=\frac{16t^4}{\Delta^2}[\frac{1}{U}+\frac{1}{2\Delta+U}+\frac{1}{2\Delta}]$. J results from the usual superexchange antiferromagnetic coupling and "ring" exchange process around a three-site plaquette.[22] In our previous paper,[13] the $O(t^3)$ term was neglected. J becomes negative for $t>0$ and $\Delta \lesssim \sqrt{2}Ut$ leading to a ferromagnetic interaction. In contrast $J_\perp$ is always antiferromagnetic.
[26] The lowest-order correction to the charge gap, in the strong-coupling limit, comes from the kinetic energy of a hole (doublon) propagating along the *B* (*A*) chains when extracting (adding) an electron to the zeroth-order ground-state configuration. Using degenerate perturbation theory we find that the gap is given, to $O(t^3)$, by $\Delta_c=\Delta-2|t|+4t^2/\Delta-8t^3/\Delta^2+E_{1D}^{t\text{-}J}$, where $E_{1D}^{t\text{-}J}$ is the energy of a hole in a half-filled *t*-*J* chain with J given by the expression in Ref. 25. $E_{1D}^{t\text{-}J}$ is given by the Bethe ansatz expression[32] for $J>0$, while $E_{1D}^{t\text{-}J}=-2|t|-J/2$ for $J<0$.
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