Proposed insulating ground state of $\text{Na}_{0.5}\text{CoO}_2$: Squaring the triangle

Ting-Pong Choy, Dimitrios Galanakis, and Philip Phillips

Loomis Laboratory of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801, USA

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We demonstrate that at a filling of $n=1.5$, a hexatic insulating state obtains in the extended Hubbard model on a triangular lattice. Composed of two tetragonal sublattices with fillings of $n=1$ and $n=2$, the insulating state is charge ordered and possesses an antiferromagnetic superlattice with a dimension of $a \times \sqrt{3}$. Two distinct energy scales arise in our model: a charge gap for the insulator and the effective exchange interaction in the antiferromagnet. Our model is capable of explaining both qualitatively and quantitatively the Hall coefficient including the sign change, the temperature dependence of the resistivity, and the persistence of antiferromagnetism above the insulating state.

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The cobaltates,¹ Na_xCoO_2 , are layered anisotropic materials that share many of the complexities of the high-temperature copper oxide superconductors. They consist of insulating layers of Na^+ ions separated by CoO_2 planes. As in the cuprates, superconductivity in the hydrated cobaltates,¹ $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, arises from doping a half-filled Mott insulating state. In the cobaltates, the half-filled band arises in the parent material, Na_0CoO_2 , from a complete filling of each of the e_g (t_{2g}) orbitals, while only a single electron resides in the d_{z^2} state.^{2,3} However, the underlying lattice is triangular as opposed to the square lattice of the cuprates. The concentration x measures the number of Co^{+4} ions converted to Co^{+3} ions for every Na atom added. Superconductivity¹ in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is confined to a domelike region as a function of the effective cobalt valence, which, in this case, is determined⁴ by the net hydronium and sodium ion contents.

While the cobaltates are generally metallic, they exhibit an insulating state⁵ at $x=0.5$. At present, the insulating behavior at $x=0.5$ remains a mystery. We propose that the key mechanism driving the insulating state is the elimination of magnetic frustration by the formation of a charge-ordered state: (1) the effective in-plane antiferromagnetic exchange coupling J and (2) the energy gap in the insulator Δ . We show that for reasonable system parameters, $\Delta < J$, and, hence, the insulating state is obtained at a lower temperature than the antiferromagnetic (AF) transition. Our model predicts an electronlike transport below the AF transition but a holelike transport above, as seen experimentally.⁵

There are now distinctly different probes of the insulating state at $n=1.5$. Transport measurements⁵ have found that the resistivity at $n=1.5$ is temperature independent in the range of $60 < T < 300$ K but undergoes a sharp upturn as the temperature decreases below 53 K. Further, the Hall coefficient⁵ changes sign from positive to negative as the temperature is lowered to 88 K. Unlike the square lattice, which is particle-hole symmetric at $n=1$, such is not the case for the triangular lattice. Hence, the vanishing of the Hall coefficient in the Na_xCoO_2 requires a nontrivial electronic state. The magnetic susceptibility χ exhibits a slight kink at 53 K, implying a phase transition. In addition, neutron diffraction^{6,7} and NMR (Ref. 8) experiments demonstrate that the Na atoms form an orthorhombic superlattice with lattice vectors $(a\sqrt{3}\mathbf{x}, 2a\mathbf{y})$. Sodium atom ordering has been promoted as the central ingredient in driving the insulating state. Consistent with such

ordering is an enhancement of the thermal conductivity⁵ below 53 K only at $n=1.5$. However, recent experiments on hydrated $\text{Na}_{0.41}\text{CoO}_2$, in which the conductivity has also been observed to diverge below 53 K, call this view into question. Electrochemical measurements⁹ indicate that charge transfer between the oxonium ion (H_3O^+) and Co results in a formal valence of Co of 3.5 rather than the nominal value of 3.59 obtained from the sodium content. Consequently, the authors conclude that the key ingredient in driving the insulating state is the presence of Co with a formal valence of 3.5 and not sodium ordering.

To understand what is special about the filling of $n=1.5$ on a triangular lattice, consider the square lattice at $n=1$. At $n=1$, the Coulomb repulsion energy is minimized and all magnetic frustration is eliminated on a square lattice by forming an antiferromagnet. Such a state is insulating because of the charge gap U for doubly occupying the same site. Our key assumption for the triangular lattice is that minimizing the Coulomb energy and eliminating Co magnetic frustration drive the insulating state at $n=1.5$. At a filling of $n=1.5$, all Coulomb repulsion energy and magnetic frustration can be eliminated by filling the lattice with alternating rows of doubly and singly occupied sites. Consequently, we consider the state in Fig. 1 in which the doubly and singly occupied sites occupy the corners of orthorhombic unit cells.

Such a state can be thought of as a triangular lattice split into two tetragonal lattices: one for the double occupancy and the other for the single occupancy with antiferromagnetic correlations. In fact, in terms of a unit cell defined by the basis vectors $(1, 0)$ and $(1/2, \sqrt{3}/2)$, the state proposed here preserves a translational symmetry but breaks rotational invariance by $2\pi/3$. Hence, the state is a hexatic nematic phase similar to that proposed for $x=1$ in the Emery model¹⁰ in which nearest-neighbor Coulomb interactions play a pivotal role. On a triangular lattice with $n=1.5$, there is another ordered ground state, the zigzag state,¹¹ which can be obtained by a zero-energy-cost rearrangement of the cobalt ions in the charge-ordered state. Consequently, as to which state is experimentally favored is determined by factors such as the lattice structure and the sodium ordering pattern. Nonetheless, to establish that either the charge-ordered or zigzag states is an insulator necessitates an analysis of the distinct transport channels, which we now present.

We analyze the energetics for transport in the context of the extended Hubbard model,

FIG. 1. Charge ordering of $\text{Na}_{0.5}\text{CoO}_2$. The circles represent cobalt atoms. Notice that the triangular lattice is broken into two orthorhombic lattices: one with double occupancies and one with antiferromagnetic ordering. Moving an electron from a doubly occupied site to a singly occupied site will increase its energy by J , where $J=4t^2/U$ is the antiferromagnetic coupling constant. A next-nearest-neighbor superexchange interaction J_1 also exists in the vertical direction. The diagonal hopping process, which leaves antiferromagnetism intact is also depicted.

$$H = -t \sum_{\langle ij \rangle} c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.} + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j, \quad (1)$$

where $c_{i\sigma}$ ($c_{i\sigma}^\dagger$) annihilates (creates) an electron with spin σ on site i , U is the energy cost for doubly occupying the same site, and V is the nearest-neighbor Coulomb repulsion. The importance of the nearest-neighbor interaction in stabilizing the insulating state can be illustrated as follows. Since along each singly occupied row, charge transport is blocked as a result of the charge gap U , it suffices to show that Fig. 1 is an insulator by demonstrating that the doubly occupied sites are immobile. Any electron in a doubly occupied site is surrounded by an equal number of spin-up and spin-down electrons in the neighboring sites, resulting in a net zero interaction energy. However, if an electron hops to a singly occupied site, it will be surrounded by three double occupancies, two electrons of the opposite spin and one of the same spin. The net increase in the energy will be $V+J$, where $J=4t^2/U$.¹² We will call such a process the creation of a doubloon (on a singly occupied row) and holon (on a doubly occupied row) pair, which costs an energy of $V+J$. Once a doubloon-holon pair has been created, there are four distinct transport mechanisms.

(1) Holon motion along the otherwise doubly occupied superlattice. The transport of the holon vertically along the superlattice requires two-step hopping, which does not cost any energy in the intermediate state. The amplitude for such a process is t .

(2) Doubloon motion in the singly occupied row. It costs an energy nJ_1 , where n is the number of hops. Hence, a doubloon is linearly confined and does not propagate along a chain.

(3) Transport of a doubloon along a diagonal through a series of concerted two-step hoppings as illustrated in Fig. 1.

Doubloon hops along the diagonal, however, do not generate any further energy costs and hence constitute the only true two-dimensional transport in the antiferromagnetic phase. As doubloon motion propagates an electron, $R_H < 0$. This type of diagonal hopping process, which leaves the antiferromagnet intact, requires both the triangular lattice and the charge-ordered state in Fig. 1.

(4) Holon transport along either one of the diagonals. Such hopping depends on the surrounding spin.

On the other hand, in the absence of antiferromagnetic correlations, both the holon and doubloon hop in their corresponding superlattices with the same hopping matrix elements but with opposite signs. All such transport mechanisms cease once the holon and doubloon are bound. The criterion for holon-doubloon binding can be derived from a two-dimensional model,

$$H = \sum_{\langle ij \rangle} t_{ij}^d (d_i^\dagger d_j + \text{H.c.}) + \sum_{\langle ij \rangle} t_{ij}^h (h_{i\sigma}^\dagger h_{j\sigma} + \text{H.c.}) + \sum_i (V + \tilde{J}) \times (h_{i\sigma}^\dagger h_{i\sigma} + d_i^\dagger d_i) - t \sum_i (d_i^\dagger h_{i\sigma}^\dagger + \text{H.c.}), \quad (2)$$

which includes all of the distinct hopping processes delineated above. The operator $d_k^\dagger$ creates a doubloon, while $h_k^\dagger$ creates a spin holon on the singly occupied row. t_{ij}^d and t_{ij}^h are the hopping matrices for the doubloon and holon, respectively,

$$t_{ij}^d = \alpha \tilde{t}_{ij}^d - (1 - \alpha) \Delta_{ij},$$

$$t_{ij}^{h\sigma} = \alpha \tilde{t}_{ij}^{h\sigma} + (1 - \alpha) \Delta_{ij}, \quad (3)$$

where $\alpha = \langle (-1)^{\mathbf{r}_i \cdot \mathbf{S}_i} \rangle^{2m}$ for some positive m is a function of the ordering parameter of the singly occupied superlattice, which is temperature dependent, and $\tilde{J} = \alpha J$. In our calculation, α has the following form:

$$\alpha(T) = \begin{cases} 0, & T > T_N \\ \left(\frac{T_N - T}{T_N}\right)^m, & T < T_N, \end{cases} \quad (4)$$

and constitutes the only free parameter in our comparison with experiment. Both α and the modified form of J reflect the fact that the hopping processes depend on the antiferromagnetic ordering. As a consequence, J enters the energy cost only if antiferromagnetism is present. $\Delta_{ij} = t(\delta_{i_x \pm 1, j_x} \delta_{i_y, j_y} + \delta_{i_x, j_x} \delta_{i_y \pm 1, j_y})$ corresponds to the hopping mechanism for both the doublon and holon in the absence of antiferromagnetism. If the electron on the singly occupied superlattice is antiferromagnetically correlated, the hopping mechanism for the doublon and holon becomes

$$\tilde{t}_{ij}^d = -t \delta_{i_x \pm 1, j_x} \delta_{i_y \pm 1, j_y},$$

$$\tilde{t}_{ij}^{h\sigma} = +t(\delta_{i_x \pm 1, j_x} \delta_{i_y, j_y} + \delta_{i_x, j_x} \delta_{i_y \pm 1, j_y} + \delta_{i_x \pm \sigma 1, j_x} \delta_{i_y \pm \sigma 1, j_y}). \quad (5)$$

Likewise, α enters the diagonal hopping term because such processes only enter if antiferromagnetism is present. Noting that the creation of a doublon-holon pair on two adjacent rows costs a total energy of $2(V+J)$, we can write the non-interacting energies of the doublon and holon as

$$\varepsilon_{d,h}(\mathbf{k}) = V + \tilde{J} + t^{d,h}(\mathbf{k}), \quad (6)$$

where $t^d(\mathbf{k}) = -2\alpha t[\cos(k_x + \sqrt{3}k_y) + \cos(k_x - \sqrt{3}k_y)] - 2t(1 - \alpha) \times [\cos(k_x) + \cos(\sqrt{3}k_y)]$ and $t^{h\sigma}(\mathbf{k}) = 2t[\cos(k_x) + \cos(\sqrt{3}k_y)] + \alpha t \cos(k_x + \sigma\sqrt{3}k_y)$ are the Fourier transforms of $\tilde{t}_{ij}^d$ and $\tilde{t}_{ij}^{h\sigma}$, respectively. Localization corresponds to a binding of a spinon and a holon. The solution to this model, obtained via a Bogoliubov rotation, has the quasiparticle spectrum,

$$E^-(\mathbf{k}) = +\cos^2 \theta_k \varepsilon_d(\mathbf{k}) - \sin^2 \theta_k \varepsilon_h(\mathbf{k}) - t \sin 2\theta_k,$$

$$E^+(\mathbf{k}) = -\sin^2 \theta_k \varepsilon_d(\mathbf{k}) + \cos^2 \theta_k \varepsilon_h(\mathbf{k}) - t \sin 2\theta_k, \quad (7)$$

where $\tan 2\theta_k = -2t/[\varepsilon_d(k) + \varepsilon_h(k)]$, corresponding to negative and positive charge excitations, respectively. As clearly seen in Fig. 2, this model admits a metal-insulator transition with a well-defined gap Δ between the localized and the extended states. This gap is zero for $V+J-4t < 0$, but is otherwise given by

$$\Delta \approx (V+J) \left(1 - \frac{4t}{V+J}\right). \quad (8)$$

Experimentally, $J \approx 10$ meV and $t = 0.2$ eV;¹³ consequently, there is no solution to Eq. (8) if $V=0$ as in the Hubbard model. However, V is not known. Hence, to determine Δ , we must rely on experiments. To describe the experimental upturn of the resistivity at 53 K, $\Delta \approx 53$ K, which results in $V \sim 880$ meV $> 4t$. This value of V is reasonable because even if we use the reduced value of the on-site energy, $U/\sqrt{3} = 4.0$ eV/1.73 = 2.3 eV (Ref. 14), reported recently for the insulating state, we find that V is of order $U/3$.¹⁵ The importance of this estimate is that V is large enough to stabilize the charge-ordered insulating phase. We computed the resistivity using the Kubo formula within the diagonalized quasiparticle spectrum in Eq. (7). Figure 2(a) shows that the

FIG. 2. (Color online) (a) Resistivity (dashed line) and band structure for the model in Eq. (2). Two bands corresponding to negative and positive charge quasiparticles with a gap Δ are shown. (b) Hall coefficient for Eq. (2). The experimental data for both the resistivity (squares) and Hall coefficient (circles) are taken from Foo *et al.* (Ref. 5).

computed resistivity adequately reproduces the experimental trends. The only free parameter is m in α , which we set to 4. We have found, however, that the resistivity is insensitive to m as the divergence is governed primarily by the gap, which is set by experiment. A key consequence of the insulating state proposed here is the emergence of an antiferromagnetic superlattice with a dimension of $a \times \sqrt{3}a$ on the singly occupied sites. In fact, this is our key experimental prediction. This can be established rigorously. There is a weak antiferromagnetic coupling J_1 between electrons separated by $\sqrt{3}a$ on neighboring singly occupied rows, which are mediated by intervening doubly occupied sites. For this exchange interaction to be well defined, doublons should not be created; hence, $V+J > 4t$. Consequently, J_1 should be a function of V .¹⁵

To determine the rough magnitude of the effective spin coupling constant J_1 in the sublattice, we consider the fourth-order perturbation process, which flips the spins with respect to the charge-ordered state and obtain $J_1 = 4(t/V)^2 J$. For the experiments at hand, $V \approx 0.88$ eV $\approx 4t$, implying that $J_1 \approx J$. Furthermore, the effective horizontal spin coupling constant J should be renormalized by the same fourth-order process such that $J \rightarrow J' = J + J_1 \approx 1.25J$. Through the identical mechanism, next-nearest-neighbor sites (that is, sites along the diagonal) in the singly occupied sublattice are also antiferromagnetically coupled. However, in this case, only *one* path exists. Consequently, the next-nearest-neighbor exchange interaction is $J_2 = J_1/2$. Hence, the singly occupied sublattice obeys the Heisenberg Hamiltonian,

$$\begin{aligned} H_{\text{singl occup}} &= J' \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{x}} + J_1 \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{y}} + J_2 \sum_{nnn} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= H_0 + J_2 \sum_{nnn} \mathbf{S}_i \cdot \mathbf{S}_j, \end{aligned} \quad (9)$$

where $\hat{x}$ ($\hat{y}$) denotes a nearest neighbor along the x axis (y axis). In the absence of J_2 , the system develops a long-range antiferromagnetic order for temperatures less than $J_{\text{eff}} \equiv \sqrt{J} J_1 \approx 13$ meV.¹⁷ For $J_2 \neq 0$, antiferromagnetism is obtained as long as $J_2 < J_{\text{eff}}/2$,¹⁶ which is satisfied in our case. As the effective low-energy description of the insulating

state has now been reduced to a half-filled rectangular lattice (by virtue of integrating out the doubly occupied sublattice), the particle-hole symmetry has now been reinstated.

Consequently, the Hall coefficient should vanish as $T \rightarrow 0$ for $n=1.5$, as observed experimentally.⁵ Once the transition to the AF phase occurs, both the noninteracting quasiparticles with negative and positive charges can contribute to the Hall coefficient, as mentioned previously. However, according to Fig. 2, the negatively charged quasiparticles have a lower energy. Hence, $R_H < 0$ below the AF transition. Above T_N , no order exists but the stripe is still stable. In this regime, the sign of the Hall coefficient is strictly determined by the filling which for $n=1.5$ should be holelike. Since the Hall coefficient vanishes at $T=0$, it is proportional to the charge difference between particles and holes. Hence, we computed the Hall coefficient by integrating $2(f(E^+(k)) - f(E^-(k)))/e$ over all momenta, where f is the Fermi function. As Fig. 2 indicates, the Hall coefficient contains a sign change and has a minimum at $T \approx 0.5J$, which are in superb quantitative agreement with experiment. Likewise, the resistivity has a plateau where R_H acquires its minimum value, as observed experimentally.⁵ Here, again, we used $m=4$ and found that the overall qualitative features are insensitive to the choice of m . The robustness of the qualitative features of R_H and the resistivity lend credence to Eq. (2) as the reductive model for the insulating state.

Within the mean-field theory,¹⁷ the upper bound to the temperature at which there is a transition to this AF state is given by $T_c = 2J_{\text{eff}}$. For reasonable system parameters, this energy scale exceeds that of the gap for the insulating state and is hence consistent with recent neutron scattering experiments,¹⁸ which find charge ordering and antiferromagnetism consistent with Fig. 1 above the temperature at which the resistivity exhibits an upturn. The relative ordering of the energy scales is as follows: The energy scale for destroying the stripe order is set by the nearest-neighbor Coulomb energy V . The antiferromagnetic order is destroyed above J_{eff} .

Between Δ and J_{eff} , the AF order exists but the holons and doublons are mobile. The antiferromagnetic order in the plane is maintained because diagonal doublon hops do not generate ferromagnetic bonds but rather exchange doublons between the two sublattices. This ultimately mixes the valence between the cobalt atoms on the singly and doubly occupied rows. Hence, rapid charge fluctuations on a time scale set by $\hbar/t \sim 10^{-14}$ s could be the origin of the absence of two distinct Co environments reported in recent near quadrupole resonance (NQR) experiments.¹⁹ Nonetheless, such mixing ceases in the insulating state as the holon and doublon are bound. Hence, our $T=0$ state contains two distinct Co environments. High-field NMR and Co NMR experiments²⁰ find, contrary to the NQR experiments, two distinct Co environments corresponding with effective moments, consistent with the charge-ordered state proposed here.

To summarize, in $\text{Na}_{0.5}\text{CoO}_2$, the ordering^{6,21} of the sodium ions induces charge ordering in the CoO_2 layers, so that both the double occupancies and the single occupancies reside on different tetragonal lattices. However, charge localization is obtained not from pinning by the sodium superlattice but by a delicate balance between local Coulomb repulsions and the kinetic energy in the CoO_2 plane. The key prediction of this work that AF order on a superlattice has a dimension of $a \times \sqrt{3}a$ has been confirmed experimentally.¹⁸ Further, the diagonal hopping mechanism identified here illustrates that the sign change of the Hall coefficient at T_N and the apparent itineracy¹⁹ of the antiferromagnetism are intimately related.

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