Electronic Model for CoO_2 Layer Based Systems: Chiral Resonating Valence Bond Metal and Superconductivity

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Takada *et al.* have reported superconductivity in layered $Na_xCoO_2yH_2O$ ($T_c \approx 5$ K). We model a reference neutral CoO_2 layer as an orbitally nondegenerate spin-$\frac{1}{2}$ antiferromagnetic Mott insulator on a triangular lattice and $Na_xCoO_2yH_2O$ as electron doped Mott insulators described by a $t-J$ model. It is suggested that at optimal doping chiral spin fluctuations enhanced by the dopant dynamics lead to a gapful d-wave superconducting state. A chiral resonating valence bond (RVB) metal, a parity and time (PT) reversal violating state with condensed RVB gauge fields, with a possible weak ferromagnetism, and low temperature p-wave superconductivity are also suggested at higher dopings.

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Recent discovery of superconductivity in $Na_xCoO_2yH_2O$ ($T_c \approx 5$ K) by Takada and collaborators [1] marks a milestone in the search for new layered transition metal oxide superconductors. In the same family of planar CoO_2 based metals weak ferromagnetism [2] and high temperature Curie susceptibility have been observed. $Na_{0.5}CoO_2$ has been shown [3] to be a very good metal with anomalously large thermoelectric power. It is becoming clear that strong electron correlation is at work, resulting in anomalous behavior and possible new electronic phases.

In this Letter we model a reference CoO_2 layer as an orbitally nondegenerate spin-$\frac{1}{2}$ antiferromagnetic Mott insulator on a triangular lattice. Consequently, $Na_xCoO_2yH_2O$ is described as an electron doped Mott insulator by a $t-J$ model. We have performed a resonating valence bond (RVB) mean-field analysis of this model. As there is a rich variety of possible phases, we do not go to the details of the mean-field theory but provide qualitative arguments (that go beyond mean-field theory) for (i) a reference chiral RVB state, (ii) a chiral RVB metallic (spin gap) state, (iii) a weak ferromagnetic state at higher doping, and (iv) Parity and time (PT) reversal violating gapful $d_1 + id_2$ and p-wave superconductivity at low temperatures.

$Na_xCoO_2yH_2O$ ($x \approx 0.35$ and $y \approx 1.3$) consists [1] of two-dimensional CoO_2 layers separated by thick insulating layers of Na^{2+} ions and H_2O molecules. CoO_2 has the structure of layers in CdI_2. It is a triangular net of edge sharing oxygen octahedra (Fig. 1); Co atoms are at the center of the octahedra forming a 2D triangular lattice. Oxygen octahedra have a trigonal distortion—a stretch along a body diagonal direction of the embedding cube. For convenience we choose the corresponding body diagonal direction as the Z axis. The trigonal stretch makes the O-Co-O angle $\approx 98°$. A simple way to understand this structure is to imagine a triangular lattice on the X-Y plane with sublattices A, B, and C. Fill the A and C sublattices with oxygen atoms and the B sublattice with Co atoms. Displace sublattice A and C layers on opposite directions along the Z axis by the same amount $\frac{z_0}{2}$. When $z_0 > (\sqrt{3/2})a$ we get the desired structure with every Co atom surrounded by an octahedron with trigonal stretching. Here a is the distance between neighboring Co atoms in the triangular lattice. Strong electron affinity of oxygen should lead to a complete electron transfer from Na atoms of $Na_{xy}H_2O$ layers in $Na_xCoO_2yH_2O$ to CoO_2 layers.

Experimentally $Na_{0.5}CoO_2$ is a strongly anisotropic [4] metal. The ab-plane resistivity is rather low with $\rho \sim 10\ \mu\Omega$ at low temperatures and $\rho \sim 200\ \mu\Omega$ at 300 K. C-axis resistivity is high indicating some kind of confinement of charges, similar to the planar cuprates, at temperatures above ~200 K. It is also interesting that such a good metal exhibits [4] Curie-Weiss $\chi \sim \frac{C}{T-\Theta}$, rather than Pauli susceptibility at high temperatures, and $\Theta \approx -118$ K. For $Na_{0.75}CoO_2$ weak ferromagnetism has been observed [2] below about 22 K. In another CoO_2 layered compound called misfit layer compound, weak ferromagnetism has been reported [2] below 3.5 K.

In a neutral reference CoO_2 layer the nominal valence of the Co atom is Co^{4+}, i.e., a $3d^5$ ion. In an octahedral environment the $3d$ levels are split (Fig. 2). The trigonal distortion of the oxygen octahedra causes further splitting of the $3d$ levels. The lower threefold degenerate t_{2g} levels are split into a nondegenerate d_{z^2} state with a doublet below, denoted as $e_g(t_{2g})$ in Fig. 2. The ground

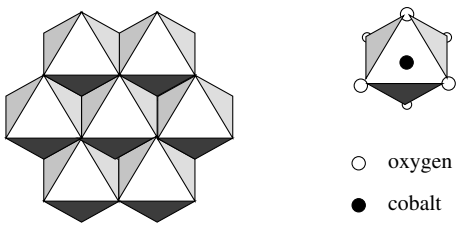

FIG. 1. Structure of CoO_2 layer. A triangular network of edge sharing oxygen octahedra. Co atoms are at the center of the oxygen octahedra.

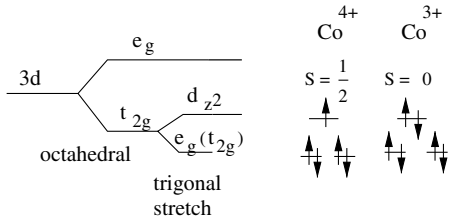

FIG. 2. Crystal field split $3d$ levels of cobalt.

state configuration is an orbitally nondegenerate spin-$\frac{1}{2}$, low spin state. In our coordinate system we choose the direction of trigonal distortion to be the z axis, so the top nondegenerate split orbital of the t_{2g} manifold is a $3d_{z^2}$ orbital. Thus in the nominal charge state Co^{4+}, we have an unpaired electron in the d_{z^2} orbital, making Co^{4+} ground state an orbitally nondegenerate spin-$\frac{1}{2}$ state. In the same way for Co^{3+} we have two electrons filling the d_{z^2} level making the ground state an orbitally nondegenerate spin-singlet. Our simple quantum chemical picture, contained in Singh's work [5] is supported by various experiments including a Co NMR study [4] in $Na_{0.5}CoO_2$. It is interesting to note that our CoO_2 layer with strong trigonal distortion has escaped some important effects which should work against superconductivity, namely, Jahn-Teller distortion, Hund coupling, and possible high spin ground states of Co ions.

As in other transition metal oxides, hybridization of d_{z^2} with symmetry adapted oxygen orbitals and the strong Hubbard repulsion in the d_{z^2} should lead to the usual superexchange interaction between neighboring magnetic Co^{4+} ions. As the superexchange paths are not 180° paths, the antiferromagnetic coupling will be reduced in strength. We make an estimate of the superexchange constant and parameters for our tight binding model using the electronic structure calculation of Singh [5] for $Na_{0.5}CoO_2$. Singh finds an electronlike Fermi surface, shown in Fig. 3. The states close to the Fermi level arise predominantly from the cobalt $3d_{z^2}$ orbitals. The bilayer type splitting found by Singh for $Na_{0.5}CoO_2$ is not important for us as our CoO_2 layers are well insulated by the

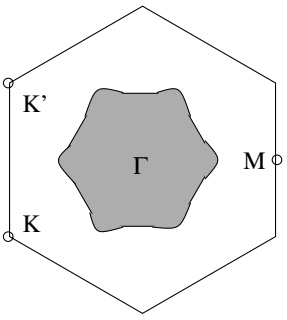

FIG. 3. Sketch of Fermi surface of electron doped CoO_2 layer, based on Singh's calculation for $Na_{0.5}CoO_2$, ignoring small Fermi surface pockets.

$Na_{xy}H_20$ layers. As a first approximation we ignore the small electronlike pockets found by Singh.

$Na_{0.5}CoO_2$ contains an equal number of Co^{3+} and Co^{4+} ions, giving an average occupancy of 1.5 electrons in the valence d_{z^2} orbital. Thus the d_{z^2} based single band is $\frac{3}{4}$ filled. In a simple tight binding model keeping only the nearest neighbor hopping we get the following band dispersion:

$$\epsilon_k = -2t\left(\cos k_x + 2\cos\frac{k_x}{2}\cos\frac{\sqrt{3}}{2}k_y\right). \qquad (1)$$

We can estimate the value of the hopping parameter t by fitting to Singh's result. We get a value of $t \approx -0.1$ eV, corresponding to a bandwidth of ≈ 1.0 eV. It is important to note that it is the negative sign of the hopping parameter that gives us a closed Fermi surface around the Γ point for our $\frac{3}{4}$ filled band. In view of the strong particle-hole asymmetry in a triangular lattice the sign of t is important; for an electron doped $t-J$ model [6] RVB states are favored for $t<0$ and ferromagnetism for $t>0$.

Since Coulomb interaction in the effective $3d_{z^2}$ orbital is $\sim$5 to 7 eV, the net superexchange interaction between two neighboring Co^{4+} ions is $J \equiv \frac{4t^2}{U} \sim 6$ to 8 meV. Using the paramagnetic Curie temperature $\Theta \approx -118$ K obtained from susceptibility measurements in $Na_{0.5}CoO_2$ we independently estimate $J \approx 7$ meV, assuming an average of three nearest neighbor Co^{4+} ions for a given Co^{4+} ion. These considerations lead us to a $t-J$ model for the electron doped CoO_2 layer:

$$H_{tJ} = -t\sum_{\langle ij\rangle} C^{\dagger}_{i\sigma}C_{j\sigma} + \text{H.c.} + J\sum_{\langle ij\rangle}\left(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{1}{4}n_i n_j\right)$$

with the local constraint $n_{i\uparrow} + n_{i\downarrow} \neq 0$. Here C's are electron operators and $\mathbf{S}$'s spin operators.

Superconductivity in a 2D $t-J$ model in a square lattice is becoming more plausible, thanks to RVB theory [7–11] and related recent [12] variational and numerical efforts. The singlet proliferation tendency arising from the superexchange, contained in the J term, seems to be sufficient to induce a robust spin-singlet superconducting state [13]. We believe the same is true for the triangular lattice. However, the enhanced frustration could modify the symmetry of the superconducting state or introduce novel quantum states such as chiral RVB metal with weak ferromagnetism. Further, the possibility of superconductivity in a repulsive Hubbard model on a triangular lattice at and close to half filling has been studied by various authors [14,15] invoking spin fluctuation mediated pairing, mainly in the context of organic superconductors. We take an RVB approach, as it is a natural way to study a system in its strong correlation limit, dominated by spin-singlet correlation and chiral fluctuation. We study the undoped case first and discuss a simple RVB mean-field theory for a chiral RVB state. The doped chiral RVB state is discussed next. As in the case of cuprates the RVB

mean-field solutions are guidelines to pick out the important phases and to map a phase diagram. Results may be improved when used in conjunction with Gutzwiller projection on the RVB mean-field states.

Spin-$\frac{1}{2}$ Heisenberg antiferromagnet on a triangular lattice has been a guiding model for Anderson's RVB theory [16], which took new meaning and new forms in the context of cuprate superconductors in the hands of Anderson, collaborators, and others. Kalmayer and Laughlin [17] proposed a novel short range RVB wave function, called a chiral spin liquid state, that violated PT symmetry; it has a nonzero expectation value of spin chirality: $\langle \mathbf{S}_i \cdot (\mathbf{S}_j \times \mathbf{S}_k) \rangle \neq 0$. This state has a certain deep connection to fractional quantum Hall states. The energy of this state per spin is higher by about 9%, compared to better ground state energy estimates. Though not better in energy, this work above established the possibility of a chiral RVB state with a spin gap that also has a manifest quantum number fractionization through the existence of well-defined spinon excitations, which are anyons. Consequently, when such a state is doped with holes, for example, the holes undergo spin charge decoupling and the holons become anyons. This prompted Laughlin [18,19] to argue for a powerful pairing correlation between holons arising from the novel exchange statistics. Later the anyon statistics was understood to have arisen from the attachment of appropriate RVB gauge field fluxes to particles.

We start with the slave boson representation for our $t - J$ model:

$$H_{t,J} = t\sum_{\langle ij \rangle} d_j^\dagger d_i s_{i\sigma}^\dagger s_{j\sigma} + \text{H.c.} - J\sum_{\langle ij \rangle} s_{i\sigma}^\dagger s_{j\sigma} s_{j\sigma'}^\dagger s_{i\sigma'} \quad (2)$$

with the local constraint, $d_i^\dagger d_i + \sum_\sigma s_{i\sigma}^\dagger s_{i\sigma} = 1$. Here $s_{i\sigma}$ are fermion operators for spin-$\frac{1}{2}$ singly occupied states and d_i are the bosonic operators for the doubly occupied spin-singlet states.

We first consider the undoped case, the spin-$\frac{1}{2}$ Heisenberg model on a triangular lattice. Lee and Feng [20] have performed RVB mean-field analysis for this case. We briefly review their results. The mean-field Hamiltonian $H_{\text{mF}} = -J\sum_{\langle ij \rangle} \chi_{ij} s_{j\sigma}^\dagger s_{i\sigma} + \cdots$ is obtained by the factorization $\tau_{ij}\tau_{ji} \rightarrow \chi_{ij}\tau_{ji}$, etc., where $\tau_{ij} \equiv \sum_\sigma s_{i\sigma}^\dagger s_{j\sigma}$. The RVB order parameter $\chi_{ij} \equiv |\chi_0| e^{i\theta_{ij}}$ with $\theta_{ij} \equiv \int_j^i \mathbf{A} \cdot d\boldsymbol{l}$. Here $\mathbf{A}$ is the spatial component of the RVB gauge field [9]. In the Lee-Feng mean-field solution $\oint \mathbf{A} \cdot d\boldsymbol{l} = \pm \frac{\pi}{2}$ in every elementary triangle.

The single spinon dispersion acquires a gap at the Fermi level and has the form

$$\varepsilon_k = \pm J\alpha \left(\cos^2 k_x + 2\cos^2 \frac{k_x}{2} \cos^2 \frac{\sqrt{3}}{2} k_y \right)^{1/2}, \quad (3)$$

where $\alpha \approx 0.603\sqrt{3}$. The chiral spin character of Lee-Feng solution is obtained through the Wen-Wilczek-Zee identity [19]

$$\mathbf{S}_i \cdot (\mathbf{S}_j \times \mathbf{S}_k) = \frac{i}{4} (\tau_{ij}\tau_{jk}\tau_{ki} - \tau_{ik}\tau_{kj}\tau_{ji}) \sim e^{i \oint \mathbf{A} \cdot d\mathbf{l}}, \quad (4)$$

which connects the spatial component of the U(1) RVB gauge field with three spin chirality. Thus the two degenerate solutions corresponding to uniform fluxes $\pm \frac{\pi}{2}$ through every elementary triangle give us the two degenerate PT violating chiral RVB states. Lee and Feng also found numerically that the energy of the above mean-field chiral RVB state on Gutzwiller projection becomes very close to Kalmayer-Laughlin state. We have also found a good overlap between Kalmayer-Laughlin wave function and Gutzwiller projected Lee-Feng RVB wave function using a procedure of Laughlin and Zou [21].

The 120° three-sublattice antiferromagnetic order with a twofold planar chirality degeneracy is to be viewed as obtained by condensing spinon pairs in a spin triplet state at the appropriate wave vector. As in cuprates, even a small amount of doping, in view of the large dopant kinetic energy removes the long range three-sublattice order. We also find from our RVB mean-field analysis of the $t - J$ model a locally stable chiral RVB state for a range of doping. *This means we may use the $\frac{\pi}{2}$ flux RVB state as a reference state for a range of doping in the metallic state.*

The situation is similar to cuprates, where Affleck-Marston's π flux RVB state [11], a state that respects PT symmetry, is useful to understand the spin gap phase. In our case, as our reference chiral RVB state has a flux of $\frac{\pi}{2}$, a strongly PT violating value, it is likely that our spin gap phase will be a chiral RVB metallic state. It will be important to look for PT violation signals in experiments.

Experiments have shown weak ferromagnetism at high electron doping. This may be explained as follows. Anderson has recently argued [22] that the effect of dopant dynamics in cuprates is to produce local spin chirality and induced ferromagnetic interaction. We apply similar arguments for our case (Fig. 4) remembering that our hopping integral has negative sign and our dopants are electrons. Here a single extra electron performing a "closed loop hopping" in a triangle induces an extra antiferromagnetic coupling; this is because the above process permutes an even number of spins. Thus we get

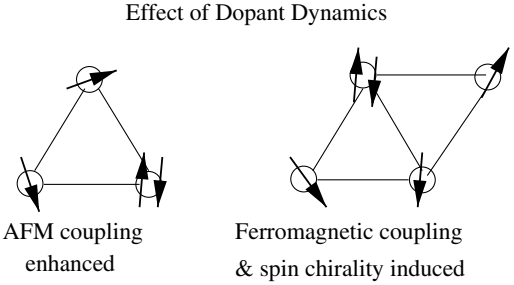

FIG. 4. Effective spin-spin coupling induced by dopant dynamics.

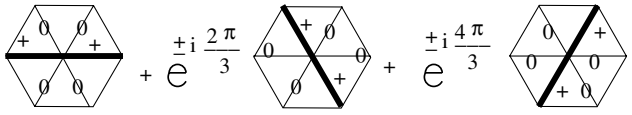

FIG. 5. Relative phases of Cooper pair amplitudes ($\Delta_{ij} \neq 0$ on dark bonds) in PT violating $d_1 \pm id_2$ states.

an effective exchange coupling $J_{\text{eff}} \approx J + x|t|$, if we focus on three sites. That is, the leading effect of doping is singlet stabilization for our t, which is negative.

However, as the doping increases, a carrier performing a closed loop hopping in a four spin cluster (Fig. 4) becomes important. As this process involves permutation of an odd number of spins, a ferromagnetic coupling is induced. Following Anderson we estimate this to be $J_{\text{eff}} \approx J - x|t|$ for large x, remembering that in our case of $t < 0$. In addition to the ferromagnetic coupling, chirality is also favored by the above process. Thus we believe that the weak ferromagnetism observed at high temperatures is a chiral RVB metal with weak ferromagnetic moments induced in a novel chiral metal, where chiral fluctuations and ferromagnetism tendencies compete. Putting in the values of J and t it is easy to explain the range of ferromagnetic $T_c \sim 3.5$ to 22 K seen in experiments.

Now let us discuss superconductivity. In the RVB mean-field theory we write, following Ref. [8], the superexchange term as a BCS interaction, $J\sum_{\langle ij\rangle}(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j) \equiv -J\sum_{\langle ij\rangle} b_{ij}^{\dagger} b_{ij}$, and perform the Bogoliubov-Hartree Fock factorization of the pairing term: $b_{ij}^{\dagger} b_{ij} \rightarrow b_{ij}^{\dagger} \Delta_{ij} + \text{H.c.}$, etc., where $b_{ij} \equiv \frac{1}{\sqrt{2}}(s_{i\uparrow} s_{j\downarrow} - s_{i\downarrow} s_{j\uparrow})$ and $\Delta_{ij} \equiv \langle b_{ij} \rangle$. For cuprates, Kotliar [11] found the $d_{x^2-y^2}$ wave state to have a lower energy.

Triangular lattice symmetry in our case leads to two degenerate d states d_1 and d_2, in the RVB mean-field theory. For small doping PT violating combinations $d_1 \pm id_2$ have lower energies. The order parameter pattern for the PT violating d-wave states are shown in Fig. 5. *Since the situation is more complex compared to cuprates, relative energetics of the extended s, d_1, d_2, or the $d_1 + id_2$, or the staggered or uniform character of the spontaneously condensed RVB flux can be determined accurately only after studying the Gutzwiller projected mean-field wave functions.*

Triplet superconductivity is also a distinct possibility as there is a latent ferromagnetic tendency, arising from the dynamics of dopant charges. We will not go into the details of this. All the above possibilities are summarized in a schematic phase diagram in Fig. 6.

As far as the scale of superconducting T_c is concerned, because of the small value of J, in our estimates we do not get T_c's far exceeding 30 K. We hope to present our quantitative analysis for the various phases discussed above in a future publication.

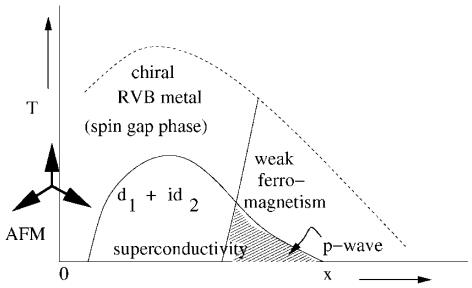

FIG. 6. The schematic $x - T$ phase diagram.

We conclude by stating that CoO_2 based metals seem to be a new class of strongly correlated systems that may stabilize novel resonating valence bond states, which was not realized in cuprates.

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