An Electronic Model for CoO_2 layer based systems: Chiral RVB metal and Superconductivity

G. Baskaran
The Institute of Mathematical Sciences
C.I.T. Campus, Chennai 600 113, India

Takada et al. have reported superconductivity in layered $Na_xCoO_2.yH_2O$ ($T_c \approx 5\ K$) and more recently Wen et al. in $A_xCoO_{2+\delta}$ ($A = Na, K$)($T_c \approx 31\ K$). We model a reference neutral CoO_2 layer as an orbitally non-degenerate spin-$\frac{1}{2}$ antiferromagnetic Mott insulator on a triangular lattice and $Na_xCoO_2.yH_2O$ and $A_xCoO_{2+\delta}$ 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 leads to a d-wave superconducting state. A chiral RVB metal, a PT violating state with condensed RVB gauge fields, with a possible weak ferromagnetism and low temperature p-wave superconductivity are also suggested at higher dopings.

Recent discovery of superconductivity in $Na_xCoO_2.yH_2O$ ($T_c \approx 5K$) by Takada and collaborators [1] marks a milestone in the search for new layered transition metal oxide superconductors. Following heels Wen et al. [2] have reported superconductivity in $A_xCoO_{2+\delta}$ ($A = Na, K$) with a high $T_c \approx 31\ K$. In the same family of planar CoO_2 based metals weak ferromagnetism [3] and high temperature curie susceptibility have been observed. $Na_{0.5}CoO_2$ has been shown [4] 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 non degenerate spin-$\frac{1}{2}$ antiferromagnetic Mott insulator on a triangular lattice. Consequently $Na_xCoO_2.yH_2O$ is described as an electron doped Mott insulator by a t-J model. We have performed an 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) PT violating d and p-wave superconductivity at low temperatures.

$Na_xCoO_2.yH_2O$ ($x \approx 0.35$ 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 inCdI_2. It is a triangular net of edge sharing oxygen octahedra(figure 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 Z-axis. The trigonal stretch makes the $O-Co-O$ angle $\approx 98^0$. A simple way to understand this structure is to imagine a triangular lattice on the XY plane with sub lattices A, B and C. Fill A and C sublattices with oxygen atoms and B sub lattice with Co atoms. Displace sublattice A and C layers on opposite directions along Z-axis by a same amount $\frac{z_0}{2}$. When $z_0 > \sqrt{\frac{3}{2}}a$ 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.

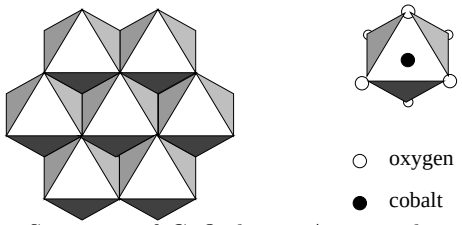

FIG. 1. Structure of CoO_2 layer. A triangular network of edge sharing oxygen octahedra. Co atoms are at the center of the oxygen octahedra.

Strong electron affinity of oxygen should lead to a complete electron transfer from Na atoms of $Na_x.yH_2O$ layers in $Na_xCoO_2.yH_2O$ and Na or K layers in $A_xCoO_{2+\delta}$, resulting in electron doped CoO_2 layers.

Experimentally $Na_{0.5}CoO_2$ is a strongly anisotropic [5] metal. The ab-plane resistivity is rather low with $\rho \sim 10\mu\Omega$ at low temperatures and $\rho \sim 200\mu\Omega$ at $300K$. C-axis resistivity is high indicating some kind of confinement of charges, similar to the planar cuprates, at temperatures above $\sim 200K$. It is also interesting that such a good metal exhibits [5] Curie-Weiss $\chi \sim \frac{C}{T-\Theta}$, rather than Pauli susceptibility at high temperatures; and $\Theta \approx -118K$. For $Na_{0.75}CoO_2$ weak ferromagnetism has been observed [3] below about $22K$. In another CoO_2 layered compound called misfit layer compound, weak ferromagnetism has been reported [3] below $3.5K$. As mentioned earlier, two groups have reported [1,2] superconductivity.

In a neutral reference CoO_2 layer the nominal valence of Co atom is Co^{4+}; i.e. a $3d^5$ ion. In an octahedral environment the 3d levels are split (figure 2); The trigonal

distortion of the oxygen octahedra causes further splitting of the 3d levels. The lower three fold degenerate t_{2g} levels are split into a non-degenerate d_{z^2} state with a doublet below, denoted as $e_g(t_{2g})$ in figure 2. The ground state configuration is an orbitally non-degenerate 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 non-degenerate 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 non-degenerate 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 non-degenerate spin singlet. Our simple quantum chemical picture is supported by various experiments including Co NMR study [5] 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.

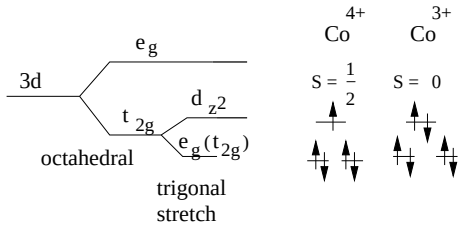

FIG. 2. Crystal field split 3d levels of cobalt.

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 super exchange interaction between neighboring magnetic Co^{4+}ions. As the super exchange paths are not 180^0 paths, the antiferromagnetic coupling will be reduced in strength. We make an estimate of the super exchange constant and parameters for our tight binding model using the electronic structure calculation of Singh [6] for $Na_{0.5}CoO_2$. Singh finds an electron like Fermi surface, shown in figure 3. The states close to the Fermi level arise predominantly from the cobalt $3d_{z^2}$ orbitals; our quantum chemical arguments are in agreement with Singh's result. 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 $Na_x.yH_20$ layers. As a first approximation we ignore the small electron like pockets found by Singh. It is likely that electron correlation will push these minority bands away from the Fermi level.

$Na_{0.5}CoO_2$ contains 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:

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

We can estimate the value of the hopping parameter t by fitting to Singh's result. We get a value of $t \approx -0.1$, corresponding to a band width of $\approx 1.0\ eV$. It is important to note that it is the negative sign of the hopping parameter that makes the Fermi surface electron like for our $\frac{3}{4}$ filled band. If t were negative we would have got hole like Fermi surfaces. In view of the strong particle hole asymmetry in a triangular lattice the sign of t is important.

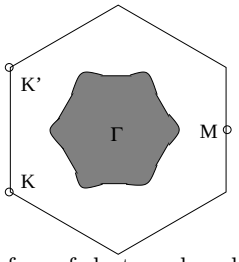

FIG. 3. Fermi surface of electron doped CoO_2 layer, as calculated by Singh for $Na_{0.5}CoO_2$, ignoring small Fermi surface pockets.

Since coulomb interaction in the effective $3d_{z^2}$ orbital is ~ 5 to $7\ eV$, the net super exchange 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 3 nearest neighbor Co^{4+} ion for a given Co^{4+} ion. These considerations lead us to a t-J model for the electron doped CoO_2 layer:

$$H_{\rm tJ} = -t\sum_{\langle ij\rangle} C^\dagger_{i\sigma}C_{j\sigma} + h.c. + J\sum_{\langle ij\rangle}(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{1}{4}n_in_j)$$

with the local constraint $n_{i\uparrow} + n_{i\downarrow} \neq 0$.

Existence of superconductivity in 2D t-J model in a square lattice is no more doubted, thanks to RVB theory [7–11] and related recent [12] variational and numerical efforts. The singlet proliferation tendency arising from the super exchange, 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, 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 and dominated by spin singlet correlation and chiral fluctuation. We study the undoped case first and discuss a simple RVB mean

field theory for 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. It becomes quantitative and accurate 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 cuprates 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 P & T symmetry; it has non-zero expectation value of spin chirality: $\langle \mathbf{S}_i \cdot (\mathbf{S}_j \times \mathbf{S}_k) \rangle \neq 0$. This state has 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 above work established the possibility of a chiral RVB state with a spin gap that also has a manifest quantum number fractionization through the existence of a well defined spinon excitation, that 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 [18,20] 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 mode:

$$H_{\rm tJ} = -t \sum_{\langle ij \rangle} s^\dagger_{i\sigma} s_{j\sigma} + H.c. - J \sum_{\langle ij \rangle} s^\dagger_{i\sigma} s_{j\sigma} s^\dagger_{j\sigma'} s_{i\sigma'} \quad (2)$$

with the local constraint, $d^\dagger_i d_i + \sum_\sigma s^\dagger_{i\sigma} s_{i\sigma} = 1$. 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 Fang [19] have performed RVB mean field analysis for this case. We briefly review their results. The mean field Hamiltonian $H_{\rm mF} = -J \sum_{\langle ij \rangle} \chi_{ij} s^\dagger_{j\sigma} s_{i\sigma} + ..$ is obtained by the factorization $\tau_{ij}\tau_{ji} \rightarrow \chi_{ij}\tau_{ji}$ etc., where $\tau_{ij} \equiv \sum_\sigma s^\dagger_{i\sigma} s_{j\sigma}$. The RVB order parameter $\chi_{ij} \equiv |\chi_0| e^{i\theta_{ij}}$ with $\theta_{ij} \equiv \int_j^i \mathbf{A} \cdot d\mathbf{l}$. Here $\mathbf{A}$ is the spatial component of the RVB gauge field [9]. In the Lee-Feng mean field solution $\oint \mathbf{A} \cdot d\mathbf{l} = \pm \frac{\pi}{2}$ in every elementary triangle.

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

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

where $\alpha \approx 0.603\sqrt{3}$. The Chiral spin character of Lee-Feng solution is obtained through the Wen-Wilczek-Zee identity [20]

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

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 Zou and Laughlin [21].

The 120^0 3-sublattice AFM order with a two fold planar chirality degeneracy is to be viewed as obtained by condensing spinon pairs in 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 3-sublattice order. We also find that 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 can 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. Absence of a sharp phase transition into the spin gap phase in the $x - T$ plane for cuprates seems to indicate that in the metallic spin gap phase the RVB flux is pinned to the PT symmetric value π. In our case, as our reference chiral RVB state has a flux of $\frac{\pi}{2}$, a strongly PT violating value, we believe 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 (figure 4) remembering that our

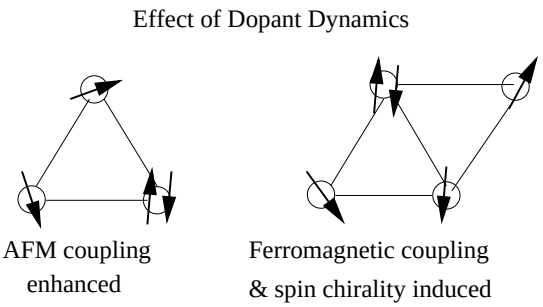

FIG. 4. Effective spin-spin coupling induced by Dopant dynamics

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 expect singlet stabilization for a range of small doping. However, as the doping increases a carrier performing a closed loop hopping in a four spin cluster (figure 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 $J_{\rm eff} \approx J + xt$, for large x (t is -ve). 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 $T_c \sim 3.5K$ to $22K$ seen in experiments.

Now let us discuss superconductivity. In the RVB mean field theory we write, following ref.8, the super exchange term as a BCS interaction, $J\sum_{\langle ij\rangle}(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}n_i n_j) \equiv -J\sum_{ij} b^\dagger_{ij} b_{ij}$ and perform the Bogoliubov-Hartree Fock factorization of the pairing term: $b^\dagger_{ij}b_{ij} \rightarrow b^\dagger_{ij}\Delta_{ij}$ + 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.

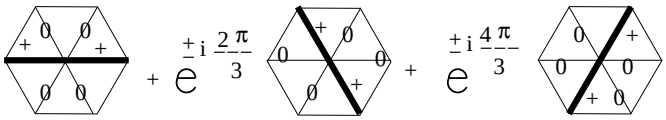

FIG. 5. Superconducting order parameter ($|\Delta_{ij}| \neq 0$ on dark bonds) and relative phases in PT violating $d_1 \pm id_2$ states.

Triangular lattice the symmetry leads to two degenerate d-states d_1 and d_2, in the RVB mean field theory. For small doping PT vilating combinations $d_1 \pm id_2$ have lower energies. The order parameter pattern for the PT violating d-wave states are shown in figure 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 latent ferromagnetic tendency, arising from the dynamics of the dopant charges. We will not go into the details of this. All the above possibilities are summarized in a schematic phase diagram in figure 6.

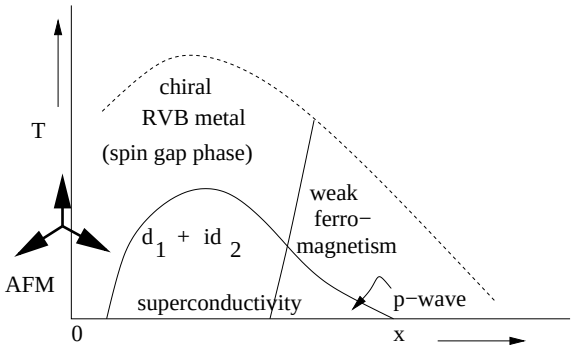

FIG. 6. The schematic $x - T$ phase diagram.

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 $30K$. We hope to present our quantitative analysis for the various phases discussed above in a future publication.

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

[1] K. Takada et al., Nature, **422** 53 (03)
[2] H.H. Wen et al., cond-mat/0303572
[3] I. Tsukuda et al., J. Phys. Soc. Japan, **70** 834 (01); T. Motohashi et al., Phys. Rev. **B 67** 064406 (03)
[4] I.Terasaki et al., Phys. Rev. **B 56** R 12685 (97)
[5] R. Ray et al., Phys. Rev. **B 59** 9454 (99)
[6] D. J. Singh, Phys. Rev. **B 61** 13397 (00)
[7] P.W. Anderson, Science, **235** 1196 (87)
[8] G. Baskaran, Z. Zou and P.W. Anderson, Sol. St. Commn, **63** 973 (87)
[9] G. Baskaran and P.W. Anderson, Phys. Rev. **B 37** 580 (88); G. Baskaran, Physica Scripta **T27** 53 (89)
[10] S.A. Kivelson, D. Rokhsar and J. Sethna, Phys. Rev. **B 35** 8865 (87)
[11] I. Affleck and B. Marston, Phys. Rev. **37** 3774 (88); G. Kotliar, Phys. Rev. **B 37** 3664 (88)
[12] A. Paramekanti et al. Phys. Rev. Lett., **87** 217002 (02); S. Sorella et al., Phys. Rev. Lett., **88** 117002 (02)
[13] G. Baskaran, Phys. Rev. **B 64** 092508 (01)
[14] M. Vojta and E. Dagotto, Phys. Rev. **B 59** R713 (99)
[15] H. Kino and K. Kontani, J. Phys. Soc. Jpn. **67** 3691 (98) H. Kondo and T. Moriya, J. Phys. Soc. Jpn. **67** 3695 (98); J. Schmalian, Phys. Rev. Lett., **81** 4232 (98);
[16] P.W. Anderson, Mat. Res. Bull. **8** 153 (73)
[17] V. Kalmayer and R. B. Laughlin, Phys. Rev. Lett., **59** 2095 (87)
[18] R. B. Laughlin, Phys. Rev. Lett., **60** 2677 (88)
[19] T.K. Lee, Shiping Feng, Phys. Rev. **B 41** 11110 (90)
[20] X.G. Wen, F. Wilczek and A. Zee, Phys. Rev. **B 39** 11413 (89); P.B. Wiegmann, Phys. Rev. Lett., **65** 2070 (90)
[21] R. B. Laughlin and Z. Zou, Phys. Rev., **B 41** 664 (90)
[22] P.W. Anderson, cond-mat/0108522