Possible spin triplet superconductivity in Na$_x$CoO$_2$·$y$H$_2$O

Akihiro Tanaka and Xiao Hu

Computational Materials Science Center, National Institute for Materials Science, Tsukuba 305-0047, Japan
(April 17, 2003)

Combining symmetry based considerations with inputs from available experimental results, we make the case that a novel spin-triplet superconductivity triggered by antiferromagnetic fluctuations may be realized in the newly discovered layered cobaltide Na$_x$CoO$_2$·$y$H$_2$O. In the proposed picture, unaccessible via resonating-valence-bond physics extrapolated from half-filling, the pairing process is similar to that advanced for Sr$_2$RuO$_4$, but enjoys a further advantage coming from the hexagonal structure of the Fermi-surface which gives a stronger pairing tendency.

Anderson’s suggestion that a doped antiferromagnet on a 2d square lattice be best described in terms of resonating valence bond (RVB) states [1], set the direction for a huge subsequent effort pursuing this picture in an attempt to understand superconductivity in the cuprate oxide compounds. While this has lead to the development of new avenues in the physics of low dimensional condensed matters, conclusive evidence of such novel states has not turned up. Meanwhile, renewed interests in RVB physics in systems on triangular lattices (TL) have been emerging recently - though the S=1/2 antiferromagnetic (AF) Heisenberg model on a TL is generally regarded as having a ground state with long range order, closely related systems such as the undoped quantum dimer model [2] and the $t$ – $J$ model on a TL with the hopping sign $t > 0$ [3] have been shown to exhibit a certain amount of stability of RVB-like states.

The discovery by Takada et al of superconductivity in Na$_x$CoO$_2$·$y$H$_2$O ($x \approx 0.35, y \approx 1.3$) [4], a system made of stacked layers of cobalt ions sitting on a 2d TL and surrounded by octahedrally displaced oxygen atoms will no doubt spark new interest in this line of investigation. Superconductivity was achieved at $T_c=5K$ by oxidation of the sodium ions (changing the effective charge density) followed by intercalation of the Co$_2$ layers in the mother compound NaCoO$_2$ with H$_2$O, thus effectively enhancing the two dimensionality of the system. Guided by analogy with the cuprates, the authors of ref [4] were lead to suggest that this system maybe understood in terms of doped AFs on TLs, which may well be related to RVB states.

As much as such directions are tempting, one must proceed with due caution since the experimental situation is rather complex. As discussed shortly, the system is actually away from the vicinity of half-filling, the regime where RVB physics is considered to be valid. It is reasonable then to resort to generic methods no more specialized than a combination of symmetry analysis and simple “fermiology”, reinforced by experimental inputs. While experiments conducted on Na$_x$CoO$_2$·$y$H$_2$O are at present basically limited to resistivity and preliminary susceptibility data, we have noticed that several conclusions -which are in fact remote from what an RVB-based investigation would lead to- can already be drawn. We therefore believe it useful at this stage to raise notice on this point with the hope of motivating further activity. The seminal work of Rice and Sigrist, who adopted a similar approach in the case of Sr$_2$RuO$_4$ [5], had played an instrumental role in the subsequent identification of the triplet superconductivity in that compound.

During the final stage of this work, we came across a preprint by Baskaran [6] addressing the same system. Although his reduction of the problem to a one-band model is similar, the discussion there is based on the RVB picture. The present work is founded on a complimentary approach as explained above. Deduction of effective theory

The first point to make is that the present system cannot be taken as a realization of the dilutely doped AF on a TL. The 3d cobalt ions in the parent compound NaCoO$_2$ with a formal valence of +3.5, are actually a mixture of the low-spin states $\text{Co}^{3+}(t_{2g}^6 e_g^0$ with $S=0)$ and $\text{Co}^{4+}(t_{2g}^5 e_g^0$ with $S=1/2)$. With no experimental indications of charge ordering in NaCoO$_2$, the most natural starting point for studying these systems is as a random mixture (1:1) of S=0 and S=1/2 states distributed on the TL. Hence instead of starting near half-filling, we must consider the case of three-quarter filling, which is a totally new situation. Superconductivity occurs after oxidation of the sodium ion so that the compound becomes Na$_{0.35}$CoO$_2$·$y$H$_2$O, in which case the system is approximately 1/3 filled. We therfore stress that RVB physics, presumably valid close to half-filling, by no means has a trivial extrapolation to this regime.

The next issue to consider is the magnetic properties of the system. The susceptibility [7] of NaCoO$_2$ contains a Curie-Weiss component with large negative Curie temperature $T_{\text{Curie}} \approx -285K$, a trend also confirmed in measurements on Na$_{0.35}$CoO$_2$·$y$H$_2$O, though with a reduced value of $T_{\text{Curie}} \approx -18.8K$ [8]. Taken together with the finding of spin density wave (SDW) like tendencies upon Co to Cu substitution in NaCoO$_2$ [9], it is natural to assume a fair amount of AF fluctuation to be present. LDA calculations show that the Fermi surface for NaCoO$_2$ sits near the top of the $a_{1g}$ like state, split off from the $t_{2g}$ manifold due to oxygen distortions.
These circumstances suggest a one-band Hubbard model \((U \approx 5-8eV, t \approx 1eV)\) on a TL around quarter to third filling as the simplest model capturing the essential physics of this system. At this point one may already expect nontrivial pairing tendencies. For instance, there are perturbative studies that claim that triplet pairing is favored over singlet pairing \([11]\). With direct quantum Monte-Carlo methods unavailable due to severe negative signs, we proceed with the generic approach mentioned earlier.

### Symmetry considerations

Group theoretical studies, valid irrespective of the pairing mechanism, have played essential roles in classifying superconductivity in heavy fermions, organics, and e.g. the ruthenate compound \([12,13]\). For the present case, the relevant symmetry group is \(\mathcal{G} = D_{6h} \otimes U(1) \otimes T\), with \(D_{6h}\) the hexagonal group together with the inversion symmetry about the plane, \(U(1)\) the gauge symmetry broken by the onset of superconductivity, and \(T\) the time reversal symmetry. For \(Na_{0.35}CoO_2\cdot yH_2O\), magnetization measurements suggest the presence of a magnetic anisotropy \([8]\). Hence the absence of \(SU(2)\) from \(\mathcal{G}\). The irreducible representation for this situation can be classified into 12 classes, \(\Gamma_a^\pm, 1 \leq a \leq 6\), with (+-) standing for spin singlet (triplet) states. States with subscripts \(1 \leq a \leq 4\), and those with \(a = 5,6\) are 1d and 2d representations respectively. The conventional point of view \([14]\) that AF fluctuations are most compatible with singlet pairing will lead us to one of these (+) representations.

A more intriguing possibility however is the case of triplet pairing. Not easily accessed from RVB treatments which deal primarily with spin singlets and their fluctuations, it is perhaps worthwhile to highlight their exotic properties. Later on we will mention that experiments so far seem to spell out such a state as the one most probable, and a novel scenario from which we recover this pairing choice will be described. As mentioned there, we will be interested in states with the d-vector perpendicular to the cobalt plane, i.e. \(\vec{d}/\hat{z}\), which ensures that the electron spins contributing to the wavefunctions have a vanishing \(z\)-component. It turns out that the \(\Gamma_5^-\) representation realizes such states. The fourth order terms in GL theory for representations \(\Gamma_5^\pm\) are

\[
\mathcal{F} = \int d\vec{r}[K_1|D_x\eta_1 + D_y\eta_2|^2 + K_2|D_x\eta_2 - D_y\eta_1|^2 + K_3 (|D_x\eta_1 - D_y\eta_2|^2 + |D_x\eta_2 + D_y\eta_1|^2)]
\]

where \(D_{\mu} = \partial_{\mu} - 2ieA_{\mu}\) the covariant derivatives. All z-derivatives are omitted on account of the two-dimensionality. Adapting a method due to Furusaki et al \([15]\) who discussed the tetragonal case \((D_{4h})\), we find that the terms in the GL Lagrangian density coupling linearly to the electric field \(\vec{E}\) read

\[
\mathcal{L}_E = c_1(E_x\eta_1^* + E_y\eta_2^*)(D_x\eta_1 + D_y\eta_2) + c.c.
\]

\[
+ c_2(E_x\eta_2^* - E_y\eta_1^*)(D_x\eta_2 + D_y\eta_1) + c.c.
\]

\[
+ c_3\{(E_x\eta_1^* - E_y\eta_2^*)(D_x\eta_1 - D_y\eta_2)
\]

\[
+ (E_x\eta_2^* + E_y\eta_1^*)(D_x\eta_2 + D_y\eta_1) + c.c.\}
\]

where the coefficients \(c_j \ (1 \leq j \leq 3\) are proportional to the \(K_j\)'s in the free energy. From these one extracts the following contribution;

\[
\mathcal{L}_{CS-like} = i(c_3 - c_1 - c_2)(\eta_1^* \eta_2 - \eta_2^* \eta_1)
\]

\[
\times (A_y \partial_y A_0 - A_z \partial_z A_0),
\]

which is of the Chern-Simons (CS) form. Several consequences follow, which are basically similar to what has been discussed in the context of \(SrRu_2O_4\). First, a zero field Hall effect is expected, due to a spontaneous (orbital) magnetization \(\vec{d} \cdot (\vec{k} \times \nabla_{\vec{k}}) \vec{d} \propto \vec{n} \times \vec{n}\), where \(\vec{n} \equiv (\eta_1, \eta_2)\). Furthermore one sees from the nonuniversality of the coefficient of the CS term that the Hall conductivity \(\sigma_{xy}\) is not quantized. The physical reason for the latter feature can be identified microscopically. (Readers are referred to refs. \([16,17]\) for the tetragonal case.) Inserting the d-vector \(\vec{d} = \Delta_1 f_1(\vec{k}) + i f_2(\vec{k})\hat{z}\), with \(f_1(\vec{k}) = 2 \sin(\frac{\pi}{2k_x})\cos(\frac{k_y}{2})\) and \(f_2(\vec{k}) = 2 \cos(-\frac{\pi}{2k_x})\sin(\frac{k_y}{2}) + 2i k_y\) into the Bogoliubov-de Gennes Hamiltonian

\[
H = \Psi^\dagger [\epsilon(\vec{k}) - \mu] \gamma_3 \otimes 1 + \gamma_1 \otimes i(\vec{d}(\vec{k}) \cdot \vec{r})\tau_2|\Psi,
\]

where \(\epsilon(\vec{k}) = -4 \cos(\frac{\pi}{2k_x})\cos(\frac{k_y}{2}) + 2 \cos(k_y)\) and performing a gradient expansion to one-loop order, one sees that the correction to the universal contribution \(\sigma_{xy} = e^2/4\pi\) comes from the normalization of the generating functional due to the Goldstone mode associated with the breaking of the gauge symmetry. This simply reflects the fact that the charge is not a well-defined quantum number in a BCS condensate \([17]\). On the other hand, the residual U(1) degree of freedom left of the SU(2) spin rotational symmetry suggests that the transport of \(S_z\) has universal features. This expectation is verified by gauging the system via the coupling to a spin-gauge field, from which one confirms that the spin Hall conductivity \(\sigma_{xy}^s\)
is quantised in integer multiples of $1/2\pi \hbar$. The integer factor is a topological invariant related to the chirality of the superconducting state, characterized in terms of the quantity $g = \langle \text{Re}d_z \tau_1, -\text{Im}d_z \tau_1, \epsilon \mathbf{1} \rangle$ as

$$N_{\text{chiral}} = \frac{\int d^2k}{(2\pi)^2} \text{tr} \left( \left[ \nabla_{k_x} g \times \nabla_{k_y} g \right] \right),$$

which is $+1$ for the present choice of d-vector (-1 for the opposite chirality). To complete the discussion on symmetries and exotic topological properties, we note that vortices obeying nonabelian statistics can be realized in this chiral p-wave state [18].

**Relation to experimental inputs**

We list the salient features of the inputs provided by experiments conducted so far [8].

1. The normal state resistivity as a function of temperature fits rather well to a $T^2$-dependence.

2. Preliminary NMR measurement of $T_1^{-1}$ at the cobalt site shows a prominent peak just below $T_c$, reminiscent of the Hebel-Schlichter peak for conventional s-wave superconductors.

3. Spins direct their moment in-plane under an applied magnetic field $\sim 8T$.

Deferring discussions on feature 3 for the moment, we focus on the first two. We take feature 1 to be an indication that the system lies in the weak coupling regime [5]. It then becomes plausible to interpret feature 2 in terms of a fully-gapped pairing state without nodes. Although this is usually considered a hallmark of s-wave pairing, it is worth recalling that the Balian-Werthamer state, with $d_{BW} = \Delta_0 \hat{k}$ has a sufficiently strong singularity of the density of states to exhibit a coherence peak as well. The chiral p-wave state (with the cylindrical Fermi surface) discussed above is the two-dimensional analogue of this situation. An in-plane measurement of the phase-sensitive thermal conductivity on single crystals, when they become available, is expected to give an isotropic result. (The absence of a peak in the case of Sr$_2$RuO$_4$, which had also been considered to be a chiral-p wave superconductor, is consistent with the existence of horizontal nodes related to interlayer pairing [19].) States such as $\vec{d} = p_x \hat{z}$ and $\vec{d} = p_y \hat{z}$, permissible on symmetry grounds, can be dismissed on bases of these observations. Alternative fully-gapped states include the singlet $d_{2-x^2-y^2} + id_{x^2-y^2}$ and $d_{x^2-y^2} + is$ states [6]. One can directly distinguish between singlet and triplet states by performing a Knight-shift measurement. For singlet pairings, the shift $K$ will drop to zero on approaching $T = 0$ for all magnetic field directions, with $K \approx Y(\vec{k}, T) \approx e^{-2\Delta_0}$, where $Y(\vec{k}, T)$ is the Yoshida function. Triples on the other hand will exhibit an anisotropic magnetic susceptibility in the superconducting state; an in-plane field $\vec{H} \perp \hat{z}$ will polarize both the Cooper pairs and the quasiparticles, so that $K / (T) = \text{const.}$ is expected, whereas the shift for $\vec{H} \parallel \hat{z}$ will lead to a behavior similar to the singlet case, $K_\perp \propto Y(\vec{k}, T)$. Remarkably, preliminary Knight shift measurements do show a temperature-independent behavior [8]. (A large $H_{c2} \sim 61 T$ [8] also is suggestive of triplet pairing.) These results, taken at face value single out the nodeless triplet pairing, of which the chiral-p state is the simplest.

**Possible scenario for triplet pairing in Na$_{0.35}$CoO$_2 \cdot y$H$_2$O**

According to LDA calculations [10], the central cylindrical Fermi surface of NaCo$_2$O$_4$, with dominant $a_{1g}$ character bears a shape close to a hexagon when viewed in the $k_z = \text{const.}$ plane. Hence there are three (approximate) nesting vectors, given by $\mathbf{Q}_i = \frac{1}{2} \Gamma K_i, i = 1, 2, 3$. Here we define the K-points as $K_i = C_6^{-1} \left( \frac{1}{3} \mathbf{G}_1 + \frac{1}{3} \mathbf{G}_2 \right)$, $G_1 = 2\pi \frac{b \times c}{a b c}$, $G_2 = 2\pi \frac{c \times a}{a b c}$, in which $a = (1, 0, 0), b = (-1/2, \sqrt{3}/2, 0), c = (0, 0, 1)$ are the primitive vectors of the layered TL. $C_6$ denotes the anticlockwise rotation about the z-axis by an angle of $\pi/6$. The presence of such nesting instabilities in the $\Gamma - K$ direction has been suggested by Terasaki et al [9] based on their observation of an order-from-disorder type emergence of a spin density wave (SDW) in Cu-substituted NaCo$_{1.8}$Cu$_{0.2}$O$_4$. We are assuming below that these qualitative Fermi surface features remain intact for Na$_{0.35}$CoO$_2 \cdot y$H$_2$O, which appears to be in accord with the observed Curie-Weiss contribution to the susceptibility.

Fermiology, the study of many-body effects with an emphasis on Fermi surface properties has been playing a central role in advancing our knowledge on superconductivity in various correlated electron systems [20]. One such scenario [21], which takes advantage of nesting tendencies and leading to triplet pairing, has been advanced for the tetragonal lattice case, with the aim of explaining the pairing in Sr$_2$RuO$_4$. We would like to point out that a very natural extension to the present TL case is possible. This argument starts by recasting of the linearized BCS gap equation at $T_c$ into the form, $T_c \propto e^{-\frac{\Delta(\mathbf{0})}{\sqrt{\phi(\mathbf{k})} \phi(\mathbf{k'})}}$, where we are following the notations of ref. [22]: $\langle \phi(\mathbf{k}) \phi(\mathbf{k'}) \rangle$ is the pairing interaction $V(\mathbf{k} - \mathbf{k'})$ averaged over the Fermi surface, i.e.

$$\langle \phi(\mathbf{k}) \phi(\mathbf{k'}) \rangle = \frac{\int_{FS} dk \int_{FS} dk' V(\mathbf{k} - \mathbf{k'}) \phi(\mathbf{k}) \phi(\mathbf{k'})}{\int_{FS} dk \int_{FS} dk' \phi(\mathbf{k}) \phi(\mathbf{k'})}.$$  

(7)

with $\phi(\mathbf{k})$ the $\mathbf{k}$-dependent part of the order parameter, i.e. $\Delta(\mathbf{k}) = \sqrt{\phi(\mathbf{k}) \phi(\mathbf{k})}$. We may view this as a sort of variational principle in which the actual pairing occurs for cases which yield a (1) positive and (2) large $\langle \phi(\mathbf{k}) \phi(\mathbf{k'}) \rangle$. In the present situation, where we are dealing with AF fluctuations, the pairing potential
\( V(Q_i) > 0 \). For this to lead to pairing requires that \( \phi(\vec{k})|\phi(\vec{k} + Q_i) < 0 \) for some \( i \). The simplest way to realize this is to introduce a nodal direction which coincides e.g. with the \( k_x \) axis, i.e. a \( p_y \)-pairing state. One immediately sees that this choice is highly beneficial as all three nesting vectors satisfy the required condition (see Fig. 1(a)), and therefore the entire Fermi surface is available for the pairing. (For this \( p_y \)-pairing, the \( Q_1 \)-channel should be the most dominant because it coincides with the direction in which the magnitude of the gap becomes maximal.) In this respect, the advantage of such node formation (vertical nodes on the central Fermi surface) is bigger than in the ruthenates where only one pair of nested segments is involved in the pairing. This state is degenerate (i.e. has the same \( T_c \)) with those in which the nodes are located at the intersections between the hexagon Fermi surface and the lines \( k_y = \pm \sqrt{3} k_x \) (Fig. 1(b) and (c)). Further gain in condensation energy is achieved by constructing a linear combination of these three states, with relative phases of \( \pi \) between (a) and (b), (c) will cancel the nodes, leading to a chiral p-wave state.

As will be discussed elsewhere, one can check that a similar construction cannot be made for an f-wave state. The appearance of the chiral p-wave state above relied on the Fermi surface geometry (reflecting the hexagonal symmetry), and the assumption of a nesting tendency. It is desirable that fine quality samples, amenable to detailed neutron scattering measurements be made in order to make a direct verification on this point possible. Further support for triplet pairing comes from the aforementioned magnetic anisotropy; when we interpret this in terms of an easy-axis along the c-axis, evaluation along the lines of ref. [22] can be used to demonstrate that the anisotropy ratio of the in-plane and longitudinal susceptibilities will directly enter into expressions for the triplet and singlet pairing potentials, and a sufficient anisotropy will eventually favor triplets (with \( \vec{d}|/\hat{z} \) ) over singlets.

We are indebted to H. Sakurai, K. Takada, T. Sasaki, M. Arai and E. Takayama-Muromachi for access to their results prior to publication, and for extensive discussions. We would also like to acknowledge K. Kindo, K. Yoshimura and their group for generously allowing us to mention their results on magnetization and NMR. The similarity of the present system with the ruthenates was pointed out to the authors by I. Terasaki. We have also meritted from discussions with T. Hikihara, T. Miyazaki, T. Sasaki, Y. Tateyama, K. Izawa, Y. Matsuda and J. Goryo.

[1] P. W. Anderson, Science 235 1196 (1987).
[2] R. Moessner and S. L. Sondhi, Phys. Rev. Lett. 86 1881 (2001).
[3] T. Koretsune and M. Ogata, Phys. Rev. Lett. 89 116401 (2002).
[4] K. Takada et al, Nature 422 53 (2003).
[5] T. M. Rice and M. Sigrist, J. Phys. Cond. Matt. 7 L643 (1995).
[6] G. Baskaran, cond-mat/0303649.
[7] Y. Ono et al, J. Solid State Chem. 166 177 (2002).
[8] H. Sakurai et al, unpublished; K. Yoshimura et al, unpublished.
[9] I. Terasaki et al, Phys. Rev. B 65 195106 (2002).
[10] D. J. Singh, Phys. Rev. B61 13397 (2000).
[11] Y. Nishikawa and K. Yamada, J. Phys. Soc. Jpn. 71 2630 (2002).
[12] M. Sigrist and K. Ueda, Rev. Mod. Phys. 63 239 (1991).
[13] V. P. Mineev and K. V. Samokhin, Introduction to Unconventional Superconductivity, Gordon and Breach Science Publishers, Amsterdam 1998.
[14] S. Nakajima, Prog. Theor. Phys. 50 1101 (1973).
[15] A. Furusaki et al, Phys. Rev. B 64 054514 (2001).
[16] J. Goryo and K. Ishikawa, Phys. Lett. A 260 294 (1999).
[17] T. Senthil, J. B. Marston and M. P. A. Fisher, Phys. Rev. B60 4245 (1999).
[18] D. A. Ivanov, Phys. Rev. Lett. 86 268 (2001).
[19] K. Izawa et al, Phys. Rev. Lett. 86 2653 (2001).
[20] D. A. Ivanov, Phys. Rev. Lett. 86 268 (2001).
[21] Kuroki et al, Phys. Rev. B 63 060506 (2001).
[22] T. Kuwabara and M. Ogata, Phys. Rev. Lett. 85 4586 (2000); M. Sato and M. Kohmoto, J. Phys. Soc. Jpn. 69 3505 (2000).