Possible Spin Triplet Superconductivity in $Na_xCoO_2 \cdot yH_2O$

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Symmetry-based considerations are combined with inputs from available experimental results to make the case that a novel spin-triplet superconductivity triggered by antiferromagnetic fluctuations may be realized in the newly discovered layered cobaltide $Na_xCoO_2 \cdot yH_2O$. In the proposed picture, inaccessible via resonating-valence-bond physics extrapolated from half-filling, the pairing process is similar to that advanced for Sr_2RuO_4, but enjoys a further advantage coming from the hexagonal structure of the Fermi surface which gives a stronger pairing tendency.

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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 led 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 interest in RVB physics in systems on *triangular* lattices (TL) has been emerging—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 are now known to exhibit a certain amount of stability of RVB-like states [3,4].

The discovery by Takada *et al.* of superconductivity at a T_c of 5 K in $Na_xCoO_2 \cdot yH_2O$ ($x \approx 0.35$, $y \approx 1.3$) [2], a system composed of stacked layers of cobalt ions residing on a 2D TL and surrounded by octahedrally displaced oxygen atoms has sparked new interest in this line of investigation. Guided by analogy with the cuprates, the authors of Ref. [2] were led to suggest that this system may be 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. Furthermore, the physical role played by the unfamiliar procedure of intercalating with H_2O is far from apparent, and incorporating its full effect into first principles calculations is formidable. It is reasonable then as a first step to resort to generic methods no more specialized than a combination of symmetry analysis and simple "fermiology," reinforced by experimental inputs. While experimental results on $Na_xCoO_2 \cdot yH_2O$ at the time of this writing are still very limited, we have noticed that several conclusions—which seem to be, 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, and of Baskaran, adopting a similar approach in the case of Sr_2RuO_4 [5], had been instrumental in the subsequent identification of the triplet superconductivity in that compound.

During the final stage of this work, we came across a work 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 complementary approach as explained above.

Deduction of effective theory.—The first point to make, in contrast to the original suggestions in Ref. [2], 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 $NaCo_2O_4$ with a formal valence of +3.5 are actually a mixture of the low-spin states Co^{3+} ($t_{2g}^6 e_g^0$ with $S = 0$) and Co^{4+} ($t_{2g}^5 e_g^0$ with $S = 1/2$). With no experimental indications of charge ordering in $NaCo_2O_4$, 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-quarters filling—a totally new situation. Superconductivity occurs after oxidation of the sodium ion so that the composition becomes $Na_{0.35}CoO_2 \cdot yH_2O$, in which case the system is approximately one-third filled. We therefore 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. The susceptibility [7] of $NaCo_2O_4$ contains a Curie-Weiss component with large negative Curie temperature $T_{\text{Curie}} \approx -285$ K, a trend also confirmed in measurements on $Na_{0.35}CoO_2 \cdot yH_2O$, though with a reduced value of $T_{\text{Curie}} \approx -18.8$ K [8]. Taken together with the finding of spin-density-wave-(SDW-)like tendencies upon Co to Cu substitution in $NaCo_2O_4$ [9], a fair amount of AF fluctuation may be assumed to be present, though neutron scattering experiments on single crystals would be

needed to gain further knowledge. Local density approximation (LDA) calculations show that the Fermi surface for $NaCo_2O_4$ sits near the top of the a_{1g}-like state, split off from the t_{2g} manifold due to oxygen distortions [10]. These circumstances suggest a one-band Hubbard model ($U \approx 5$–$8eV$, $t \approx 1eV$) on a TL about one-quarter to one-third filling as the simplest model capturing the essential physics of this system. At this point one may already anticipate nontrivial pairing tendencies. For instance, perturbative studies incorporating vertex corrections claim that triplets are favored over singlets [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 hexagonal case, the relevant symmetry group is $\mathcal{G} = D_{6h} \otimes \mathrm{U}(1) \otimes T$, where U(1) is the gauge symmetry broken by the onset of superconductivity, and T the time reversal symmetry. Magnetization measurements on $Na_{0.35}CoO_2 \cdot yH_2O$ infer the presence of strong magnetic anisotropies [8], and hence the absence of SU(2) from $\mathcal{G}$. The irreducible representation for this situation is classified into 12 classes, $\Gamma_a^{\pm}$, $1 \le a \le 6$, with $+$ ($-$) standing for spin singlet (triplet) states. States with subscripts $1 \le a \le 4$, and those with $a = 5$ and 6 are 1D and 2D representations, respectively. The conventional wisdom [14] stating 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. We mention later on that several experiments do seem to spell out such a state as being the one probable, and a novel scenario from which we recover this pairing choice will be described. There we will be interested in states with the d vector perpendicular to the cobalt plane, i.e., $\vec{d} \parallel \hat{z}$, which ensures that the electron spins contributing to the wave functions have a vanishing z component. It turns out that the Γ_5^- representation realizes such states. The fourth order terms of the Ginzburg Landau (GL) free energy,

$$\mathcal{F}_{\mathrm{quart}} = \int d^2\vec{r}[\beta_1(|\eta_1|^2 + |\eta_2|^2)^2 + \beta_2(\eta_1^*\eta_2 - \eta_1^*\eta_2)^2], \qquad (1)$$

where η_1 and η_2 are coefficients of the two basis functions $\hat{z}k_x$ and $\hat{z}k_y$, give rise to a T-violating state with $\vec{d} = \hat{z}(k_x + ik_y)$ when $\beta_2 > 0$. Group theoretically, this belongs to the magnetic superconducting class [13] $D_6(E) = \{e^{i\pi n/3}C_n, e^{i\pi n/3}TU_n\}$ ($0 \le n \le 5$), and the T violation is most dramatically manifested in electric/magnetic properties. A method due to Furusaki *et al.* [15] who discussed the tetragonal case D_{4h} can be adapted, to find that the terms in the GL Lagrangian density coupling linearly to the electric field $\vec{E}$ read

$$\mathcal{L}_E = c_1(E_x\eta_1^* + E_y\eta_2^*)(D_x\eta_1 + D_y\eta_2) + \mathrm{c.c.} + c_2(E_x\eta_2^* - E_y\eta_1^*)(D_x\eta_2 + D_y\eta_1) + \mathrm{c.c.} + c_3\{(E_x\eta_1^* - E_y\eta_2^*)(D_x\eta_1 - D_y\eta_2) + (E_x\eta_2^* + E_y\eta_1^*)(D_x\eta_2 + D_y\eta_1) + \mathrm{c.c.}\}, \qquad (2)$$

where the coefficients c_j ($1 \le j \le 3$) are each proportional to the K_j's appearing in the gradient terms of the GL free energy for $\Gamma_5^{\pm}$ which may be found in Ref. [10]. From these one extracts the following contribution:

$$\mathcal{L}_{\text{CS-like}} = i(c_3 - c_1 - c_2)(\eta_1^*\eta_2 - \eta_2^*\eta_1)(A_y\partial_x A_0 - A_x\partial_y A_0), \qquad (3)$$

which is of the Chern-Simons (CS) form. Several consequences, basically similar to what has been discussed in the $SrRu_2O_4$ context, follow. First, a zero field Hall effect is expected, due to a spontaneous (orbital) magnetization $\vec{d} \cdot (\vec{k} \times \nabla_{\vec{k}})\vec{d} \propto \vec{\eta}^* \times \vec{\eta}$, where $\vec{\eta} \equiv (\eta_1, \eta_2)$. One further sees from the nonuniversality of the coefficient of the CS term that the Hall conductivity σ_{xy} is not quantized. The physical origin of the latter feature can be identified microscopically (consult Refs. [14,15] for the tetragonal case) and reveals that it 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 universal transport features. This expectation is verified by gauging the system via the coupling to a spin-gauge field, from which one confirms the spin Hall conductivity σ_{xy}^s to be quantized 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 pseudospin matrix $\mathbf{g} = {}^t(\mathrm{Re}d_z\tau_1, -\mathrm{Im}d_z\tau_1, \epsilon\mathbf{1})$ as

$$N_{\mathrm{chiral}} = \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathrm{tr}(\mathbf{g} \cdot \nabla_{k_x}\mathbf{g} \times \nabla_{k_y}\mathbf{g})}{\mathrm{tr}|\mathbf{g}|^{3/2}}, \qquad (4)$$

which is $+1$ for the present choice of d vector (-1 for the opposite chirality).

Though strong-coupling approaches are not invoked below, we pause to note that the well-known Kalmeyer-Laughlin state [18] for the bosonic Hubbard model on a TL at filling $\nu = 1/2$ has a fermionic counterpart, the $\nu = 1/2$ Pfaffian state, which can continuously be deformed into the so-called {331} paired state realized at $\nu = 5/2$. The latter is precisely a chiral p-wave superconductor with $\vec{d} \parallel \hat{z}$ [19], obeying the CS physics mentioned above. Such deformation involves tuning the spin

anisotropy, and bears relations to the arguments given below which will be discussed elsewhere.

Relation to experimental inputs.—We list some 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) Some NMR measurements of T_1^{-1} at the cobalt site show a prominent peak just below T_c, reminiscent of the Hebel-Schlichter (HS) peak. (3) Spins direct their moment in-plane under an applied magnetic field $\sim$8 T. 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 perturbative Fermi-liquid regime [5]. It then becomes plausible to interpret feature (2) in terms of a fully gapped BCS pairing state without nodes. This is usually considered a hallmark of s-wave pairing. It is worth recalling though that the Balian-Werthamer state with $\vec{d}_{\rm BW} = \Delta_0 \vec{k}$, despite the absence of diverging coherence factor effects, still has a sufficiently strong singularity of the density of states to exhibit an HS peak as well. The fully gapped chiral p-wave state (with the cylindrical Fermi surface) discussed above, is the 2D analogue of this situation, and a numerical evaluation of a peak in a related situation may be found, e.g., in Ref. [18]. 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_2RuO_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 [21].) States such as $\vec{d} = p_x \hat{z}$ and $\vec{d} = p_y \hat{z}$, permissible on symmetry grounds, can be dismissed on the bases of these observations. Alternative fully gapped states include the singlet $d_{x^2-y^2} + id_{xy}$ 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 $K \propto Y(\vec{k}, T) \approx e^{-\Delta_0/T}$, where $Y(\vec{k}, T)$ is the Yoshida function. Triplets, 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 $\vec{H} \| \vec{z}$ will lead to a behavior similar to the singlet case, $K_\perp \propto Y(\vec{k}, T)$. Remarkably, Waki *et al.* report the preliminary Knight-shift measurements which show a temperature-independent behavior [8]. (A large $H_{c2} \sim$ 61 T [8] well exceeding the Pauli limit also is suggestive of triplet pairing.) These results, taken at face value, would single out the nodeless triplet pairing, of which the chiral-p state is the simplest.

Possible scenario for triplet pairing.—According to LDA calculations [10], the central cylindrical Fermi surface of $NaCo_2O_4$, 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 $\mathbf{Q}_i = \frac{4}{5}\Gamma K_i$, $i = 1, 2, 3$. Here we define the K points as $K_i = C_6^{i-1}(\frac{1}{3}\mathbf{G}_1 + \frac{1}{3}\mathbf{G}_2)$, $\mathbf{G}_1 = 2\pi \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}$, $\mathbf{G}_2 = 2\pi \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}$, in which $\mathbf{a} = (1, 0, 0)$, $\mathbf{b} = (-1/2, \sqrt{3}/2, 0)$, $\mathbf{c} = (0, 0, 1)$ 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 Γ-K direction has been suggested by Terasaki *et al.* [9] based on their observation of an order-from-disorder-type emergence of a 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 $Na_{0.35}CoO_2 \cdot yH_2O$, which appears to be in accord with the observed Curie-Weiss contribution to the susceptibility.

Fermiology of correlated electrons, i.e., the study of many-body effects with an emphasis on Fermi-surface properties plays a central role in advancing our knowledge on superconductivity in various systems [22]. It is known to lead, e.g., to the qualitatively correct deduction of the nodal directions and a $d_{x^2-y^2}$-wave pairing in the cuprates near half-filling. (Applied to the TL, this argument may suggest f-wave tendencies.) Meanwhile, a new scenario [23], 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_2RuO_4. Here we point out that a very natural extension to the TL case is possible, which may have relevance to $Na_{0.35}CoO_2 \cdot yH_2O$ or related materials. This argument starts by a recasting of the linearized BCS gap equation at T_c into the form, $T_c \propto e^{-1/N(O)\langle\langle V_\phi\rangle\rangle_{FS}}$, where we are following the notations of Ref. [22]: $\langle\langle V_\phi\rangle\rangle_{FS}$ is the pairing interaction $V(\vec{k} - \vec{k}')$ averaged over the Fermi surface, i.e.,

$$\langle\langle V_\phi\rangle\rangle_{FS} = -\frac{\int_{FS} d\vec{k} \int_{FS} d\vec{k}' V_\phi(\vec{k} - \vec{k}')\phi(\vec{k})\phi(\vec{k}')}{[\int_{FS} d\vec{k}'] \int_{FS} d\vec{k} \phi^2(\vec{k})}, \quad (5)$$

with $\phi(\vec{k})$ the $\vec{k}$-dependent part of the order parameter, i.e., $\Delta(\vec{k}) = \Delta_0 \phi(\vec{k})$. 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 $\langle\langle V_\phi\rangle\rangle_{FS}$. In the present situation, where we are dealing with AF fluctuations, the pairing potential $V(\mathbf{Q}_i) > 0$. For this to lead to pairing requires that $\phi(\vec{k})\phi(\vec{k} + \mathbf{Q}_i) < 0$ 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 $\mathbf{Q}_1$ 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 vertical node formation on the central Fermi surface is bigger than in the ruthenates where only

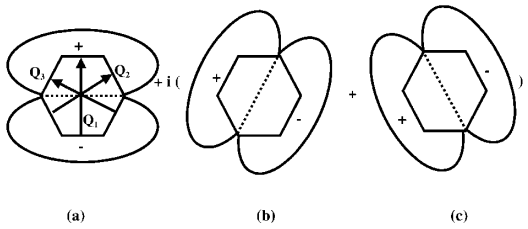

FIG. 1. Illustration of pairing via nesting of Fermi surface segments. (a) Node located at $p_y = 0$, corresponding to p_y pairing. (b) and (c) denote the case where the nodal directions are rotated by 60° and 120°, respectively. Superposition of the three states, with relative phases of $\frac{\pi}{2}$ between (a) and (b), (c) will cancel the nodes, leading to a chiral p-wave state with enhanced condensation energy.

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 $k_y = \pm\sqrt{3}k_x$ [Figs. 1(b) and 1(c)]. Further gain in condensation energy is achieved by constructing a linear combination of these three states in such a way that the nodes will cancel one other, opening a full gap at all points on the Fermi surface. This becomes possible through the construction

$$\phi(\vec{k})_{p_y+ip_x} \propto \phi_{p_y}(\vec{k}) + i[\phi_{p_y}(C_6\vec{k}) + \phi_{p_y}(C_6^2\vec{k})]. \quad (6)$$

One can check that a similar construction cannot be made for an f-wave state. (A d-wave pairing also fails to take full advantage of the considered Fermi-surface geometry.) The magnetic anisotropy mentioned earlier also plays a role in this scenario; evaluation along the lines of Ref. [22] reveal that the anisotropy ratio of the in-plane and longitudinal susceptibilities, $\alpha = \chi_{\pm}(q)/\chi_{zz}(q)$, will directly enter into expressions for the triplet (V_t) (with $\vec{d} \parallel \hat{z}$) and singlet ($V_s$) pairing potentials, $V_t = \frac{1}{2}V^{zz}_{\rm spin} - V^{\pm}_{\rm spin}$ and $V_s = \frac{1}{2}V^{zz}_{\rm spin} + V^{\pm}_{\rm spin}$, where we are omitting a weak charge channel contribution. The longitudinal part $V^{zz}_{\rm spin}$ will dominate over the transverse portion $V^{\pm}_{\rm spin}$ as α decreases, and the triplet channel will begin to have a magnitude comparable to that of the competing singlet channel [24]. The above nesting argument will then lead to the triplet pairing.

The appearance here of the chiral p-wave state relies on the Fermi-surface geometry (reflecting the hexagonal symmetry), and the assumption of a nesting tendency. Such scenarios in $Na_{0.35}CoO_2 \cdot yH_2O$ or related materials must await verification by detailed neutron scattering measurements made on high quality samples. Nevertheless, the findings of Ref. [2] have revealed that new physics lie ahead within the still largely unexplored domain of electrons on TLs, of which we consider the present work to be one.

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Note added.—We have been informed after posting this work on the e-print archive that Wang *et al.* [25] also find support for the absence of singlet pairing in the highly electron doped t-J model.

[1] P.W. Anderson, Science **235**, 1196 (1987).
[2] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
[3] R. Moessner and S. L. Sondhi, Phys. Rev. Lett. **86**, 1881 (2001).
[4] T. Koretsune and M. Ogata, Phys. Rev. Lett. **89**, 116401 (2002).
[5] T. M. Rice and M. Sigrist, J. Phys. Condens. Matter **7**, L643 (1995); G. Baskaran, Physica (Amsterdam) **223–224B**, 490 (1996).
[6] G. Baskaran, Phys. Rev. Lett. **91**, 097003 (2003). Brief mention of a possible triplet pairing is also made in this Letter.
[7] Y. Ono *et al.*, J. Solid State Chem. **166**, 177 (2002).
[8] H. Sakurai *et al.*, Phys. Rev. B **68**, 132507 (2003); T. Waki *et al.*, cond-mat/0306036; H. Sakurai (unpublished).
[9] I. Terasaki *et al.*, Phys. Rev. B **65**, 195106 (2002).
[10] D. J. Singh, Phys. Rev. B **61**, 13 397 (2000).
[11] Y. Nisikawa 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. B **60**, 4245 (1999).
[18] V. Kalmeyer and R. Laughlin, Phys. Rev. Lett. **59**, 2095 (1987).
[19] T.- L. Ho, Phys. Rev. Lett. **75**, 1186 (1995).
[20] Y. Hasegawa and H. Fukuyama, J. Phys. Soc. Jpn. **56**, 2619 (1987).
[21] K. Izawa *et al.*, Phys. Rev. Lett. **86**, 2653 (2001).
[22] For a review, see H. Aoki, in *Recent Progress in Many-Body Theories*, edited by R. F. Bishop *et al.* (World Scientific, Singapore, 2002).
[23] K. Kuroki *et al.*, Phys. Rev. B **63**, 060506 (2001).
[24] T. Kuwabara and M. Ogata, Phys. Rev. Lett. **85**, 4586 (2000); M. Sato and M. Kohmoto, J. Phys. Soc. Jpn. **69**, 3505 (2000).
[25] Q. Wang *et al.*, cond-mat/0304377.