A critical assessment of the pairing symmetry in \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \)

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We examine each of the symmetry-allowed pairing states of \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) and compare their properties to what is experimentally and theoretically established about the compound. In this way, we can eliminate the vast majority of states that are technologically allowed and narrow the field to two, both of \( f \)-wave type states. We discuss the expected features of these states and suggest experiments that can distinguish between them. We also discuss odd-frequency gap pairing and how it relates to available experimental evidence.

\( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) is a novel superconductor which, despite a relatively low superconducting temperature of only \( \sim 5\text{K} \), has recently attracted substantial experimental and theoretical interest. Much of the interest is driven by an as-of-yet unforeseen pairing state that is presumed to be highly unusual and possibly (as we will argue in this Letter, likely) even more unconventional than the \( d \)-wave superconductivity of the cuprates or \( p \)-wave superconductivity of the ruthenates. A survey of the current literature for \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) reveals that in the two years since its discovery, various groups have proposed \( s \)-wave, \( f \)-wave \( \mathbf{z}(x+iy) \), \( d \)-wave \( x^2 - y^2 + 2ixy \), and various versions of \( f \)-wave states, as well as an odd-frequency triplet state. To our knowledge, \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) holds the record for the greatest number of different superconducting symmetries proposed for one compound.

Synthesis of single crystal \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \) is difficult and polycrystalline samples often exhibit inhomogeneities in Na distribution and \( \text{H}_2\text{O} \) accumulation. The compound is furthermore chemically unstable at ambient temperature and humidity, making it difficult to handle and characterize. For these reasons, well-reproducible and reliable experimental results that could be expected to unravel the precise superconducting state have been slow to emerge. Still, there are several experimental facts that are rather well established, reproducible and which bear immediate relevance to the superconducting symmetry. Other facts that follow from confirmed knowledge about the crystal and electronic structure allow the exclusion of at least a few of the symmetry-allowed pairing states. An absence of knowledge about which states conform to symmetry requirements, which are excluded by experiment and which are physically unreasonable has frequently lead both theorists and experimentalists to concentrate on those pairing symmetries which are compatible with a specific data set or a specific theory of pairing to the detriment of a broader, consistent picture.

In this Letter, we list all the different symmetry representations that are compatible with a hexagonal crystal structure, according to the seminal work of Sigrist and Ueda. Based on what is currently known experimentally about \( \text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O} \), we discuss which states can be eliminated from consideration with a reasonable degree of confidence. We will show that surprisingly few candidates survive this scrutiny, and that all of these are highly unconventional and, in a sense, more exotic than either the high-\( T_c \) cuprates or the \( p \)-wave ruthenates. The list of allowed symmetries is up to \( L=3 \) (i.e. up to the \( f \)-states) is given in Table I.

There are 25 states in this table, excluding the last one which will be discussed separately later. We will show that all but two of them are incompatible with the

| TABLE I: Symmetry-allowed pairing states for hexagonal symmetry | 2D | DOS | \( \mu \text{SR} \) |
|---|---|---|---|
| 1 | \( x \) | Y | N | Y | s |
| 2 | \( y \) | Y | N | Y | s |
| 3 | \( z \) | Y | Y | Y | s |
| 4 | \( x \) | Y | Y | Y | s |
| 5 | \( y \) | Y | Y | Y | s |
| 6 | \( (x+iy) \) | Y | N | N | p |
| 7 | \( z \) | N | Y | Y | p |
| 8 | \( y \) | N | Y | Y | p |
| 9 | \( x \) | N | N | N | p |
| 10 | \( y \) | N | N | N | p |
| 11 | \( x \) | N | N | N | p |
| 12 | \( y \) | Y | N | N | p |
| 13 | \( x \) | N | N | N | p |
| 14 | \( y \) | Y | N | N | p |
| 15 | \( z \) | N | Y | Y | p |
| 16 | \( (x+iy)^2 \) | Y | Y | Y | d |
| 17 | \( xy \) | Y | Y | Y | d |
| 18 | \( (x+iy)^2 \) | Y | N | N | d |
| 19 | \( xz \) | N | Y | Y | d |
| 20 | \( yz \) | N | Y | Y | d |
| 21 | \( x \) | N | N | N | d |
| 22 | \( y \) | Y | Y | Y | f |
| 23 | \( z \) | Y | Y | Y | f |
| 24 | \( x \) | N | Y | Y | f |
| 25 | \( y \) | N | Y | Y | f |
| 26 | \( s \) | Y | Y | Y | s |

(a) These states are excluded because of their proximity to a fully-gapped state. In Table III of Ref. 12 this state is printed with a typo, which is corrected here. In Table VI of Ref. 12 this state is printed with a typo, which is corrected here.
Experimental data.

First, we decide which facts are to be considered as firmly established. Some potentially very important probes, such as the temperature dependence of the Knight shift, are still controversial in the sense that different authors report contradictory results. We have therefore singled out three pieces of evidence on which all or practically all publications agree. These are:

**Two-dimensionality.** Electronic structure calculations for the hydrated compound show an anisotropy in the Fermi velocity of at least an order of magnitude, which is supported by an experimentally measured resistive anisotropy of $10^3 - 10^4$, corresponding to a Fermi velocity anisotropy of 30 to 100 (the resistivity anisotropy of the unhydrated, high Na content compound, Na$_{0.75}$CoO$_2$, which should be substantially lower than that of Na$_{0.3}$CoO$_2$·$y$H$_2$O, was found to be as high as 500), indicating that the transport along $c$ is probably incoherent. This is firm evidence that the electronic structure is very strongly 2D.

As found experimentally and explained theoretically, the magnetic anisotropy of the unhydrated high-Na compound is very small, primarily because each Co couple with 7 Co atoms in neighboring layers. While there are no data on the magnetic coupling at $x = 0.3$, nor for the hydrated compound, one can estimate the reduction in magnetic coupling from the ratio of the squared Fermi velocities, which is about 20. Thus in the hydrated compound, magnetic interaction should also be 2D.

Finally, in an interesting difference from both the cuprates and ruthenates, the Co and O phonons should also be 2D in this system. Of course, water vibration need not be such, but the absence of the hydrogen isotope effect clearly indicates their irrelevance for the superconducting pairing.

Therefore, we conclude that the superconducting order parameter in Na$_{0.3}$CoO$_2$·$y$H$_2$O should be 2D.

Absence of superconductivity-induced spontaneous magnetic moments below $T_c$. Some of the superconducting states listed in Table II (#9,12) are nonunitary and have a spontaneous magnetization in the superconducting state. Others (#6,18,21) break the time-reversal symmetry for a Cooper pair by virtue of a nonzero pair orbital moment. In both cases, the resulting nonzero local magnetic moments are supposed to be detectable. Note that net magnetization is not present in the latter case, due to domain formation and internal Meissner screening, but crystallographic defects and grain or domain boundaries should still host nonzero local moments. One of the main arguments in favor of the axial $(x + iy)\hat{z}$ state in Sr$_2$RuO$_4$ is the fact that muon spectroscopy revealed the appearance of disordered static magnetic moments below $T_c$. The accepted interpretation of this finding is that the pairing symmetry has a nonzero orbital moment. Muon spin rotation experiments for Na$_{0.3}$CoO$_2$·$y$H$_2$O have been reported and no indications of static moments below $T_c$ have been found. To our knowledge, there are no other works reporting detection or non-detection of static magnetic moments in this compound. We nevertheless feel confident to include this fact in our compendium for two reasons: i) one of the reports comes from a group which has performed similar measurements on other superconductors and was previously able to detect local moments in PrOs$_4$(Sb$_7$)$_2$, and ii) this is a rare example of an experiment in which poor sample quality makes the effect more pronounced rather than obscuring it.

Therefore, we conclude that neither nonunitary nor $L \neq 0$ states are possible in Na$_{0.3}$CoO$_2$·$y$H$_2$O.

Absence of a finite superconducting gap. Several experimental groups have reported experiments indirectly probing the density of states (DOS) in the superconducting phase. Such experiments, primarily calorimetry, were instrumental in clarifying the symmetry of pairing in such novel superconductors as SrRuO$_4$ and MgB$_2$. These experiments measure the temperature dependence of either specific heat or relaxation rates (NMR, NQR, or $\mu$SR). In all work that we are aware of, the authors agree that the low temperature behavior of the DOS is not exponential. As of yet, no group has reported measurements at temperatures low enough to allow for a reasonably confident determination of the exact temperature dependence, but most authors suggest a $T^3$ (line nodes) behavior for $T > 2$ K and finite-DOS linear behavior at lower $T$.

These results exclude states with a fully developed sizeable gap on all Fermi surfaces.

Armed with these three facts, let us now test the 25 states listed above against them. First, we eliminate all states that have, by symmetry, strong $z$-dependence of the order parameter. These are the ten states #3, 7, 8, 9, 15, 19, 20, 21, 24, 25. Of the remaining 15 states, #1, 2, 10, 11, 12, 13, 14, and 18 have no symmetry restriction that would require them to have node lines or points. In general, there exists the possibility of accidental rather than symmetry-induced nodes, or regions with a finite but extremely small order parameter, similar to the so-called “extended s” state, earlier considered for superconducting cuprates. In the case of Na$_{0.3}$CoO$_2$·$y$H$_2$O, such accidental nodes seem highly unlikely due to its specific fermiology. The Fermi surface of Na$_{0.3}$CoO$_2$·$y$H$_2$O consists of one relatively small nearly circular cylinder, and, possibly (predicted by the theory, but not yet confirmed experimentally) six tiny pockets surrounding the first Fermi surface. Whether the latter actually exist or not, a pairing interaction that would be consistent with the hexagonal symmetry and at the same time enforce sign change of the order parameter on these small Fermi surfaces should itself change sign with a variation of the wave vector on the order of 0.2–0.25 of the Brillouin zone dimension. It is hardly possible to imagine a physically meaningful pairing interaction of this sort.

Finally, the $\mu$SR experiment allows us to exclude the non-unitary state #12. Note that several states that we have already excluded because they are allowed by sym-
We are left with the stabilization of the other states highly questionable. The same amplitude of the order parameter and makes full gap. This should lead to a considerable difference on the surface, the latter state has a node line on all three states belong to the same symmetry representation to second order in the order parameter, they are degenerate with each other and with state #6, \( x^2 - 3y^2 \)). Strong coupling effects, the spin-orbit interaction and other effects can, formally, tilt the energy balance in favor of these states, but only in the 4th order in the order parameter (the distinction between the states themselves appears only in the 6th order). However, all three states belong to the same symmetry representation and the first two have node lines, while (\#3 and \#4). Given the small size of these pockets, the \( s \) and \( s \) case above, \( s \) and \( s \) are also isotropic and thus do not have any additional disadvantage in terms of the pairing energy. The ground state in this case is defined either by the spin-orbit induced magnetic anisotropy (if the easy magnetization axis is in the plane, \( s \) is favored, otherwise \( s \)), or by the spin-orbit induced anisotropy of the pairing interaction.

Finally, we would like comment on the (still controversial) Knight shift experiments. The absence of a Knight shift decay below \( T_c \) has been taken as a decisive argument in favor of the \( (x \pm iy) \) state in \( Sr_2RuO_4 \). The \( f \) state that has emerged from our discussion also corresponds to Cooper pairs with spins in the \( xy \) plane and thus to a constant Knight shift. The same is true for the \( s \) state. On the other hand, \( s \) or \( s \) would show a reduced, though not exponentially reduced, Knight shift below \( T_c \). Of the states with an even frequency gap (\#1-25), the states which, formally, should not show a Knight shift reduction below \( T_c \) along some directions are \#4, 5, 6, 15, 22 and 23.

In conclusion, we have shown that, based on established experimental evidence and a knowledge of the electronic structure of \( Na_{0.3}CoO_2 \cdot yH_2O \), many superconducting states that are allowed by symmetry can be eliminated from consideration. Of those with an even-frequency gap, only the \( f \) states, \( x^2 - 3y^2 \) and \( y(y^2 - 3x^2) \) are fully compatible with what is known about this compound. The former has no line nodes along the \( e_y \) hole pockets and is therefore energetically favorable, given the existence of \( e_y \) states at the Fermi level. In terms of odd-frequency gap states, \( s \) and \( s \) and \( s \) are all consistent with experimental reports.

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