Orbital-singlet pairing and order parameter symmetry in Sr$_2$RuO$_4$

Ralph Werner

Institut für Theorie der Kondensierten Materie, Universität Karlsruhe, 76128 Karlsruhe, Germany

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Based on the degeneracy of the $d_{zx}$ and $d_{yz}$ orbitals in Sr$_2$RuO$_4$ it is argued that the Cooper pairs condense in orbital singlets. Together with the spin-triplet wave functions the real-space wave function then is symmetric. Considering interaction effects the order parameter is found to have $A_{1g}$ symmetry consistent with a number of experimental observations. The sensitivity of the material on non-magnetic impurities follows in a straightforward manner from the orbital-singlet configuration.

With the discovery of the high temperature superconductors a whole class of transition metal oxides became a focal point in condensed matter research. These materials exhibit many unconventional properties whose interpretation has so far generally proved controversial. An example that attracted a lot of attention is Sr$_2$RuO$_4$. Its normal state properties are Fermi liquid like in the temperature range $T_c < T < 30$ K but below $T_c \leq 1.5$ K the material is an unconventional superconductor since a number of experimental probes show that the paired electrons carry a magnetic moment. In spite of the large interest that the superconductivity in Sr$_2$RuO$_4$ has attracted an unambiguous understanding of the electronic correlations has not yet evolved.

Rice and Sigrist proposed that the superconducting order parameter has $p$-wave symmetry promoted by ferromagnetic correlations by analogy with $^3$He. This idea is supported by experiments that show that the static magnetic properties of Sr$_2$RuO$_4$ are the same in the normal and the superconducting phase. However, there is no conclusive experimental proof for the $p$-wave symmetry of the superconducting order parameter and no indications of ferromagnetic correlations have been found either in neutron scattering investigations or other approaches.

Furthermore, the specific heat, nuclear quadrupole resonance (NQR), and thermal conductivity are consistent with two-dimensional gapless fluctuations in the superconducting phase of Sr$_2$RuO$_4$, which are incompatible with the analogy to superfluid $^3$He. One possible scenario is the existence of line nodes similar to those in the superconducting cuprates. Since vertical line nodes have been ruled out by thermal conductivity measurements horizontal line nodes in the subsystem of the $d_{zx}$ and $d_{yz}$ electrons have been proposed. One weakness of the latter picture is that it requires the fine tuning of various interaction strengths, while no double gap structures have been observed in Andreev reflection spectroscopy data.

In this letter it is shown how the degeneracy of the Ru$^{4+}$ $d_{zx}$ and $d_{yz}$ orbitals allows for a straightforward description of the unconventional superconductivity in Sr$_2$RuO$_4$ that is consistent with the experimental observations. The possibility of mixed orbital pairing leading to $S = 1$ spin-triplet Cooper pairs through Hund’s rule coupling has been raised implicitly by Baskaran. The “active” $d_{zx}$ and $d_{yz}$ orbitals drive the superconducting instability because they have the larger inter-plane electronic overlap. This is supported by the recently implied increase of $T_c$ upon uniaxial pressure along the crystallographic c axis since the inter-plane coupling is increased. Such pairing is umklapp scattering enhanced by the body centered tetragonal lattice.

The results of the approach can be summarized as follows. The Cooper pairs form orbital singlets allowing for an even parity real-space wavefunction in spite of the spin-triplet configuration. Taking into account the relatively strong interaction effects in the system this allows for an almost homogeneous gap function, consistent with the experimental observations. Any impurity or defect locally breaks the symmetry of the $d_{zx}$ and $d_{yz}$ orbitals and thus acts as a pair breaker in strict analogy to magnetic impurities in a spin-singlet superconductor. The quadratic temperature dependence of the specific heat follows from fluctuations of the internal degrees of freedom of the order parameter. On the other hand, the pair correlations for the $d_{yz}$ electrons are induced by the interband proximity effect. Since this effect is usually strong a single gap is assumed leading to consistency with Andreev reflection experiments.

In the subspace of the degenerate $d_{zx}$ and $d_{yz}$ orbitals the possible order parameters can be classified in standard notation as orbital-singlet spin-triplet components

$$\langle P_{s,\mu}^{\uparrow} \rangle = \sum_{n,\sigma,\nu,\nu',\sigma'} \sigma_{n,\nu,\sigma}^\dagger \sigma_{n,\nu',\sigma'}^\dagger \langle c_{n,\nu,\sigma}^\dagger c_{n,\nu',\sigma'} \rangle$$

and orbital-triplet spin-singlet components

$$\langle P_{s,\mu}^{\dagger} \rangle = \sum_{n,\nu,\nu',\nu''} \sigma_{n,\nu,\sigma}^\dagger \sigma_{n,\nu',\sigma}^\dagger \sigma_{n,\nu'',\sigma}^\dagger \langle c_{n,\nu,\sigma}^\dagger c_{n,\nu',\sigma}^\dagger c_{n,\nu'',\sigma} \rangle.$$
orbital-singlet \( \lambda/J_\parallel \) is odd and the spin-triplet is even under electron permutation is \([31]\):

\[
H_{\parallel} \lambda/J_\parallel
\]

larger Hund’s rule coupling

Cooper pair condensate. Possible effects from spin-orbit

singlet states and thus form the ground state of the

triplet states are energetically favored over the spin-

Cooper pairs. Possible effects from spin-orbit coupling

on the real or Fourier space projection of the pair wave function

Eq. \([4]\). In the presence of Hund’s rule coupling the spin-

singlet superconductor. In the latter the magnetic impurities locally break spin-rotational invariance

impurities \([25]\) and crystal defects \([26]\), which can be understood by analogy to the effect of magnetic impurities in a spin-singlet superconductor. In the latter the magnetic impurities locally break spin-rotational invariance and thus act as pair breakers for spin-singlet Cooper pairs \([27]\). Similarly, any impurity—magnetic, non-magnetic, or crystal defect—locally breaks the rotational symmetry of the lattice and thus the symmetry between the \(d_{xz}\) and \(d_{yz}\) orbitals. Consequently impurities are pair breaking in the orbital-singlet superconductor described by Eq. \([2]\) in strict analogy to magnetic impurities in a spin-singlet superconductor. The resulting quantitative applicability of the theory of Abrikosov and Gor’kov to \(\text{Sr}_2\text{RuO}_4\) is impressively demonstrated in Refs. \([25,24]\).

As a next step it is necessary to study the superconducting gap function in order to interpret the numerous directionally dependent experimental probes. The gap function \(\Delta_k = (\Delta_{k,x}, \Delta_{k,y}, \Delta_{k,z})\) is given in the Fourier representation of Eq. \([1]\) with \(\langle P^{s\dagger}_k \rangle = \sum_k \Delta^*_k \) via

\[
\Delta^*_k = \sum_{\sigma,\sigma',\sigma''} \sum_{\nu,\nu',\nu''} \sigma^\mu_{\sigma,\sigma',\sigma''} \sigma^\nu_{\nu,\nu',\nu''} \langle \psi^\dagger_k,\nu,\sigma \psi_k,\nu',\sigma' \rangle.
\]

(4)

It is determined in principle by solving the Eliashberg equations

\[
\sum_k \Delta^*_k = -\frac{T}{V_{0,2}} \nabla_{\Delta_k} \ln \int \mathcal{D}[\phi_k] e^{-S_{\text{SG}}[\phi_k]}
\]

self-consistently. \(V_{0,2}\) is the effective pairing potential. The action \(S_{\text{SG}}[\phi_k]\) has been derived using the quasi one-dimensionality of the kinetic energy of the \(d_{xz}\) and \(d_{yz}\) electrons and includes the intermediate coupling on-site interaction non-perturbatively \([12]\). It depends on the four Bose fields, which can be considered as charge, flavor, spin and spin-flavor fields in analogy to the two-channel Kondo problem \([33]\), and includes mass generating terms in the superconducting state \([24]\). The treatment of such a four-component, two-dimensional sine-Gordon action is quite involved and is only possible using approximations.

However, to investigate the gap function in \(\text{Sr}_2\text{RuO}_4\) it is sufficient to apply qualitative physical arguments. Starting with the investigation of the wavefunction symmetry within the non-interacting, local picture and then analysing the expected influence of strong interactions it turns out that a rather homogenous gap function must be expected.

To establish the wavefunction symmetry in momentum space it is useful to write \([34]\)

\[
\exp(\ii kr) = 4\pi \sum_{lm} \frac{F_l(kr)}{kr} Y^*_l m (k/kr) \ii \nu Y_{l m}(r/kr),
\]

so that the angular components in real and Fourier space factorize. \(F_l(kr)\) is a regular spherical Bessel function and does not depend on the magnetization quantum number \(m\). Since the \(d_{xz}\) and \(d_{yz}\) orbitals are linear combinations of the orthogonal spherical harmonics \(Y_{2 \pm 1}\) the angular part of the pair wavefunction projection onto Fourier space, \(\langle k|\psi_s^\dagger \rangle\), has the same symmetry as in real space, i.e., \(d_{xz}(r/kr)d_{yz}(r/kr) = d_{xz}(k/kr)d_{yz}(k/kr)\) [Fig. \([1]\)]. Introducing the rotation operator \(R_{\pi/2} : k_x \rightarrow k_y, k_y \rightarrow -k_x\) one has

\[
R_{\pi/2} d_{xz}(k/kr) d_{yz}(k/kr) = -d_{xz}(k/kr) d_{yz}(k/kr),
\]

(7)

\[
R_{\pi/2} |x, y\rangle_s = -|x, y\rangle_s,
\]

(8)

and \(R_{\pi/2} |\uparrow, \downarrow\rangle_\mu = |\uparrow, \downarrow\rangle_\mu\). Consequently

\[
R_{\pi/2} \langle k|\psi_s^\dagger \rangle = \langle k|\psi_s^\dagger \rangle.
\]

(9)

In other words the wavefunction is even under a rotation of 90° since both angular and orbital-singlet contributions are odd under that rotation. We therefore expect the gap function to be of extended s-wave symmetry.
In a group theoretical context the six possible pairing states described by the pair operators in Eqs. (1) and (2) find their analogies in the possible pairing states of the tetragonal point group $D_{4h}$ [2]. Since the angular Fourier space part $d_{zx}(k/k)d_{yz}(k/k)$ has even parity and the pair wavefunction is invariant under rotation of $90^\circ$ the state with either $A_{1g}$ or $A_{2g}$ symmetry must be realized. It is useful to define the mirror operators $M_x : y \rightarrow -y$ and $M_y : x \rightarrow -x$ as well as $M_\pi : \vec{\pi} \rightarrow -\vec{\pi}$ and $M_\tau : \vec{\tau} \rightarrow -\vec{\tau}$ with $\vec{\pi} = (x+y)/\sqrt{2}$ and $\vec{\tau} = (x-y)/\sqrt{2}$. Note that $\vec{\pi}$ and $\vec{\tau}$ define a reference frame rotated by $\pi/4$. Applying these to $d_{zx}(k/k)d_{yz}(k/k)$ and $\langle x, y \rangle_s$ reveals the $A_{2g}$ symmetry of $\langle k|\psi^s_\mu\rangle$.

However, in the real system the symmetry of the gap function will be significantly altered by hybridization and—more importantly—interaction effects. Starting out by considering the non-interacting case the orbital-singlet superconducting instability can be formulated following BCS [23] and electrons with opposite momentum can only pair at the four points (small black dots in Fig. 2) of the Brillouin zone where the idealized, one-dimensional Fermi surfaces [36] of the $d_{zx}$ and $d_{yz}$ bands cross (dashed lines in Fig. 2). In a more realistic picture the $d_{zx}$ and $d_{yz}$ bands are weakly hybridized [34,35] and form the $\alpha$ and $\beta$ sheets of the Fermi surface (full lines in Fig. 2). It can be shown that then only the eight points on the $\alpha$ and $\beta$ sheets indicated by the larger dots in Fig. 2 contribute to the pair formation. Such a small phase space for the pairing is consistent with the $A_{2g}$ symmetry discussed above but would be inconsistent with the large specific heat anomaly at the superconducting phase transition [37].

That the neglect of the interaction clearly represents an unjustified oversimplification of Eq. (1) becomes obvious from the significance of the on-site interactions [22] for the observed [1,37] strong magnetic in-plane correlations. An estimate of how the interactions increase the pairing phase space is possible by noting that the dominant magnetic correlations can be described as gapless, quasi one-dimensional fluctuations at momentum transfer $q_i = (\pm 2k_F, \pm 2k_F)$ modulus a reciprocal lattice vector $G_i$. The arrows in Fig. 3(a) show the momentum transfer $q_1 = (2k_F, 2k_F)$ and three combinations with reciprocal lattice vectors $G_0 = (0, 2\pi)$, $G_1 = (2\pi, 2\pi)$, and $G_2 = (2\pi, 0)$ in units of the reciprocal lattice spacing $1/a$.

The back-scattering terms in the action of Eq. (3) couple magnetic and charge degrees of freedom [22]. The Cooper pairs can thus scatter elastically off the gapless magnetic excitations modulus any reciprocal lattice vector $G_i$, i.e., $\langle c_{-k,y,\sigma} c_{k,\pm q,\mp \sigma}^\dagger G_{i,y,\sigma} \rangle \neq 0$ as indicated by the black arrows in Fig. 3(b). The resulting momentum transfer allows for mixed orbital pairing on many points of the Fermi surfaces formed by the idealized one-dimensional $d_{zx}$ and $d_{yz}$ bands as indicated in Fig. 3(b) and (c). Including also higher order contributions allows for an even more homogeneous distribution of paired electrons across the Fermi surfaces as indicated for $(\pm 4k_F, \pm 4k_F)$ in Fig. 3(d).

This qualitative discussion shows that interactions can be held accountable for a rather homogeneous gap function in Sr$_2$RuO$_4$. Moreover, the action $\mathcal{S}_{SC}[\phi]$ in Eq. (3) as a function of the charge, flavor, spin, and spin-flavor Bose fields is manifestly invariant under the mirror operations $M_\nu$ [22]. The action including the interaction thus points towards a $A_{1g}$ symmetry of the gap function.
This results from the fact that the charge, flavor, spin, and spin-flavor fields are linear combinations of the fields of the $d_{x^2}$ and $d_{y^2}$ orbitals. The $A_{1g}$ symmetry is consistent with thermal conductivity measurements \cite{8} as well as with the geometry of the upper critical fields \cite{24}. Point contact experiments also do not reveal any significant in-plane anisotropy of the superconducting order parameter \cite{23}.

Finally, from the back-scattering terms in the action $S_{SC}[\phi]\|$ the existence of two degenerate superconducting saddle points leading to two degenerate order parameter components can be deduced \cite{23}. Each component has a two-fold symmetry axis. Indeed, the existence of such two order parameter components with a slight spatial anisotropy in Sr$_2$RuO$_4$ is implied by the existence of two upper critical fields \cite{24,39}. Comparison with the critical field measurements suggests \cite{10} that the components are 93\% isotropic. The two components are classified as flavor components $\Omega_{i,x}$ and $\Omega_{i,y}$ \cite{23}.

Since $\Omega_{i,x}$ and $\Omega_{i,y}$ are degenerate in the absence of fields breaking the $\frac{\pi}{2}$-rotational symmetry the system can fluctuate between the two components in the ordered phase giving rise to a Goldstone mode \cite{41}. This mode accounts for the gapless quasi two-dimensional excitations observed in the superconducting phase in various experiments \cite{15,10}. The presence of such a mode in the superconducting state finds support in the softening of the in-plane elastic constants recently observed in ultrasonic measurements \cite{22}.

In summary the notion of spin-triplet, orbital-singlet pairing in Sr$_2$RuO$_4$ leads to a straightforward physical picture that is consistent with fundamental experimental observations such as the sensitivity to impurities, the symmetry of the two upper critical fields and the fluctuations in the ordered phase. Unlike previous theories predicting $p$ wave symmetry the two-component order parameter can be considered as an extended $s$ wave with $A_{1g}$ symmetry and only slight anisotropy. The interactions play a crucial role in the in-plane correlations. Details of the non-perturbative approach and comparisons to experiments as well as the $p$-wave approach \cite{35} are given in Refs. \cite{23,10}.

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\begin{thebibliography}{36}
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[1] Y. Maeno et al., J. Phys. Soc. Jpn. 66, 1405 (1997).
[2] K. Ishida et al., Phys. Rev. Lett. 84, 5387 (2000).
[3] Y. Maeno, T. M. Rice, and M. Sigrist, Physics Today 54, 42 (2001).
[4] K. Ishida et al., Nature (London) 396, 658 (1998).
[5] G. M. Luke et al., Nature (London) 394, 558 (1998).
[6] J. A. Duffy et al., Phys. Rev. Lett. 85, 5412 (2000).
[7] T. M. Rice and M. Sigrist, J. Phys.: Condens. Matter 7, L643 (1995).
[8] F. Laube et al., Phys. Rev. Lett. 84, 1595 (2000).
[9] M. A. Tanatar et al., Phys. Rev. Lett. 86, 2649 (2001).
[10] K. Izawa et al., Phys. Rev. Lett. 86, 2653 (2001).
[11] Y. Sidis et al., Phys. Rev. Lett. 83, 3320 (1999).
[12] I. I. Mazin, D. A. Papaconstantopoulos, and D. J. Singh, Phys. Rev. B 61, 5223 (2000).
[13] A. Damascelli et al., Phys. Rev. Lett. 85, 5194 (2000).
[14] K. M. Shen et al., Phys. Rev. B 64, 180502(R) (2001).
[15] S. Nishizaki, Y. Maeno, and Z. Q. Mao, J. Phys. Soc. Jpn. 69, 572 (2000).
[16] M. Suzuki et al., Phys. Rev. Lett. 88, 227004 (2002).
[17] C. C. Tsuei and J. R. Kirtley, Rev. Mod. Phys. 72, 969 (2000).
[18] M. E. Zhitomirsky and T. M. Rice, Phys. Rev. Lett. 87, 057001 (2001).
[19] H. Kusunose and M. Sigrist, cond-mat/0205050 (2002).
[20] G. Baskaran, Physica B 223-224, 490 (1996).
[21] C. Bergemann et al., Phys. Rev. Lett. 84, 2662 (2000).
[22] N. Okada et al., J. Phys. Soc. Jpn. 71, 1134 (2002).
[23] R. Werner, cond-mat/0208307 (2002).
[24] H. Yaguchi et al., submitted to Phys. Rev. B (2002), cond-mat/0106492.
[25] A. P. Mackenzie et al., Phys. Rev. Lett. 80, 161 (1998).
[26] Z. Mao, Y. Morii, and Y. Maeno, Phys. Rev. B 60, 361 (1999).
[27] A. A. Abrikosov and L. P. Gor’kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960), [Sov. Phys. JETP 12, 1243 (1961)].
[28] G. E. Volovik, Exotic properties of superfluid $^3$He, Series in Condensed Matter Physics, Vol.1 (World Scientific, Singapore, 1992).
[29] K.-K. Ng and M. Sigrist, J. Phys. Soc. Jpn. 69, 3764 (2000).
[30] A. Liebsch and A. Lichtenstein, Phys. Rev. Lett. 84, 1591 (2000).
[31] In a $p$-wave superconductor the wavefunction of the electrons in the condensate has different parity then the electronic orbital wavefunctions.
[32] R. Werner and V. J. Emery, cond-mat/0208306 (2002).
[33] V. J. Emery and S. A. Kivelson, Phys. Rev. B 46, 10812 (1992).
[34] A. Lindner, Dreihimpulse in der Quantenmechanik (Teubner, Stuttgart, 1984).
[35] M. Sigrist et al., Physica C 317-318, 134 (1999).
[36] I. I. Mazin and D. Singh, Phys. Rev. Lett. 79, 733 (1997).
[37] M. Braden et al., cond-mat/0206304 (2002).
[38] The differential resistance data from point contact experiments \cite{8} have been argued to be inconsistent with an isotropic $s$-wave superconductor but since a $s$-wave model including gapless excitations might also account for the spectra this is not conclusive \cite{23}.
[39] D. F. Agterberg, Phys. Rev. B 64, 052502 (2001).
[40] R. Werner, cond-mat/0208308 (2002).
[41] The tetragonal structure of Sr$_2$RuO$_4$ has been found to be very stable [M. Braden et al., Phys. Rev. B 57, 1236 (1998)] and consequently the degeneracy of the two order parameter components is quite robust.
\end{thebibliography}