UNCONVENTIONAL SUPERCONDUCTIVITY IN A NUTSHELL

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SUMMARY

During the last few decades, superconductivity research has mainly focused on the materials that cannot be described by the Bardeen-Cooper-Schrieffer theory. In this overview I present a brief introduction into key features of unconventional superconductors, along with a discussion of some real-life examples.

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Superconductivity was discovered by Kamerlingh-Onnes one hundred years ago, in 1911, but it was not until 1957 that a truly microscopic theory of this phenomenon was developed by Bardeen, Cooper, and Schrieffer (BCS). The current understanding of superconductivity in solids, as well as superfluidity in ^{3}He, rests on the following main ideas of the BCS theory [1,2]: (i) The effective force between quasiparticles in a fermionic many-body system can be attractive, leading to the formation of bound states of two quasiparticles, known as the Cooper pairs; (ii) The Cooper pairs "condense" into the ground state characterized by a macroscopically coherent wave function, in which the gauge symmetry of the normal state is broken.

In the original BCS model, the effective attraction between quasipartcles with opposite momenta, $\boldsymbol{k}$ and $-\boldsymbol{k}$, was attributed to the exchange of the crystal lattice vibrations, or phonons. Due to the locality of the phonon-mediated attraction, the wave function of the Cooper pairs is $\boldsymbol{k}$-independent, corresponding to a zero angular momentum, or *s*-wave, orbital state. The Pauli principle then dictates that the paired quasiparticles form a singlet spin state, with the total spin $S = 0$.

The BCS model in its "conventional", *i.e.* singlet *s*-wave, form, along with its more quantitatively rigorous extension known as the strong-coupling, or Eliashberg, theory [3], has been remarkably successful in explaining the properties of many superconducting materials, especially the classical superconductors, such as Al or Pb. However, it fails in the case of the superfluid phases of ^{3}He, discovered in 1972. Although the possibilities of a higher angular momentum and/or triplet Cooper pairing had been discussed already in 1960s, it was the superfluid ^{3}He that provided the first real-life example of what is now known as unconventional pairing. The Cooper pairs in ^{3}He are in a *p*-wave triplet state [4], *i.e.* the pairs have angular momentum $L = 1$ and spin $S = 1$. The effective attraction between quasiparticles is due to magnetic fluctuations, enhanced by the proximity to a ferromagnetic instability. Similar features, *i.e.* the intrinsic anisotropy of pairing, either in spin-singlet or spin-triplet states, and the importance of magnetic fluctuations, either in antiferromagnetic or ferromagnetic channels, are shared by other systems that exhibit unconventional superconductivity.

The spin and momentum structure of the Cooper pairs is encoded in the gap function, which plays the role of the superconducting order parameter and is directly related to the pair wave function. In the singlet state, the pairing is described by a single complex function $\psi(\boldsymbol{k})$, while in the triplet state there are three possible values of the spin projection and, therefore, the gap function has three complex components, which are combined into a spin vector $\boldsymbol{d}(\boldsymbol{k})$. Due to the Pauli principle, $\psi(\boldsymbol{k})$ is always even in $\boldsymbol{k}$, while $\boldsymbol{d}(\boldsymbol{k})$ is odd.

The intrinsic anisotropy of pairing, reflected in the $\boldsymbol{k}$-dependence of the gap function, is a consequence of the crystal lattice symmetry breaking. That the point symmetry of the normal state is broken in the superconducting state, in addition to the gauge symmetry, is a defining property of unconventional superconductors [5]. Physically, the origin of the gap anisotropy can be traced to nonlocality of the pairing interaction in real space. If the *s*-wave pairing is suppressed by the short-range repulsion between ^{3}He atoms or between electrons in strongly correlated metals, then a higher angular momentum pairing state, in which quasiparticles avoid getting close to each other, might be realized.

The gap function determines the spectrum of quasiparticle excitations, which control thermal and transport properties in the superconducting state. For instance, in the singlet case the excitation energy has a gap near the Fermi surface, given by $|\psi(\boldsymbol{k})|$. In the original BCS model the pairing is isotropic and $\psi(\boldsymbol{k}) = \Delta$, where Δ is a function of temperature, vanishing in the normal state. In this case the number of thermally excited quasiparticles at temperatures well below the critical temperature T_c is exponentially small, leading to the characteristic activation behaviour, *e.g.* for the electronic specific heat one has $C(T) \sim e^{-\Delta/k_B T}$. However, if $\psi(\boldsymbol{k})$ vanishes somewhere on the Fermi surface, then so does the energy gap, producing a "gap node". In triplet superconductors the situation is more complicated and relatively simple expressions are available only in the so-called unitary case, when $\boldsymbol{d}^* \times \boldsymbol{d} = 0$ and the energy gap is given by $|\boldsymbol{d}(\boldsymbol{k})|$.

If the gap nodes are present, then quasiparticle excitations can be easily created in their vicinity and the exponential BCS behaviour is replaced by various power laws. For instance, the electronic specific heat is proportional to T^3, if the gap goes to zero at isolated points at the Fermi surface, or to T^2, if it does along whole lines. Similar power laws are found for the spin susceptibility, nuclear magnetic resonance relaxation, thermal conductivity, and other properties that are determined by quasiparticle excitations. Knowledge of the type (*i.e.* point versus line) and location of the gap nodes from experiment helps to understand the internal structure of the Cooper pairs, which in turn might yield important clues about the nature of the microscopic interactions responsible for superconductivity.

In addition to the gap nodes, other tell-tale signs of unconventional superconductors include a strong sensitivity to disorder, *e.g.* impurities, in the crystal, or the multicomponent structure of the order parameter, which manifests itself in multiple superconducting phases depending on temperature, pressure, and/or magnetic field [5].

The first examples of unconventional superconductivity in solids were discovered in 1970s, in heavy-fermion [6] and organic [7] compounds. The former are mostly uranium and cerium based intermetallics, such as $CeCu_2Si_2$, $CeCoIn_5$, UPt_3 [8], and many others, in which the fermionic quasiparticles have anomalously large effective masses due to strong many-body effects. The order parameter structure has been established with some degree of certainty only in few cases. For instance, in $CeCoIn_5$, which has tetragonal crystal symmetry, the pairing is singlet, with vertical lines of nodes, either along the basal plane axes, with $\psi(\boldsymbol{k}) \sim k_x k_y$ (called d_{xy} state), or along the basal plane diagonal, with $\psi(\boldsymbol{k}) \sim k_x^2 - k_y^2$ ($d_{x^2-y^2}$ state).

Probably the most popular class of unconventional superconductors are high-T_c copper oxides, such as $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-x}$, and others [9]. The layered crystal structure of these materials makes the electronic properties essentially two-dimensional. The Cooper pairing is singlet and strongly anisotropic in the Cu-O planes, corresponding to the $d_{x^2-y^2}$ state. There are gap nodes along the Brillouin zone diagonals that support low-energy quasiparticles. Despite many years of considerable experimental and theoretical efforts, the fundamental questions about the superconducting pairing mechanism [10] as well as the nature of the puzzling "pseudogap" normal state [11] in the cuprates remain unanswered.

The view that a high value of T_c is an exclusive property of copper oxides had been challenged recently by the discovery of superconductivity in iron-based compounds, in particular, iron pnictides, such as $LaFeAsO_{1-x}F_x$ [12]. The most popular order parameter candidate is the so-called $s\pm$-state, in which the gap function is isotropic and singlet, but, in a marked contrast to the BCS model, reverses its sign between different sheets of the Fermi surface.

The layered structure of high-T_c compounds is shared by another oxide superconductor, Sr_2RuO_4. Unlike the cuprates, however, there is strong evidence that the pairing in the strontium ruthenate is triplet, with the order parameter given by $\boldsymbol{d}(\boldsymbol{k}) \sim \hat{z}(k_x + ik_y)$, known as the chiral *p*-wave state [13]. The fact that the gap function is intrinsically complex, *i.e.* $\boldsymbol{d}^*(\boldsymbol{k})$ cannot be transformed into $\boldsymbol{d}(\boldsymbol{k})$ by a global gauge transformation, means that time-reversal symmetry is broken in the superconducting state and the Cooper pairs have a nonzero internal magnetic moment. In addition, nontrivial topology of the chiral order parameter in $\boldsymbol{k}$-space leads to the existence of peculiar gapless excitations, known as Majorana fermions, which are localized near the order parameter inhomogeneities, such as magnetic vortices and interfaces.

Other materials of recent interest include noncentrosymmetric superconductors, such as $CePt_3Si$ and $Li_2(Pt,Pd)_3B$. Their crystal lattices lack inversion symmetry, which means that the classification of the gap functions as purely singlet or triplet is no longer valid and the order parameter is represented by a mixture of singlet and triplet components. In contrast to centrosymmetric superconductors, the spin-orbit coupling of electrons with the lattice ions leads to a number of unusual magnetic effects [14].

This short review has covered just a fraction of the large and diverse family of unconventional superconductors. Many more materials, or even whole classes of materials, have not been mentioned here. The field of unconventional superconductivity has remained at the forefront of the condensed matter research for several decades and shows no signs of running out of steam, as new exciting materials are discovered every year.

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39. I have some expertise in this area, having succeeded in not doing this to date in six distinct cases.
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