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Exotic magnetic states in Pauli-limited superconductors

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1. Introduction

Magnetism and superconductivity compete in many materials. Magnetic order can generate sufficiently strong magnetic fields that alter the phase coherence of a superconductor or break up the Cooper pairs. Further, the microscopic mechanisms for magnetic order and superconductivity rely both on the same quasiparticles close to the Fermi surface, which can lead to a direct microscopic competition.

The interplay between magnetism and superconductivity has been studied for about 60 years. Early work was performed right after the development of the Bardeen–Cooper–Schrieffer (BCS) theory in the 1950s [1]. In 1957, Ginzburg predicted that magnetic impurities in a superconductor have a detrimental effect on superconductivity [2]. Shortly afterwards, Matthias showed experimentally that 1–2% of Gd destroys superconductivity in the single-element superconductor La before ferromagnetic order is established at about 3% doping [3]. In this case, superconductivity is suppressed because of exchange fields between the magnetic moments of the impurities and the spins of the itinerant electrons forming the superconducting Cooper pairs. Excellent reviews have been written about these early studies of magnetism in conventional superconductors [4, 5].

In the early 1970s, the first superconductors were found that also feature magnetic order, and they were heavily studied for several decades. These include molybdenum chalcogenides (Chevrel phases) MM06S68 where M stands for a transition metal ion, and the rare-earth (RE) rhodium borides (RERhB44). In most of these conventional superconductors, the order is antiferromagnetic. In these materials, the internal magnetic fields generated by the magnetic order fluctuate on a length scale that is often much shorter than the coherence length, so magneto-static effect do not break up the s-wave Cooper pairs [6]. Magnetic order arises from localized electrons of the rare-earth ions. In contrast, superconductivity is the result of mobile electrons that interact weakly with each other and form Cooper pairs through the virtual exchange of phonons. Several reviews have been published on the subject [7, 8].

However, magnetic order and superconductivity in these antiferromagnetic superconductors compete on a microscopic
level. This is evident in the field ($H$)—temperature ($T$) phase diagrams of the magnetic and superconducting phases: when the field strengthens the magnetic phase, this leads to a decrease of superconductivity and vice versa. This competition arises because magnetic exchange interactions depend on quasiparticles close to the Fermi surface, whose density also affect superconductivity. This effect is particularly strong in $s$-wave superconductors that feature a uniform energy gap near the Fermi surface. The more recently studied borocarbide superconductors also belong to this class of magnetic superconductors. More exotic phenomena are observed in ferromagnetic superconductors in this materials class. Recent reviews about these materials have been written by Gupta [9] and Mazumdar and Nagarajan [10].

Towards the end of the 1970s, two new material classes were discovered that had a lasting impact in the research community. Steglich et al discovered superconductivity in CeCu$_2$Si$_2$, that proved to be the first heavy-fermion superconductor [11]. In the same year, Jérome et al discovered superconductivity in (TMTSF)$_2$PF$_6$ under a pressure of about 0.9 GPa: the first organic superconductor [12]. The most important aspect of these two materials classes is the presence of strong electronic correlations. This is different from previously studied superconductors where electron–electron interactions are weak.

In the heavy-fermion superconductors, the $f$-electrons of rare-earth ions can hybridize with conduction electrons. Because of the tendency to be localized, the $f$-electrons can lead to an increase of the effective electron mass by orders of magnitude [13]. At the same time, the magnetic interactions between localized and mobile $f$-electrons can lead to strong fluctuations and instabilities. These effects can be further enhanced if the electronic structure is low-dimensional or the magnetic interactions are frustrated. Even in the absence of $f$ electrons, novel phases can emerge in the presence of strong correlations: organic superconductors are strongly low-dimensional electric conductors with strong electronic correlations and can give rise to emergent phases such as charge ordered or spin Peierls phases [14, 15].

In metals with strong electronic correlations, the relationship between magnetic correlations and superconductivity is more intricate than in metals with weak correlations. In strongly-correlated metals, both electronic and magnetic fluctuations can be intertwined and may contribute towards the emergence of superconductivity. Strong fluctuations are thought to provide the binding potential for electrons to form Cooper pairs in a number of strongly-correlated metals. In some of these materials, superconductivity emerges when magnetic order is suppressed in a continuous quantum phase transition, but not in the absence of strong magnetic or charge fluctuations.

Magnetic order and superconductivity have even been found to coexist microscopically in a number of heavy-fermion and organic superconductors [13, 15]. Superconductivity in these materials is often unconventional, which means that the superconducting gap function breaks at least one symmetry of the crystalline space group [16]. Due to the antisymmetric nature of Cooper pairs, either singlet superconductivity with $s$- and $d$-wave symmetry or triplet superconductivity with $p$- and $f$-wave symmetry is phenomenologically possible. For unconventional superconductivity, the superconducting gap function may contain nodal regions with a vanishing gap. This is the case for singlet $d_{x^2−y^2}$ and $d_{xy}$-wave superconductivity. The associated nodal regions can provide low-energy quasiparticles that can participate in magnetic ordering phenomena, and are thus compatible with the coexistence of magnetic order and superconductivity.

An entirely different class of materials that features coexisting magnetic and superconducting order are the $p$-wave superconductors. In this case, superconductivity emerges from triplet Cooper pairs that can feature non-zero magnetic moment. As a result, magnetic fluctuations and superconductivity can naturally coexist because the magnetic moment of the Cooper pair can couple to other magnetic degrees of freedom in the material. There are only few such materials known [17]. One possible superconductor of this kind is UGe$_2$ which is ferromagnetic at fairly high temperatures ($T_C = 53$ K). Near the critical regions where ferromagnetism is suppressed with pressure, superconductivity emerges. Superconductivity exists only as long as the material is ferromagnetic, providing evidence for an intimate coupling between magnetic order and superconductivity. Another material that may fall in this category is UCoGe that also becomes superconducting inside a ferromagnetic phase. However, superconductivity in UCoGe survives outside the ferromagnetic phase when it is suppressed under pressure.

A relatively new concept are superconducting phases that lead to changes of the magnetic properties or generate magnetic order. This exotic magnetism in strongly-correlated electron systems is the focus of this review. In such phases, magnetic correlations or magnetic order do not only coexist with superconductivity, but they are caused by superconductivity (as shown in figure 1(d)). As we will discuss, such phenomena have been discussed theoretically for some time, and important first experiments provide evidence for some of these predictions. An open question is under what circumstances such phases or effects can occur, and what distinguishes them from the more generally observed competition between superconductivity and magnetism.

Particularly promising for superconductivity-driven novel magnetism are superconducting pair-density waves (PDW), which are described by a spatially modulated superconducting order parameter. These were originally predicted independently by Fulde and Ferrell [18] and Ovchinnikov and Larkin [19] (FFLO) for $s$-wave superconductors. However, they can also exist for unconventional superconductors. They are predicted for Pauli-limited type-II superconductors at high magnetic fields, where orbital effects are weak and the upper critical field of superconductivity is not determined by orbital supercurrents of the vortices.

Orbital supercurrents can be weak in materials that feature a low-dimensional electronic structure, because the motion of the electrons perpendicular to the magnetic field is inhibited. Pauli-limiting effects can be strong for superconductors with a short coherence length, leading to high orbital limiting fields. This makes heavy-fermion and low-dimensional metals prime candidates for PDW superconductivity at high
magnetic fields. A recent review on the subject was published by Matsuda and Shimahara [20].

An important microscopic mechanism for PDW superconductivity involves a magnetic field that splits the conducting bands, and leads to different energies for spin-up and spin-down electron bands. As a consequence, the spin–up and spin–down bands have a different Fermi vector in the normal phase. When the material undergoes the transition to superconductivity, spin–up and spin–down electrons are combined into singlet Cooper pairs whose momenta do not add up to zero, and so the Cooper pairs have a finite momentum. The macroscopic wave-function that describes the superconducting condensate is a singlet and is modulated with a wave-vector that is incommensurate with the underlying structural lattice. This is what is commonly referred to as FFLO superconductivity, and is a special case of PDW superconductivity [18, 19].

There are other microscopic mechanisms that have been suggested to yield PDW superconductivity. In Mott insulators such as the parent compounds of the high-$T_c$ cuprate superconductors, it is well established that the introduction of mobile carrier can stabilize charge (CDW) or spin density wave (SDW) order. It was argued that CDW or SDW also leads to a modulation of the superconducting condensate and can induce PDW superconductivity.

There is also the possibility that two electrons with different momentum form triplet Cooper pairs with finite momentum. This kind of modulated triplet superconductivity is different from singlet FFLO superconductivity—and also the microscopic origin is different. Shimahara argued that electron pairing interactions mediated by spin fluctuations quite generally can lead to both singlet and triplet superconductivity [21]. While singlet superconductivity is dominant in most superconductors at zero field, he argued that Pauli-limited superconductors at high magnetic fields favor triplet superconductivity. This effect may be additionally enhanced for materials close to quantum critical points which can be sensitive to small energy scales.

This review is organized as follows: in section 2 we will first cover theories of exotic magnetism that can emerge from superconductivity. In section 3, we will discuss experimental results obtained in the heavy-fermion superconductors. Section 4 presents experiments on organic superconductors, and section 5 gives a survey of superconductivity-driven magnetism in other types of materials. The review will finish with a summary of the theoretical and experimental state of research and the formulation of open fundamental questions.

2. Theories for exotic magnetism in superconductors

Magnetic interactions in a metal depend on the electronic structure of the material. For metals with localized magnetic moments, an important magnetic interaction is the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction. The RKKY interaction is an indirect exchange interaction that is mediated by the conduction electrons and depends on the overlap of the localized electronic wave-function with that of the mobile carriers. For metals without localized magnetic degrees of freedom, there can be instabilities of the Fermi sea that lead to magnetization densities, either ferromagnetic order or spin density waves. Such instabilities towards static magnetic order are particularly strong when Fermi surface regions contain large regions separated by a similar wave-vector. This leads to an increase of the spin susceptibility for this particular wave-vector—the nesting wave-vector—and to a static modulation of the spin density. For low-dimensional conductors, this effect can be strong, because the density of states can be high at the Fermi surface.

For a conventional s-wave superconductor, where superconductivity induces a uniform gap in the Fermi surface, there are no low-energy quasiparticles that can participate in the formation of magnetic order. Unconventional superconductors can have point or line nodes in the superconducting state, and so they have low-energy particles that can mediate interactions. It is plausible that, for magnetic order and superconductivity to coexist microscopically, the nesting vector and the line nodes have to coincide. At first sight, this appears not to be the case in some materials. For example, CeCu$_2$Si$_2$, the ordering wave-vector is $Q = (0.21, 0.21, 0.47)$, which is not along the nodal direction of the $d_{xy}$ wave-order parameter in the $ab$ plane. However, it is in fact observed that superconductivity and SDW order do not microscopically coexist in CeCu$_2$Si$_2$. This is consistent with the expectation that the SDW ordering wave-vector should lie along the nodal direction in order to allow a coexistence of magnetic order and superconductivity.

Furthermore, the electronic structure of a type-II superconductor is altered at finite field, because the magnetic field can penetrate the material in the form of vortices. This has been realized early on, and one of the first studies was that by
Caroli, De Gennes and Matricon [22] who found the presence of bound fermion states in the vortex line of a type-II superconductor whose energy is much lower than the superconducting gap $\Delta$. Kramer and Pesch in 1975 also found evidence for low-lying bound states in the core, which results in a change of the core density [23]. Poettinger and Klein found that the electronic density of states inside a vortex oscillates strongly [24]. All these theoretical studies predict that the introduction of low-energy states in the superconducting condensates adds degrees of freedom that can affect the magnetic properties.

Additional effects occur if the magnetic field primarily couples to the spin of the electrons, and orbital effects are less important. Fulde and Ferrel [18] and independently Larkin and Ovchinnikov [19] analyzed the case of the $s$-wave superconductor. They found that modulated singlet superconductivity is possible in the presence of magnetic fields. It is stabilized either through an external field or exchange fields. This leads to a modulated singlet PDW phase at high fields, as schematically shown in figure 2. The modulation vector $q$ is expected to be proportional to the field-induced electronic band splitting and increases linearly with magnetic field. Such modulated superconductivity is now generally termed FFLO superconductivity. For the case of external high magnetic fields, FFLO superconductivity is separated from unmodulated superconductivity by either a first or second order transition.

Yang and Sondhi in 1998 analyzed the case of a 2D $d_{x^2-y^2}$-wave superconductor where the magnetic field interacts solely through the Zeeman interaction with the Cooper pairs [25]. The nodal nature of the electronic structure leads to the suppression of superconductivity for those parts of the Fermi surface where the Zeeman energy is larger than the gap energy (figure 3). The resulting normal electrons are aligned paramagnetically with the field. Superconductivity becomes modulated at high fields and low temperatures, forming a singlet PDW. The prediction of Yang and Sondhi is that this FFLO phase in a $d$-wave superconductor is separated from the uniform phase by a first order transition. The effects on the magnetic properties were not discussed in this study, but it can be expected that paramagnetic moments along the nodes will have a strong effect on the microscopic magnetism of a material.

More generally, Psaltakis and Fenton studied the case where superconductivity and SDW order arise from the same electrons, and they showed that both spin-singlet and spin-triplet Cooper pairing must occur simultaneously [26]. Similarly, Shimahara argued that superconducting pairing interactions that are mediated by spin fluctuations always include an attractive potential for both singlet and triplet Cooper pairs [21]. The author considered the case where the pairing interaction arises solely from antiferromagnetic fluctuations in two dimensions. He found that singlet pairing is realized at zero field, but at high fields where singlet superconductivity is weakened or suppressed by Pauli paramagnetic effects, triplet superconductivity is favored. He argued that in an FFLO state, singlet and triplet superconducting components are always mixed because the finite momentum of the pairs breaks the symmetry of real space. Similar results were obtained for quasi-one-dimensional models, where interchain interactions lead to triplet pairing that is of the same order of magnitude as the singlet pairing [27, 28].

Inspired by the prominence of the experimentally studied high-$T_c$ superconductors, there were a number of studies that focused on the coexistence of SDW order and $d$-wave superconductivity. A study of the Hubbard model showed that for $d$-wave superconductivity, coexistent SDW order and triplet superconductivity arise generally at half filling [29]. It was also shown that in a two-dimensional spin lattice with competing nearest and next-nearest neighbor interactions, $d$-wave superconductivity can coexist with modulated triplet superconductivity [30]. Zhang derived a $SO(5)$ symmetry principle...
that unifies antiferromagnetism and d-wave superconductivity, and furthermore explains their coexistence [31].

Lebed analyzed a clean singlet d-wave type-II superconductor and argued that, if triplet pairing is active, the parity and the spin-rotational symmetry of the superconducting order is broken [32]. In particular, he argued that the singlet-triplet coexistence is strong when the orbital critical field is of the order of the Pauli-limiting field. Additionally, he found that in the presence of magnetic fields, the spin of the triplet Cooper pairs are perpendicular to the external magnetic field.

With the observation of SDW order in CeCoIn$_5$, which only exists in the superconducting phase and is therefore coupled to superconductivity, it was argued that a SDW within a d-wave superconducting condensate always couples to a superconducting PDW [33]. These authors also proposed a Landau theory describing the coupling of the superconducting and magnetic order parameters, whose symmetry properties were determined for CeCoIn$_5$ by Agterberg et al [34]. A somewhat different way to couple different SDW and superconducting order parameters was proposed by Miyake [35].

Almost simultaneously, Aperis et al determined the phases of a mean-field model Hamiltonian that can feature d-wave superconductivity, SDW order and modulated triplet superconductivity (sometimes called π-triplet superconductivity) [36]. Their numerical results show that particle-hole asymmetry leads to a coexistence of all three order parameters. In a separate manuscript, they computed the field-temperature phase diagram and showed that a novel phase emerges at high fields close to the upper critical field $H_c^2$ that consists of both SDW order and triplet superconductivity (figure 4) [37]. They argued that this phase is driven by triplet superconductivity which induces SDW order as a secondary order parameter.

It is important to note that the PDW found by Aperis et al [36] is a triplet PDW and is different from the modulated superconductivity of the FFLO state that is a singlet. Another important difference concerns the modulation vector. In a FFLO phase, the modulation $q$ is proportional to the magnetic field, while the modulation of the triplet phase arises from the electronic nesting properties of the material.

The analysis of a microscopic model related to the Hubbard model by Yanase and Sigrist [38] on the basis of the Bogoliubov-de Gennes equations provided further evidence for novel phases at high magnetic fields. They found that a d-wave superconductor in high fields undergoes a second-order transition to a modulated singlet d-wave FFLO phase that appears for fields higher than the initially expected critical field. This FFLO order features an energy gap that is modulated relatively slow over tens of lattice sites (and is thus of LO type [19]), consistent with the general expectation for FFLO superconductivity. Magnetic degrees of freedom develop as a result of Andreev bound states. With decreasing temperature, SDW order is established. It was also found that an additional triplet component can emerge, and is induced by the SDW order. This lowers the energy of the SDW-DDLO phase further and makes it more stable. Further, depending on the degree of electron localization, different types of magnetic structures are realized [39], and double-q magnetic structures are possible [40, 41].

As Yang and Sondhi had shown [25], the magnetic field can lead to normal electrons and enlarged polarized Fermi pockets. Kato et al [42] studied how this affects the magnetic properties of a two-dimensional d-wave superconductor. For the microscopic model they considered, they found an instability towards a SDW order for wave-vectors connecting opposite nodes of the superconducting gap function. Interestingly, they also found that the SDW instability is equivalent to spin triplet superconductivity of the Bogoliubov quasiparticles of their model. Studying the coupling between different nesting vectors, they also found the possibility of double-q phases [43]. Similarly, Ikeda et al [44] found that the SDW order close to the upper critical field $H_c^2$ is a direct result of strong paramagnetic Pauli deparing and the nodes of the superconducting gap function. In this model, SDW develops without triplet PDW order. These authors found that FFLO is not needed for SDW order, but makes magnetic order stronger if present.

The electronic structure in the vortices can be different and it can be strongly affected by Pauli deparing effects. This was studied in great detail by Suzuki et al [45] using a quasiclassical microscopic Eilenberger theory for a clean $d_{x^2-y^2}$-wave superconductor, giving direct information about the quasiparticles in the vortices in both real and reciprocal space. They find that the density of states along the nodal direction is enhanced and can lead to SDW instabilities not present in the normal phase. An entirely different scenario was proposed by Michal and Mineev [46]. They considered a two-dimensional metal with a low-temperature $d_{x^2-y^2}$ superconducting phase that is Pauli limited. They found that $d_{x^2-y^2}$-wave spin excitons condense at high fields into the ground state, resulting in coexisting magnetism and superconductivity.

These theories all deal with non-trivial mechanisms how magnetic and superconducting order can coexist or emerge from each other. What is currently not clear is which of these microscopic models apply to real materials, and what phenomena are realized experimentally. As we will see, only very
few materials have been studied experimentally in the Pauli limit and with the necessary sensitivity to distinguish various theoretical scenarios. This is partly due to the exacting experimental conditions that have to be met: often the phenomena occur at very low temperatures and at high fields, making them inaccessible to many experimental techniques.

In particular, detecting PDW superconductivity has been a challenge. This is because there is no established method for the measurement of modulated superconducting order parameters, and all the existing evidence is indirect. Most of the employed methods are mostly sensitive to the presence of a phase transition, i.e. specific heat capacity and ultrasound measurements. Other measurements, such as Andreev reflection or nuclear magnetic resonance (NMR) are difficult to interpret if multiple order parameters are present.

3. Heavy-fermion superconductors

Heavy-fermion superconductors are important model materials to study exotic magnetism in superconductors. This has two main reasons. Firstly, the materials can often be synthesized in very pure form, leading to long mean-free lengths and the absence of spin scattering that could suppress exotic quantum phases. Secondly, the energy scale is low, and the magnetic and superconducting phases can be experimentally explored as a function of magnetic field and pressure. In addition, new heavy-fermion superconductors are regularly discovered. All this has led to steady progress in the study of heavy-fermion superconductors [47, 48].

Heavy-fermion superconductors are intermetallic materials that contain rare-earth ions forming a regular lattice, which is also termed the Kondo lattice. Many (but not all) of the heavy-fermion superconductors feature stronger electronic correlations in two dimensions with respect to the third direction and two-dimensional or quasi-two-dimensional Fermi surfaces. The rare-earth ions introduce f-electrons which can be hybridized with the conduction bands if the f-electron band is close to the Fermi energy $E_F$. This can have a strong effect on the physical properties, as can be the case for rare-earth ions such as Ce$^{3+}$, Pr$^{3+}$ or Yb$^{3+}$.

The presence of f-electrons close to the Fermi energy and arranged on a regular lattice can have two effects in materials. One effect is that the f-electrons can be either localized or itinerant. This ultimately depends on the degree of hybridization between the f-electron wave-functions with those of the itinerant electrons. Many novel phenomena in these materials occur in the proximity of the transition to itinerancy, which is also called Kondo breakdown or local quantum critical point [49].

The second effect is that the local magnetism arising from the orbital and spin degrees of freedom of the f-electrons can lead to long-range magnetic order. The magnetic interactions, $J$, between localized f-electrons depend on an overlap of the f-electron orbitals with those of the conduction electrons. However, the presence of a local magnetic moment requires that the f-electrons are only weakly hybridized with the conduction electrons. There are two competing energy scales that determine the ground state: the Kondo energy $T_K \propto \exp\left(-\frac{1}{J g(E_F)}\right)$ and the interaction energy $T_{\text{RKKY}} \propto J^2 g(E_F)$, where $g(E_F)$ is the electron density of states at the Fermi energy $E_F$. These competing effects are described in the Doniach phase diagram [50, 51] shown in figure 5.

A single rare-earth impurity in a metal causes the scattering of conduction electrons. This can lead to localized bound states around the rare-earth impurities. In the Kondo lattice, there is an additional effect that arises from the hybridization of the f-electrons with the conduction bands. At high temperature, the rare-earth ions act mainly as scatterers, but at low temperatures the local f-electron bands can form new bands through the hybridization with the conduction bands. This happens for temperatures that are below the characteristic energy scale of these novel bands, and is called the Kondo temperature. Because the f-electrons have a strong local character, they have a weak dispersion leading to flat bands in reciprocal space. As a result, the hybridization of the f-electron and conduction bands leads to weakly curved electron bands near the Fermi surface which is the origin of the high effective masses in heavy-fermion metals. Below the Kondo temperature, the hybridized bands are coherent. It is generally believed that a high degree of coherence is a prerequisite for the emergence of novel phases in the heavy-fermion metals.

The question to what degree the Kondo breakdown quantum critical point is coupled to the magnetic quantum critical point is currently under investigation. It has been proposed that depending on the material, these quantum critical points can occur together, or only one or none of them can occur (figure 6) [52]. Experimentally, it was found that materials can feature only a magnetic quantum critical point [53] or only a Kondo breakdown critical point [54]. There is also evidence that in some materials both quantum critical points occur together [55].

Superconductivity in heavy-fermion metals emerges at low temperatures, and is formed by the heavy
fermionic quasiparticles that emerge from the hybridization. Superconductivity in most heavy-fermion metals is unconventional. The first heavy-fermion superconductor that was discovered was CeCu$_2$Si$_2$ in 1979 [11]. It took 20 more years to identify other examples of ambient-pressure superconductivity in Ce-based heavy-fermion metals, namely CeCoIn$_5$ and CeIrIn$_5$ [56, 57]. Superconductivity in heavy-fermion metals is believed to be driven by either magnetic or charge fluctuations [58, 59]. Compared to actinide superconductors, Ce-based superconductors are ideally suited for experiments, because they do not contain radioactive isotopes. Radioisotopes represent safety risks and complicate the execution of many experimental investigations, particularly neutron and x-ray scattering experiments.

3.1. The well-studied case of CeCoIn$_5$

CeCoIn$_5$ features the highest superconducting transition temperature $T_c = 2.3$ K of all Ce-based superconductors at ambient pressure [56]. It crystallizes in the tetragonal P4/mmm space group. The crystal structure can be pictured as CeIn$_2$ planes separated by CoIn$_2$ planes along the c-axis. Its low-temperature physical properties are related to those of CeIn$_2$ that is antiferromagnetically ordered at ambient pressure and features pressure-induced superconductivity around a pressure of $p \sim 2.5$ GPa [60].

One of the major advantages for experimental studies of CeCoIn$_5$ is that it can be grown as ultraclean single crystals from an In flux and an equal amount of Ce and Co. Crystals are typically thin rectangular platelets of about 0.1 mm thickness and 1–10 mm edges. The residual resistance ratio (RRR), defined as the resistance at room temperature divided by the resistance at $T_c$ is typically over 10. This indicates a very low concentration of impurities in single crystals of CeCoIn$_5$. The material is in the superclean limit with a mean free path $l > 1 \mu$m that is much larger than the superconducting coherence length ($\xi \sim 200$) [61].

The Sommerfeld constant, defined as the ratio of the specific heat and the temperature, is $\gamma = C/T = 290$ mJ mol$^{-1}$ K$^{-2}$ for temperatures just above $T_c$, and reflects that the f-electrons are strongly hybridized with the conduction electrons (figure 7). This provides evidence for a sizeable renormalization of the effective electron mass. The change in the specific heat at the superconducting transition $\Delta C$ is large, and the ratio $\Delta C/\gamma T_c = 4.5$ indicates that superconductivity in CeCoIn$_5$ is in the strong coupling limit. Superconductivity is suppressed by magnetic fields in a strongly anisotropic manner: the upper critical field for fields along the c-axis is $H_{c2} = 4.95$ T and close to 12 T for fields in the tetragonal plane (figure 8).

CeCoIn$_5$ features a so-called large Fermi surface, where the f-electrons are mobile and mostly itinerant [62, 63]. As a result, CeCoIn$_5$ is not in the proximity of a Kondo breakdown quantum critical point. However it is close to a magnetic quantum critical point. The electronic correlations are strong in the tetragonal plane, and weaker perpendicular to it, and the Fermi surface contains quasi-two-dimensional features. Applying a magnetic field along the tetragonal c-axis leads to a power-law behavior in the physical properties such as the specific heat [64] and electrical resistivity [65], suggesting the presence of a quantum critical point close to $H_{c1}$ (figure 9). The origin of this magnetic quantum critical point and its relation to superconductivity is still under debate at this point.

Superconductivity in CeCoIn$_5$ is unconventional and is of $d_{x^2−y^2}$-wave symmetry. Evidence for this has first been provided by a number of macroscopic techniques, such as the temperature and angular dependence of the thermal conductivity [66, 67], and angular-dependent specific heat measurements [68]. First microscopic evidence for singlet superconductivity was provided by nuclear magnetic resonance (NMR) measurements [69, 70]. Additional microscopic evidence for $d_{x^2−y^2}$-wave superconductivity consists in the
observation of a spin resonance using neutron spectroscopy similar to those in the cuprate superconductors \[71\], and in point-contact spectroscopy \[72\] and quasiparticle interference measurements \[73, 74\].

3.1.1 Pauli-limited superconductor and spin depairing. Particularly important for this review is that CeCoIn\(_5\) is a Pauli-limited superconductor. This means that superconductivity is not destroyed by orbital supercurrents, but by the coupling of the magnetic field to the spin of the electrons. For one-band BCS superconductors, the upper critical field from orbital effects \(H_{c2}^{orb}(T = 0)\) is generally estimated by \(H_{c2}^{orb}(T = 0) = 0.73 \frac{dH_{c2}}{dT} T_c\) in the clean limit \[75\]. For CeCoIn\(_5\) this estimate yields \(H_{c2}^{orb}(0) \approx 13\) T for fields along the \(c\)-axis and \(H_{c2}^{orb}(0) \approx 35\) T for fields in the basal plane \[76\]. The experimentally observed critical fields are considerably lower, which is strong evidence that superconductivity in CeCoIn\(_5\) is Pauli limited. The relative importance of orbital and Pauli paramagnetic effects is described by the Maki parameter, \(\alpha = \sqrt{2} \frac{H_{c2}^{orb}(0)}{H_d(0)}\) \[77\], where \(H_d(0)\) is the Pauli limiting field. For CeCoIn\(_5\), it is found that \(\alpha > 3.5\), suggesting the presence of relatively strong spin paramagnetic effects at high fields. De Haas-van Alphen oscillation measurements showed a strong spin dependence of the quasiparticle mass enhancement at high magnetic fields along mostly the tetragonal axis \[78\].

A decade after the development of the BCS theory, it was predicted that for a Pauli limited superconductor, the transition from the superconducting to the normal phase is first order at low temperature \[79\]. The transition is first order because at high fields there are two energies that compete: the condensation energy of the Cooper pairs and the Zeeman energy of the normal electron spins in a magnetic field. This effect was revealed experimentally in CeCoIn\(_5\) using specific heat and thermal expansion measurements \[76, 80\]. For magnetic fields along the \(c\)-axis, the transition from the superconducting to the normal phase is of first order for temperatures \(T < T_0 = 0.31 T_c\), and of second order for higher temperatures. This is interpreted as further evidence for the strength of spin-paramagnetic effects, and is an indication of novel physics close to the upper critical field that was experimentally not investigated at the time. Evidence for field-dependent paramagnetic effects was also found with specific heat \[81\] and spin-torque measurements \[82\].

Microscopic evidence for spin-paramagnetic effects was also found in studies of the field dependence of the vortex lattice in the mixed state. For a Pauli limited type-II superconductor such as CeCoIn\(_5\), the Meissner phase is unconventional because of the simultaneous presence of orbital and spin depairing \[83, 84\]. Ichioka and Machida showed in 2007 using a quasiclassical theory that for a superconductor with strong Pauli-paramagnetic effects, the vortex structure features paramagnetic moments around its core \[85\]. Indeed,

Figure 8. \(HT\) phase diagram of CeCoIn\(_5\) for fields along the [1 0 0] and [1 1 0] direction in (a), and in (b) for fields along the [0 0 1] direction. The transition from the normal to the superconducting phase is of first-order for \(T < T_0\). For \(T < 250\) mK there is an additional phase boundary for \(H > 10\) T. Figure reproduced with permission from \[99\]. Copyright 2003 by the American Physical Society.

Figure 9. Phase diagram of CeCoIn\(_5\) as a function of field and temperature, showing the transition between the normal and superconducting phase for \(H < H_{c2}(T = 0) = 4.95\) T, and a transition between non-Fermi-liquid (NFL) and Fermi-liquid (FL) behavior for higher fields. This phase diagram indicates the presence of a quantum critical point near \(H_{c2}(T = 0)\). Reproduced with permission from \[64\]. Copyright 2003 by the American Physical Society.
small-angle neutron scattering experiments provided evidence for very unusual properties of the vortex lattice in CeCoIn$_5$ [86–88]. The key results are reproduced in figures 10 and 11.

Figure 10 shows that the Bragg peak intensity of the vortex lattice increases with field. This is in complete contrast to previously studied superconductors. For type-II superconductors with no or weak spin depairing, the vortex Bragg peak intensity always decreases with field because the scattering contrast decreases as the vortex density increases with increasing field. The increasing intensity observed in the experiment is thus evidence for an additional scattering cross-section that emerges with increasing field. The experiment was interpreted as evidence for spin-paramagnetic effects that increase in strength with increasing field [89]. The first results were observed for magnetic fields along the $c$-axis, but similar results were also observed for magnetic fields in the basal plane [90].

Several groups carried out calculations of the vortex form factor in the presence of orbital and spin depairing. Ichioka and Machida investigated the vortex structure of a type-II superconductor with strong Pauli-paramagnetic effects using the Eilenberger theory. They found the presence of paramagnetic moments around the vortex core that leads to an increase of the vortex lattice form factor [85, 91]. Michal and Mineev found similar results using a generalized Clem variational method and a Abrikosov-inspired theory [92]. A Ginzburg–Landau analysis at intermediate temperatures where the upper critical field is still of second order yields an increase of the form factor with increasing fields, and a gradual decrease to zero at the upper critical field [93]. Experimentally, it is clear that there must be an additional field-induced scattering potential in CeCoIn$_5$, but it is not clear whether it arises from paramagnetic or antiferromagnetic effects. The second possibility was considered by Aoyama and Ikeda who found that antiferromagnetic fluctuations lead to an increase of the vortex lattice form factor [94, 95]. The vortex structure of CeCoIn$_5$ can thus be considered a complex composition of orbital supercurrents and magnetic moments with both paramagnetic and antiferromagnetic character. This is also consistent with a NMR study that revealed the presence Zeeman and Dooperler-shifted quasi-particles extending outside the vortex core [96].

Figure 11 shows another remarkable effect. The symmetry of the vortex lattice changes with field, and at high field shows reentrant behavior. The vortex lattice features successively a triangular, rhombic, square, rhombic and at the highest fields again a triangular arrangement. At least some of these transitions are of first order, which is consistent with a combined quasi-classical Eilenberger and non-local London theory [97]. A triangular arrangement can be expected at low fields where the vortices are far apart from each other and the gap symmetry plays a small role. With increasing field, and decreasing vortex distance, a transition towards a square lattice can be expected with the increasing importance of the symmetry of the gap function. At higher fields, a Ginzburg–Landau theory
of a two-dimensional BCS Hamiltonian can explain that the square-lattice vortex lattice becomes unstable and transforms into a rhombic phase [98]. At the highest fields just below $H_{c2}$ it appears that the symmetry of the superconducting gap plays again no role. This suggest that at such fields, the paramagnetic or antiferromagnetic effects are dominant for the interaction of the vortices.

3.1.2. Second superconducting phase: Q phase. Specific heat capacity measurements reveal an additional phase boundary inside the superconducting phase for magnetic fields in the basal plane (figure 12) [99, 100]. This second superconducting phase exists below $T \approx 0.3$ mK and above $H_0 \approx 10$ T close to the upper critical field $H_{c2}$, and is now generally referred to as the $Q$ phase. The $HT$-phase diagram for fields in the basal plane shows only a weak dependence on the field direction. There is also some evidence of a second superconducting phase for fields along the tetragonal axis [99]. Specific heat measurement can not provide information about the microscopic nature of the $Q$ phase. However, based on the fact that CeCoIn$_5$ is a clean Pauli-limited superconductor, it was argued that this second superconducting phase is the realization of an FFLO superconducting phase [99].

The existence of this additional superconducting phase was confirmed by a number of macroscopic and microscopic measurements. Linear magnetostriction as a function of field and temperature provides evidence of a second order phase transition below the upper critical field $H_{c2}$, but only for fields within $20^\circ$ of the basal plane [101]. Overall these macroscopic measurements identify an additional superconducting phase that is most stable for fields in the basal plane and gets rapidly suppressed when the field is turned away from this plane. Ultrasound measurements provide evidence for an anomaly of the transverse sound velocity in the $Q$ phase, and the $HT$ phase diagram for magnetic fields along the[1 1 0] direction is consistent with that obtained from specific heat [102].

The first microscopic observation of the $Q$ phase was achieved with NMR measurements for fields in the basal plane [103]. These measurements revealed a distinct change in the $115^\text{In}$ NMR spectrum at the phase boundary of the $Q$ phase with the appearance of a new resonance line which was attributed to normal quasiparticles. These results were interpreted as evidence for inhomogeneous FFLO superconductivity. Similar
results were also observed for magnetic fields along the tetragonal axis [104], which constitutes some of the only clear evidence to date that a $Q$ phase also exists for this field direction.

Independent $^{115}$In NMR measurements yielded somewhat different results with a strong enhancement of the spin susceptibility, from which it was argued there are no normal state regions [105]. These measurements are not consistent with an FFLO state that consists of sheets of superconducting and normal regions. Instead it was argued the $Q$ phase is a more complex phase with an intricate interplay of magnetism and superconductivity that could involve static ferromagnetic or antiferromagnetic moments or a mixture of singlet and triplet superconductivity. Such scenarios were confirmed by a separate $^{115}$In NMR study that revealed the presence of static spin moments in the vortex cores [106] and the presence of Zeeman and Doopler-shifted quasiparticles extending outside the vortex core [96]. The first microscopic evidence for field-induced long-range magnetic order in the $Q$ phase was provided by Young et al [106], and is shown in figure 13.

Direct evidence for long-range SDW order in the $Q$ phase was obtained from neutron diffraction [33]. Figure 14 shows a magnetic Bragg peak for different magnetic fields and temperatures. It is observed for a wave-vector $(q, q, 0.5)$ with $q \approx 0.44$ and describes the modulation of a small magnetic moment of the order of $0.1 \mu_B$. The incommensuration $q$ does not show a detectable field or temperature dependence.

Figure 15 shows that as a function of increasing field, the SDW order has a continuous onset, and vanishes in a sharp transition at the upper critical field $H_{c2}$. As a function of temperature, the magnetic Bragg peaks intensity vanishes also in a first-order transition for $H > 11.5$ T, and in a second order transition at lower fields. This is consistent with a first-order phase transition at the upper critical field for $T < T_0$ seen with macroscopic measurements.

The remarkable aspect of the magnetic order in the $Q$ phase is that it does not exist outside the superconducting phase (figure 16), and its existence thus requires superconductivity. In this regard, this is in complete contrast to all previously known examples of magnetically ordered superconductors, which feature a mere coexistence of competing magnetic and superconducting order parameters.

In the first neutron diffraction experiment [33], the modulation wave-vector of the SDW was observed to be perpendicular to the magnetic field direction. This raised the possibility that the SDW modulation is perpendicular to the flux lines in the mixed state. However, in a follow-up experiment it was shown that the modulation vector remains unchanged and thus always points along a nodal direction of the $d_{x^2-y^2}$ superconducting order parameter [107]. The SDW modulation is thus not related to the flux line direction, but is pinned to the crystal lattice. Further, it was observed that the SDW occurs only for fields close to the tetragonal plane and is suppressed when the field is turned away from the basal plane by more than about $20^\circ$ ([108]), which is consistent with magnetostrictive measurements [101].

The fact that the modulation vector of the SDW order is pinned to the lattice and points along the nodal direction is evidence that electronic nesting plays a role in the formation of the SDW order. For FFLO superconductivity, the incommensuration $q$ is small and proportional to the energy difference of the spin-split bands, which scales with the magnetic field $H$. The field-independent incommensurrate $q$ in CeCoIn$_5$ suggests that the SDW is not directly connected with the modulation of a FFLO gap function if present at all.

The origin of the SDW order in CeCoIn$_5$ is not understood at present. A number of microscopic theories have been developed, which have already been mentioned earlier [38–41]. They can be grouped roughly in two main groups: the first group of theories contains an instability towards an
FFLO state of modulated $d$-wave superconductivity at high fields close to the upper critical field. Superconductivity in this FFLO state features a long-wave length modulation. Magnetism occurs in the FFLO nodal regions as Andreev bound states, and is thus a consequence of the modulated nature of superconductivity [38].

The second group are theories that do not rely on FFLO superconductivity. Magnetism in these theories arises for different reasons: (1) as a result of normal Fermi pockets around the nodal regions of the $d$-wave superconducting gap [42], (2) as a result of the confined nature of the vortex structure [45], or (3) as a result of the emergence of triplet superconductivity at high fields that drives magnetic order [36]. In the scenarios (1) and (2) the SDW is driven by circumstances that are not present at zero field, such as the presence of enhanced spin-split Fermi pockets in the nodal $d$-wave directions or due to the presence of vortices. In the scenario (3), the magnetism emerges as a secondary order parameter that only exists because of triplet superconductivity.

The debate which of these approaches best describes the $Q$ phase in CeCoIn$_5$ is ongoing. The coexistence of magnetic and superconducting order parameters has made it difficult to unambiguously identify the nature of the $Q$ phase and its origin. In the following, we will review some of the most recent experiments that were performed, and discuss how they compare with the proposed scenarios.

On a phenomenological level, it is an important observation that the onset of the $Q$ phase inside the superconducting phase occurs through a second-order phase transition. There is no evidence of a first-order phase transition anywhere inside the superconducting phase, apart from those of the vortex lattice [109]. This is in contrast to many of the FFLO scenarios that predict a first-order transition that separates a uniform $d$-wave phase from a high-field modulated $d$-wave phase. However, some theories also predict a second-order phase transition to an FFLO phase [110]. The entropy change at the $Q$ phase transition is relatively small, and consistent with the formation of SDW order, but not with a transition into an FFLO phase [109].

One possibility is that $d$-wave superconductivity remains the dominant order parameter in the $Q$ phase, and that additional order parameters emerge at this second-order phase transition [33]. Several microscopic theories describe the possibility that SDW order emerges within a uniform $d$-wave condensate and is coupled to modulated superconductivity, or vice versa [36]. This possibility has been analyzed phenomenologically, and results in rather stringent symmetry conditions for the modulated superconducting order parameter [34]. The symmetry analysis yields that the SDW is coupled to both a singlet and a triplet superconducting order parameter that is modulated incommensurately. This result follows purely from the translational invariance of the crystal in real space, and leads to the conservation of momentum in reciprocal space. However, this is a lowest-order coupling theory. It is not impossible that higher-order terms could describe a coupling between a slowly modulated FFLO order and a more rapidly modulated SDW order. However, such a Landau theory has not been developed so far.

The most recent NMR measurements all confirm the presence of magnetic order. Koutraoulakis et al [111] corroborated the presence of an incommensurate SDW order with the magnetic moments pointing along the $c$-axis, and confirmed that the SDW order is independent of the magnetic field direction in the basal plane. Their NMR spectra suggest that the incommensurate SDW order coexists with a novel modulated superconducting state, leading to an increase of the spin susceptibility. They also found evidence for an additional phase at lower fields in which SDW is absent, but where modulated superconductivity exists. However, the existence of such a phase could not be confirmed by other techniques.
Another NMR experiment performed by Kumagai et al [112] found evidence for an increase of the paramagnetic quasiparticle spectrum in the $Q$ phase. Figure 17 shows that this increase is particularly strong upon entering the $Q$ phase, and was interpreted as direct evidence for modulated normal quasiparticle regions resulting from FFLO superconductivity. It is however not clear whether PDW superconductivity of a different microscopic origin could also lead to similar phenomena.

The question arises whether an additional phase also exists for fields along the $c$-axis. Kumagai et al reported evidence of an FFLO-type phase for this field direction [104], but other techniques have failed to provide clear evidence of an additional phase. For example, high-resolution specific heat measurements provided evidence for the absence of an additional phase for this field direction [109], consistent with magnetization measurements [113]. It is conceivable that the magnetic field along the $c$-axis makes the SDW with its antiferromagnetic moments along the same direction unstable, so that no ordered phase can exist.

Due to the lack of suitable experimental tools, it is difficult to study the properties of the putative modulated superconducting order parameter. In contrast, the study of the magnetic order is easier. The SDW in CeCoIn$_5$ can order with two related ordering wave-vectors ($q$, $q$, 0.5) and ($q$, $-q$, 0.5). The resulting magnetic structures with longitudinally-modulated magnetic moments along the $c$-axis are either spatially modulated along the [1, 1, 0] real space direction, or alternatively along the [1, −1, 0] direction. The nearest-neighbor magnetic moments along the $c$-axis are always perfectly antiparallel. Experimentally, these two domains can be easily distinguished: the first domain will lead to Bragg peaks at reciprocal lattice positions that are equivalent to ($q$, $q$, 0.5), the second domain will lead to peaks equivalent to ($q$, $-q$, 0.5).

Gerber et al [114] found that only one of these magnetic domains is populated for a particular field direction, but never both domains at the same time. This is even true for magnetic fields along the [1, 0, 0] direction, where both domains should be identical by symmetry. Changing the magnetic field direction with respect to [1, 0, 0], it was demonstrated that the domain population associated with the two wave-vectors can be switched in a hysteretic and sharp fashion, as seen in figure 18. From these experiments, it can be concluded that there exists an interaction that makes the $Q$ phase extremely sensitive to the field direction around the [1, 0, 0] direction. Because the ordered moment points along the $c$-axis and thus always perpendicular to the magnetic field, the selection of the SDW domain can not be explained with a coupling of the magnetic structure to the magnetic field through a Zeeman term.

The switching of the domains can not be explained by theories that describe the $Q$ phase as a purely magnetic phase. $d$-wave superconductivity is a macroscopic singlet state, and with the absence of paramagnetic effects, it also cannot lead to a selection of one of the domains. However, there are several theories that involve modulated superconductivity in form of FFLO or a more general PDW, and that provide an explanation for the switching.

Gerber et al [114] interpreted their results as evidence for the presence of triplet superconductivity in the $Q$ phase. These conclusions were reached on the basis of a phenomenological theory that describes the coupling of the SDW to a putative PDW in the $Q$ phase [33, 34]. A group theoretical analysis of the possible PDW order parameters in this scenario shows that the PDW is a mixture of singlet and triplet components, whose symmetry is determined from very general symmetry principles [34]. Most importantly, this symmetry analysis suggests that the two SDW domains belong to different irreducible representations. Thus only one of them can occur for a particular field direction, but never both of them together. The experiment is consistent with the presence of two triplet components $d_1(k) = (0, 0, k_x - k_y)$ and $d_2(k) = (k_x, -k_y, 0)$. The switching between the two SDW domains is driven by an anisotropy of the magnetic susceptibility of the $d$: triplet component. These results are consistent with Lebed’s theory for a type-II superconductor with comparable orbital and Pauli limiting fields, for which both singlet and triplet superconductivity should be present, and the moment of the triplet component is perpendicular to the magnetic field [32].

Microscopically, this interpretation may be consistent with Mineev’s theory, where $d_{x^2-y^2}$ spin excitations condense at high fields into the ground state, thereby creating a novel superconducting state [46]. The field dependence of the spin resonance shows that it splits in field, and that the lowest energy excitation decreases its energy with increasing field [115, 116]. An extrapolation of the decrease in energy...

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**Figure 17.** Field evolution of the NMR spectra at one of the Indium sites. The green shaded area corresponds to the paramagnetic quasiparticle spectrum in the $Q$ phase. Reproduced with permission from [112]. Copyright 2011 by the American Physical Society.
indicates this excitation could condense into the ground state around $H = 10$ T, where the $Q$ phase emerges in a second-order phase transition. Furthermore it was argued that the spin resonance is incommensurate already at zero field [117].

An alternative explanation of the switching was given by Hatakeyama and Ikeda [118]. They find that the switching of the SDW modulation can not occur in a uniform superconducting phase, confirming that the switching of the SDW domains must be mediated by a modulated superconducting order parameter. Using a two-dimensional Hamiltonian in a mean-field approximation, they find the SDW order that emerges from paramagnetic effects within a $d$-wave superconducting condensate is sensitive on the field direction and leads to a sudden switch of the modulation direction.

3.2. Other Pauli-limited $d$-wave superconductors

3.2.1. CeCu$_2$Si$_2$. There are a number of other heavy-fermion superconductors that may feature similarly exotic phases as CeCoIn$_5$. Among the known Pauli-limited heavy-fermion singlet superconductors are CeCu$_2$Si$_2$, and UPd$_2$Al$_3$ which all feature superconductivity at ambient pressure. CePd$_2$Si$_2$ becomes superconducting under pressure. CeRh$_2$Si$_2$ and UNi$_2$Al$_3$ are orbitally limited, and are thus less likely to exhibit exotic magnetism.

CeCu$_2$Si$_2$ was the first unconventional superconductor discovered [11], and has been argued to be a $d_{15}$ superconductor [119], although more recent evidence is consistent with a gap function of $s_\pm$ symmetry [120]. CeCu$_2$Si$_2$ is located close to a magnetic quantum critical point. The mean free path is relatively short and about 10 nm ([121]). Depending on the exact stoichiometry, both an antiferromagnetic SDW order and superconductivity exist at sub-Kelvin temperatures, sometimes in the same sample. These samples are called A-type, S-type or A/S type CeCu$_2$Si$_2$, respectively. The SDW order is described by an ordering wave-vector $Q = (0.28, 0.28, 0.53)$ and competes with superconductivity [122]. If the two orders exist in the same sample, SDW order and superconductivity are spatially separated [123]. This competition is consistent with a gap function that features a gap along the reciprocal $(h, h, l)$ direction, as is the case for both the $d_{15}$ and $s_\pm$ symmetry.

The field-temperature phase diagram of the superconducting phase has been studied with different techniques. A/S-type samples were studied using magnetization to very low temperatures [124]. An anomaly for fields somewhat below $H_{c2}$ was observed that could indicate a change of microscopic magnetism. Alternatively, it could also be related to the pinning of vortices. The $HT$ phase diagram of a S-type sample was recently studied with specific heat. These measurements (figure 19) show an increase at very low temperatures for fields close to $H_{c2}$ that may reflect the proximity to a phase transition [125].

There is no evidence that the transition at the upper critical field $H_{c2}$ is of first order. This is not necessarily in disagreement with the expectation that CeCu$_2$Si$_2$ is a Pauli-limited superconductor for which novel physics could be expected at high fields: it was argued that for a multiband superconductor in the Pauli limit, the transition at $H_{c2}$ can remain second order to low temperatures [126]. The presence of multiple bands

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Figure 18. (a) Magnetic Bragg peak intensity measured using neutron diffraction as a function of the angle $\Psi$ between the magnetic field and the [100] crystallographic direction. (b) Definition of $\Psi$ and a representation of the two SDW domains. (c) Hysteresis of magnetic Bragg peak intensity during rotation of the magnetic field by $\Psi$. Figure reproduced with permission from [114]. Copyright 2014 by the American Physical Society.
Antiferromagnetic order is established below $T_N = 14$ K and superconductivity is present below $T_c = 2$ K. Antiferromagnetic order and superconductivity coexist microscopically. The magnetic order is commensurate and is described with the ordering wave-vector $Q = (0, 0, 1/2)$ [132]. The ordered magnetic moment is $0.85 \mu_B$ per $U^{4+}$, reflecting the tendency that the $f$-electrons are localized. UPd$_2$Al$_3$ features an enhanced spin susceptibility, and it is generally accepted that UPd$_2$Al$_3$ is a Pauli limited superconductor. However, there is only limited experimental evidence for Pauli paramagnetic effects at high magnetic fields, neither from NMR or small angle neutron scattering experiments. The $HT$ phase diagram of superconductivity is weakly dependent on the field direction (figure 20) [133]. Neutron scattering showed weak anomalies in the antiferromagnetic structure across the superconducting phase transition [134].

Thermal expansion features anomalies in the vicinity of $H_{c2}$, which was initially interpreted to be a realization of an FFLO state [133]. However, these anomalies exist for all temperatures, in contrast to theory (although triplet pairing at finite field would alter these predictions [135]). For various reasons, it is now generally believed that these features arise from enhanced vortex lattice pinning [136]. The mechanism for this so-called ‘peak effect’ remains poorly understood. It was argued that vortex pinning should be weak for vortices with paramagnetic cores, requiring a change of the superconducting order parameter, such as as modulated superconductivity [131] or other effects [137]. Not clear is how static magnetic order would modify the paramagnetic effects that may appear in the vortices. The energy scale associated with antiferromagnetic order has a higher energy scale than superconductivity, because $T_N > T_c$. It is possible that the paramagnetic moments in the vortices interact with the static magnetic moments, leading to a qualitative change of the paramagnetic effects. For magnetic fields where paramagnetic effects emerge, this may also lead to a coupling between the vortices and the lattice.

### 3.3. Other heavy-fermion superconductors

Other Pauli-limited heavy-fermion superconductors could show similar physics. However, most heavy-fermion superconductors become superconducting only at very low temperatures $T < 0.5$ K or under high pressure. For example, $\beta -$ YbAlB$_4$ is only superconducting for temperatures below $T = 80$ mK [138], making the measurement of exotic magnetic effects in the superconducting phase a challenge. Other examples include CeIrIn$_5$ and CeFeCoIn$_5$ that become superconducting at $T_c = 0.4$ K and $T_c = 0.68$ K, respectively [57, 139]. CeRhIn$_5$ and CePtIn$_3$ feature superconducting domes centered at pressures of 2.5–3.2 GPa, respectively [140, 141]. Unconventional transuranium superconductors feature high superconducting transition temperatures and there is evidence that at least some of them are paramagnetically limited, for example NpPd$_2$Al$_2$ [142]. However, the radioactivity of the transuranium ions greatly limits the experimental methods with which these materials can be studied.

We now review a few other heavy-fermion superconductors with regards to exotic magnetic effects. We will not include in our discussion some important superconductors,
such as Sr$_2$RuO$_4$. This is a $p$-wave superconductor and thus falls outside the scope of this review. An excellent review has been written by Mackenzie and Maneo [143].

UPt$_3$ is a heavy-fermion metal that features three superconducting phases below $T_c = 0.54$ K and weak antiferromagnetic order below $T_N = 5$ K [144]. Because of transitions in the superconducting phase, superconductivity has to be unconventional. It has been proposed that superconductivity is of triplet type, but the exact symmetry of the three different phases is still under debate. Superconductivity is most probably Pauli limited. The mean-free path is with 500 nm much longer than the coherence length of about 12–15 nm, making UPt$_3$ a superconductor in the clean limit.

Although magnetic fluctuations probably mediate superconductivity in UPt$_3$, there is only weak evidence for changes of magnetism in the superconducting phases. Magnetic correlations appear to be complex, with relatively fast fluctuations around $(0, 0, 1)$ and slower fluctuations around $(\frac{1}{2}, 0, 1)$ where the weak order condenses [145, 146]. The antiferromagnetic order changes only very weakly at the transition from the normal to the superconducting phase, reducing the ordered moment by about 20% [147]. The diffraction intensity of the flux line lattice decreases continuously as a function of increasing field, showing no sign of paramagnetic effects [148]. AC magnetic susceptibility measurements indicate an unusually strong pinning of the vortex lattice close to the upper critical field $H_{c2}$ [149]. Overall, these results suggest that the field-induced magnetic effects are weak, or absorbed by the presence of long-range magnetic order that sets in at higher temperature.

UBe$_{13}$ is an unconventional superconductor for $T < T_c = 0.9$ K [150], with an upper critical field in excess of $H_{c2} = 10$ T at very low temperatures. The gap symmetry is not known, and was argued to be either of singlet or triplet type. The temperature dependence of the critical field shows an unusual upward curvature with decreasing temperature below about $T = 0.5$ K. Upon doping of non-magnetic Th, a second phase transition appears for temperatures below $T_c$ [151]. The nature of this additional phase is unclear. It was argued to consist of SDW order or of superconductivity with different symmetry [152, 153].

DC magnetization measurements provide evidence for a magnetic anomaly as a function of magnetic field at low temperatures [154]. The magnetization shows irreversible behavior below about half the upper critical field, and an anomaly between $H = 2$ and 3 T. Upon doping of non-magnetic Th, the magnetic anomaly may become sharper and develop into the second phase of Th-doped UBe$_{13}$ ([153]). Below the irreversibility line seen in the magnetization around 8 T there is a peak effect similar to those observed in other unconventional superconductors, that probably arises from the vortex lattice.

Superconductivity in UBe$_{13}$ survives to much higher magnetic fields than the Pauli limiting field, which was estimated to be around 1.7 T. It was recently argued that paramagnetic effects are present in UBe$_{13}$ ([155]). Overall, UBe$_{13}$ features various magnetic effects that occur only in the superconducting phase, and that reflect a sensitivity to small magnetic fields that is typical for superconductivity with nodes. It is likely that these effects reflect magnetic fluctuations associated with the superconducting order parameters. It is possible that the low-temperature phase in Th-doped UBe$_{13}$ could be a phase with coupled SDW-PDW order.

4. Organic superconductors

A particularly interesting materials class for novel magnetic and superconducting phases are organic superconductors. These are materials that consist of donor and acceptor molecules that form charge transfer salts. Among the most important ones are the Bechgaard salts, (TMTSF)$_2$X with X = ClO$_4$, PF$_6$ and AsF$_6$, where the tetramethyltetraselenafulvalene (TMTSF) molecules act as donors. These salts contain a one-dimensional stacking of TMTSF molecules. They are conducting mostly because of $\pi$-orbital overlap between neighboring molecules. Superconductivity in this class of materials was first found in (TMTSF)$_2$PF$_6$ in 1979 [12].

![Figure 20. HT phase diagram of UPd$_2$Al$_3$ for magnetic fields along the [0 0 1] and [1 1 0] axes, compiled from thermal expansion measurements [133]. There is a hysteretic region close to $H_c$ that is thought to arise from vortex pinning. Reproduced with permission from [133]. Copyright 1993 by the American Physical Society.](image-url)
There are other important donor molecules for the synthesis of conducting organic materials, including bis(ethylenedithio)tetrafulvalene (BEDT-TTF) and bis(ethylenedithio)tetraselenafultale (BETS). Crystalline structures built up of BEDT-TTF form dimerized layered structures, leading to quasi-two-dimensional electronic properties. A number these materials also feature superconducting phases at low temperatures, for example for the acceptors Cu(NCS)$_2$ ([156]), Cu[N(CN)$_2$]Cl ([157]) and Cu[N(CN)$_2$]Br ([158]).

Correlations are strong in both TMTSF and BEDT based conductors, and they lead to a plethora of phases as a function of acceptor molecules and pressure [159]. For (TMTSF)$_2$X-based materials, ground states such as an antiferromagnetic SDW phase (for X = As$_2$F$_6$ and Br) [160], an insulating spin-Peierls phase (X = PF$_6$) [161], and superconductivity (X = PF$_6$ under pressure) [12] have been observed. Charge order was observed for X = As$_2$F$_6$ and PF$_6$ ([162]). BEDT-based materials either feature insulating or superconducting phases at the lowest temperatures, separated by what appears to be a first-order transition [160].

The two most prominent superconductors among these organic conductors are (TMTSF)$_2$PF$_6$ and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. (TMTSF)$_2$PF$_6$ has been argued to be a $p$-wave superconductor under pressure [159]. (TMTSF)$_2$ClO$_4$ is a zero-pressure superconductor [163] that is thought to be similar to (TMTSF)$_2$PF$_6$ [164, 165]. Both (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ feature upper critical fields $H_{c2}$ that exceed their Pauli limit [166].

There is an upturn of $H_{c2}$ with decreasing temperature in (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ that is seen in transport and magnetization measurements and is not well understood. It was proposed that (TMTSF)$_2$ClO$_4$ features triplet superconductivity for fields close to $H_{c2}$ [166]. A thermodynamic phase transition from a low-field phase with line nodes to a different superconducting phase above the Pauli limiting field has been identified [164]. However, field-dependent NMR measurements do not provide evidence for a change in the superconducting order parameter at this field, and merely show a change in the spin relaxation at significantly lower fields [165]. Due to the absence of a thermodynamic transition for fields greater than the Pauli limiting field, it has been argued that long-range superconducting order does not exist at high fields, although the resistivity is zero [164]. This would imply that there is no modulated superconductivity in (TMTSF)$_2$ClO$_4$ at high fields.

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is probably a singlet $d$-wave superconductor [167]. It also features a rather unusual HT phase diagrams with a upturn of $H_{c2}$ with decreasing temperature (figure 21). Pauli paramagnetic effects have been observed using $^{13}$C NMR [168]. For magnetic fields in the plane of the dominant electronic correlations, the transition from the superconducting into the normal phase is of first-order for fields larger than 21 T, indicating the Pauli limiting field [169, 170]. For higher fields, an additional first-order transition appears inside the superconducting phase that was interpreted as a transition to an FFLO phase [170]. Magnetic torque measurements confirm the presence of a high-field phase whose magnetic response is distinctly different from that below the Pauli limiting field [171].

Recently, unusual effects were observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ using $^{13}$C NMR measurements [172]. These measurements provide clear evidence of a change of the NMR spectra in the low-field superconducting phase, and for superconductivity for fields higher than the Pauli limiting field. The NMR relaxation rate increases in the putative FFLO phase. This was interpreted as evidence for polarized Andreev bound states at the nodal regions of FFLO superconductivity. This is also consistent with theories developed by Yanase and Sigrist [38].

5. Other superconductors

High-$T_c$ superconductors also feature unusual magnetic properties. A number of them have been argued to be Pauli-limited unconventional superconductors. This includes both hole and electron doped cuprates for magnetic fields applied in the CuO$_2$ layers. Sekitani et al studied films of optimally doped YBa$_2$CuO$_4$ with a thickness of 30 µm in two separate high-field experiments with fields up to 600 T. They found that the temperature dependence of the upper critical field shows paramagnetic limiting effects [173]. Resistivity measurements on slightly underdoped Bi$_2$Sr$_2$CuO$_{6+x}$ as a function of magnetic field also revealed a temperature dependence of $H_{c2}(T)$ that

![Figure 21. HT phase diagram of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ for fields in the two-dimensional plane of the dominant electronic correlations, assembled from differential susceptibility measurements [169]. The upper critical field is indicated with $B_c$. There is a second characteristic field, $B_p$, that appears at low temperatures at somewhat lower fields, and that is thought to be the transition between the uniform and modulated FFLO-type superconductivity. Reproduced with permission from [169].](image-url)
is indicative for the presence of paramagnetic effects [175]. In films of electron doped Pr_{2−x}Ce_xCuO_{4−δ} with thickness of 0.25 μm resistivity measurements suggest that the upper critical field is determined by Pauli limiting effects [176]. Most recently, angular-dependent magnetoresistance measurements on Bi_{1.15}Sr_{0.9}CuO_{6+δ} with Tc = 4 K provide evidence for an anisotropy in Hc2 that decreases with increasing field and decreasing temperature, which was interpreted as evidence for paramagnetically limited superconductivity [177].

Also some of the iron pnictide and chalcogenide superconductors were argued to be Pauli-limited superconductors. For FeTe$_{0.65}$Se$_{0.4}$ resistivity measurements for magnetic fields up to 45 T show an upward curvature in Hc2(T) with decreasing temperature, which was explained with Pauli limiting effects [178]. For the presence of Pauli paramagnetic effects argued Braithwaite et al [179] using resistivity and specific heat measurement of FeSe$_{1−x}$Te$_x$ for x = 0.52.

The minimal critical fields in high-Tc superconductors is typically around 50 T, and it can reach several hundred Tesla. This has made the study of the physical properties in the Pauli limit difficult, and mostly only the aforementioned resistance and magnetic susceptibility measurements have been carried out.

Some high-Tc superconductors feature unusual effects at zero or low magnetic fields, with multiple order parameters. The literature on this subject is vast and we only briefly mention a few aspects of these materials and how they relate to the effects at high-magnetic fields described in this review. An excellent review was recently published by Fradkin, Kivelson and Tranquada [180].

Some time ago it was observed that SDW order and superconductivity occur below the same temperature Tc = 42 K for La$_x$CuO$_{4+δ}$ with y = 0.12 [181]. Small magnetic fields induce SDW order in related La$_{2−x}$Sr$_x$CuO$_4$ with x = 0.10 ([182]). An interesting example is La$_{2−x}$Ba$_x$CuO$_4$ near x = 0.125 which features CDW order below T = 54 K. SDW order exists below T = 42 K, and the temperature dependence of the resistivity suggests an intermediate phase transition at T = 16 K, which is interpreted as a transition to a PDW state, before the material adopts bulk superconductivity at Tc = 10 K ([183]).

The cuprates also show a fascinating interplay between CDW order and superconductivity. There are different ways to interpret these experimental findings. One particularly interesting way, in view of this review, is that these different order parameters are coupled on some level, while they may still compete under certain circumstances [184]. It has been theoretically suggested that SDW order may appear in the high-Tc cuprates that feature correlations that break the rotational symmetry when high magnetic fields are applied [185]. Such high-field SDW order would induce triplet superconductivity not unlike the scenario described for CeCoIn$_5$.

### 6. Conclusions

This review summarizes the extensive progress of our understanding of exotic magnetic phenomena in superconductors. We define exotic magnetism as magnetism that is intrinsic to superconductivity and does not exist without superconductivity. There is a relatively long history of theoretical work that explored such effects. Particularly in unconventional superconductors with nodal regions in the superconducting gap function, novel magnetic effects have been predicted. Many of these effects are related to Pauli spin depairing effects and the emergence of PDW superconductivity.

Experimentally, the evidence for superconductivity-induced exotic magnetism is limited. Important progress has been achieved in at least two model superconductors. One of these is CeCoIn$_5$ where field-induced SDW order was observed that does not exist in the normal phase, and collapses together with superconductivity in a first order transition. The other example is κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ where Andreev bound states have been observed recently that reflect novel magnetic states in type-II superconductors near the Pauli limit.

The magnetic phenomena observed in CeCoIn$_5$ and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ appear to be generic features of unconventional superconductors near the Pauli limit. Given the increasing number of known unconventional superconductors, the question may arise why not more exotic magnetic states have been observed. This review gives an overview of the known and well studied unconventional superconductors. It identifies materials for which exotic superconductivity-induced magnetism could be found in the future. It also attempts to provide at least a partial answer why only few materials have been found to exhibit such properties so far. Firstly, only few known materials feature Hamiltonians that place them near the Pauli limit. Secondly, experimental studies require high sample quality and relatively large samples. Thirdly, the novel phases have to occur at an experimentally accessible magnetic field and temperature range, preferably at ambient pressure. Only few materials fulfill all these conditions.

Theoretically, it appears that there are two main scenarios for novel phases in a Pauli-limited superconductor at high fields: firstly FFLO type superconductivity arising from spin-split bands leading to a slowly-modulated singlet PDW, and secondly modulated superconductivity arising from nesting of field-induced normal electrons leading to a triplet PDW. Which of these two scenarios is realized in a particular material probably depends on the microscopic details. The balance between orbital and paramagnetic effects certainly plays a crucial role. The proximity of the material to a quantum critical point may also be important, but its role is not clear. There is increasing evidence that in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ the FFLO scenario is realized, while for CeCoIn$_5$ the nature of the Q phase is still under discussion.

An important lesson from recent research is that exotic superconducting states, whether they are FFLO type or other types of PDW, have an intimate relationship with magnetism. They can be coupled with SDW order or lead to novel magnetic correlations. While this has been realized by a number of theorists for decades, it is only recently that experiments have provided evidence that such complex coupled quantum phases do in fact exist. The most recent progress in this area should serve as both a theoretical and experimental guide to search and study more such phenomena in the future.
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