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Superconductivity and magnetism/Supraconductivité et magnétisme

Magnetism and superconductivity of heavy fermion matter

Jacques Flouquet [a,*], Georg Knebel [a], Daniel Braithwaite [a], D. Aoki [b], Jean-Pascal Brison [c], Frédéric Hardy [a], Andrew Huxley [a], Stéphane Raymond [a], Bernard Salce [a], Ilya Sheikin [d]

[a] *Département de la recherche fondamentale sur la matière condensée, SPSMS, CEA Grenoble, 17, rue des Martyrs, 38054 Grenoble cedex 9, France*
[b] *IMR, Tohoku University, Oarai, Ibaraki 311-1313, Japan*
[c] *Centre de recherche sur les très basses températures, CNRS, 38042 Grenoble cedex 9, France*
[d] *Grenoble High Magnetic Field Laboratory, MPI-FKF/CNRS, BP166, 38042 Grenoble cedex 9, France*

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Abstract

The interplay of magnetism and unconventional superconductivity (d singlet wave or p triplet wave) in a strongly correlated electronic system (SCES) is discussed with recent examples found in heavy fermion compounds. A short presentation is given on the formation of the heavy quasiparticle with the two sources of a local and intersite enhancement for the effective mass. Two cases of the coexistence or repulsion of antiferromagnetism and superconductivity are given with $CeIn_3$ and $CeCoIn_5$. A spectacular example is the emergence of superconductivity in relatively strong itinerant ferromagnets UGe_2 and $URhGe$. The impact of heavy fermion matter among other SCES as organic conductor or high T_C oxide is briefly pointed out. ***To cite this article: J. Flouquet et al., C. R. Physique 7 (2006).***

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Résumé

Magnétisme et supraconductivité de la matière fermion lourd. L'interférence entre magnétisme et supraconductivité non conventionnelle (de type singlet d ou triplet p) dans les systèmes électroniques fortement corrélés est discuté en prenant comme exemple les composés à fermions lourds. La formation des quasiparticules lourdes est le résultat de fluctuations locales et d une augmentation supplémentaire par les corrélations magnétiques. Nous discutons deux exemples ($CeIn_3$ et $CeCoIn_5$) de coexistence ou répulsion entre antiferromagnétisme et supraconductivité. Une surprise a été la découverte de la supraconductivité dans les composés ferromagnétiques itinérants UGe_2 et $URhGe$. L'impact des résultats obtenus sur la matière fermion lourd dans les autres systèmes fortement corrèlés comme les composés organiques ou les oxydes supraconducteurs est souligné. ***Pour citer cet article : J. Flouquet et al., C. R. Physique 7 (2006).***

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Keywords: Heavy fermion; Superconductivity; Antiferromagnetism; Ferromagnetism

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1. Conventional case

The interplay of magnetism and superconductivity covers quite different situations. In the past decade, the novelty has come with the discovery of new materials where the electronic correlations are strong: organic conductors [1], high T_C oxides [2], or heavy fermion systems [3]. The localisation or the motion of the quasiparticles leads often to competing ground states with transitions from insulator to metal or from well ordered magnetic phases to a paramagnetic (PM) state associated or not with the appearance of superconductivity (S) [4]. In these strongly correlated electronic systems (SCES) quite different facets can be stressed: for example for superconductivity the pairing mechanism, the stability of superconductivity, the nature of the order parameter, the consequences on the low energy excitations, and the feedback on the vortex matter [5]. Here we will focus mainly on the experimental determination of the temperature (T), pressure (P) and magnetic field (H) phase diagram of heavy fermion compounds (HFC). A new type of matter may occur at the boundary between two ground states which can be tuned under P or H.

In the conventional case with weak correlations between the itinerant quasiparticles, two different baths exist: the magnetism is carried by localised moments which interact weakly with the other electronic bath formed by the Fermi sea [6,7]. The peaceful coexistence of antiferromagnetism (AF) and superconductivity was discovered in 1975 at the University of Geneva in ternary compounds of rare earth (RE) elements and molybdenum sulfide (REMo$_6$S$_8$) [6], later in a series of rhodium boride alloys (RERh$_4$B$_4$) [8,9], and more recently in RE borocarbide [10]. Often most of these compounds are superconducting below a critical temperature $T_C \approx 2$ to 10 K and undergo phase transition to an antiferromagnetically ordered state at $T_N \leqslant T_C$. The simple argument is that at the scale of the superconducting coherence length ξ_0 the Cooper pair will feel an average zero magnetic field so that ξ_0 will be larger than the magnetic period d. This length d extends usually only to few atomic distances with also short magnetic correlation $\xi_m \leqslant \xi_0$. The superconducting pairing leads to the so called s-wave pairing: the spin up and spin down paired electrons have zero orbital angular momentum and the mechanism of attraction is due to the electron–phonon interaction.

A magnetic field can destroy singlet superconductivity in two ways. The orbital effect is simply the manifestation of the Lorentz force; the corresponding orbital limit $H_{C2}(0)$ at $T \to 0$ K varies as ($m^{*2}T_C$), where m^* is the effective mass of the quasiparticle. The paramagnetic limitation (H_p) occurs when a strong magnetic field attempts to align the spins of both the electrons: $H_p(0) = 1.8T_C$ in T. In conventional superconductors, as $H_{C2}(0) \leqslant H_p(0)$ due to the weakness of m^*, the Pauli limit is often irrelevant. However in HFC with $m^* \approx 100m_0$ (m_0 the free electron mass), a competition will occur between the two mechanisms at least for singlet pairing. However, for triplet superconductivity with equal spin pairing between up up or down down spins, there will be no Pauli limitation and superconductivity can only be destroyed by the orbital effect.

In conventional superconductors, as observed in ErRh$_4$B$_4$ and HoMo$_6$S$_8$, the superconductivity is destroyed by the onset of a first order ferromagnetic transition. The energy gained by the atoms carrying the ferromagnetic moment below T_{Curie} exceeds the energy gained by the electrons as they form Cooper pairs at T_C. Superconductivity cannot prevent the magnetic transition but can only modify it slightly in a narrow temperature range. Furthermore, it is very unlikely for singlet superconductivity to also survive in the ferromagnetic (FM) state because the exchange interaction H_{ex} often forbids the formation of Cooper pairs [11].

2. The heavy fermion matter

The heavy fermion compounds are inter-metallic compounds of 4f or 5f electrons where on cooling, very large effective masses often $100m_0$ appears due to the weak delocalisation of the 4f or 5f particle from its site produced by the hybridisation with the other initial light itinerant electrons (s, p, d) [4]. Basically on cooling below 10 K the remaining large magnetic entropy ($S = R \log 2$ for a doublet crystal field ground state) is transferred for the formation of heavy quasiparticle with an effective low Fermi temperature (10 K instead of 10 000 K for noble metals). However the duality between the localised and itinerant character leads to the competition between long range magnetic order (AF or FM) and PM. The popular picture is that the switch at $T \to 0$ K will appear at a magnetic quantum critical point (QCP) via a smooth second order phase transition. For example under pressure, that will occur at P_C (Fig. 1).

We will not enter into the present debate on heavy fermion descriptions. Qualitatively, at least on the PM side, their properties are rather well described by an itinerant spin fluctuation approach with vanishing crossover temperatures T_I and T_{II} where respectively Fermi liquid properties are well obeyed below T_I and the usual high temperature behaviour of Kondo impurities is recovered above T_{II}. In the temperature window $T_{III} - T_I$ the so called non Fermi liquid
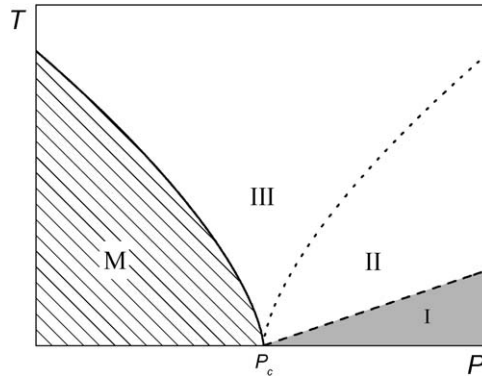
Fig. 1. Magnetic phase diagram predicted for an itinerant spin fluctuation system. In the domain I, Fermi liquid properties will be achieved. In the domains II and III, non Fermi-liquid behaviour will be found. Depending on the nature of the interactions (AF or F), the contour lines I, II, III change. Here the contour is drawn for antiferromagnetism. In case of ferromagnetism, the T_I line starts as $(P - P_C)^{3/2}$.

properties are observed. The underlining question is the location of P_C with respect to the pressure P_{KL}, where the 4f electrons participate ($P \geqslant P_{KL}$), or not ($P \leqslant P_{KL}$), to the Fermi sea and to the pressure P_V where for $P \geqslant P_V$ the 4f electron looses their orbital sensitivity to the local environment (the crystal field effect) due to the hybridisation with the other electrons. At least P_C must be between P_V and P_{KL}. The physical image of HFC is that, through strong local fluctuations reminiscent of the Kondo effect of a single impurity characterised by its Kondo temperature (T_K), the renormalised band corresponds already to a heavy particle with a band mass near $m_b \cong 50m_0$. Antiferromagnetic fluctuations produced by the intersite coupling give only an extra factor of 2. A strong support for this statement is that a self-consistent fit of the superconducting upper critical field $H_{C2}(0)$ including orbital, Pauli plus strong coupling limits with λ coefficient $\lambda = m^*/m_b - 1$ indicates a moderate value of $\lambda \approx 1.2$, i.e., a ratio of $m^* = 2.2m_b$.

For different cerium HFC–AF, a superconducting dome appears tight to P_C with the appearance and disappearance of superconductivity at P_{-S}, P_{+S} (Fig. 2). The nearly coincidence of the maxima $T_C^{\max}$ of T_C near P_C is an indirect strong support for a magnetic origin of the superconducting pairing. At P_C, slow magnetic fluctuation occurs: T_I vanished linearly with $P - P_C$ for AF and m^*/m_b reaches its maxima. As the characteristic temperatures (T_N, T_I) collapses at P_C, their strong pressure dependence leads to a huge corresponding Grüneisen coefficient $\Omega^* = -\frac{\partial \log T_I}{\partial \log T_V}$ (V: volume molar). Through the Maxwell relation, a huge electronic thermal expansion occurs basically $\alpha \approx m^{*2}$ for $P \geqslant P_C$ [4]. The combined effects of large spin and density fluctuations can induce a Cooper pairing with an unconventional order parameter [5] (at least different from the previous s wave case) since the local strong coulomb repulsion precludes the simultaneous presence of the Cooper pair on a given site: singlet d wave or triplet pairing have been reported.

There is now an extensive literature on superconductivity induced by spin fluctuation [12,13]. The energy window between the frequencies $\hbar\omega_{sf} = k_B T_I$ and $\hbar\omega_K = k_B T_K$ play a key role in the pairing. Even if the transition at P_C is not of second order but weakly first order there will be no strong effect on the appearance of superconductivity. When $P_C \approx P_V$ (CeIn$_3$, CePd$_2$Si$_2$, CeRh$_2$Si$_2$ cases) $T_C^{\max}$ seems located near P_C. For CeCu$_2$Si$_2$ or CeCu$_2$Ge$_2$ where $P_C \leqslant P_V$ two different regimes occur in the pressure variation of T_C (Fig. 3) [14,15]. This suggests two different mechanisms for the Copper pairing mediated by spin or valence fluctuations.

The magnetic field leads to the creation of a vortex lattice with the mixed phase of normal and superconducting components. In the special situation of SCES, it may lead to new phenomena: (i) the restoration of specific magnetic properties inside the vortex core as recently reported in high T_C superconductors [16]; (ii) a displacement of the frontier between AF and S phases when it occurs.

In this very narrow band an extra effect may occur due to the field variation of the ground state itself but also in the nature of the magnetic fluctuation. In the (H, P) phase diagram at 0 K (Fig. 2), the superconducting upper critical field $H_{C2}(0)$ must be located by comparison to characteristic fields for the magnetism: H_C for the transition from AF to PM states below P_C, H_m inside the PM phase for the entrance in the polarised PM state (PPM). Above H_m, the static ferromagnetic component increases continuously, but the q dependence of the dynamical response is flat. If the local magnetism is of the Ising type (the magnetic anisotropy axial) H_m is the continuation above P_C of H_C which ends up at a critical point at P_C: H_m is roughly equal to the Kondo field $H_K = k_B T_K/9\mu_B$ [4]. For a planar
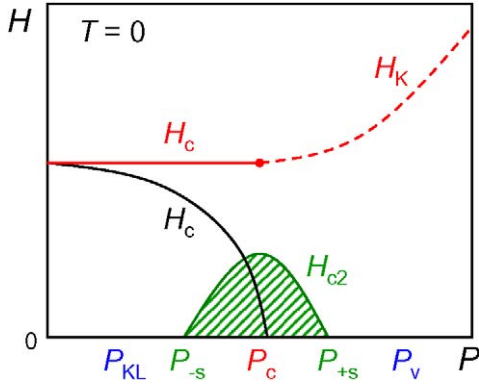
Fig. 2. At $T = 0$ K, characteristic pressure of HFC: P_{KL} when the 4f electrons are itinerant, P_{-S} and P_{+S} for the onset and disappearance of superconductivity, P_C the magnetic quantum critical point and P_V when strong valence or orbital fluctuations exist as the Kondo temperature overpasses the crystal field splitting. H_C represents the critical field from AF to PM state. Depending of the magnetic anisotropy, it ends a critical point or collapses at P_C. H_K represents the entrance in a Kondo polarised PM state.
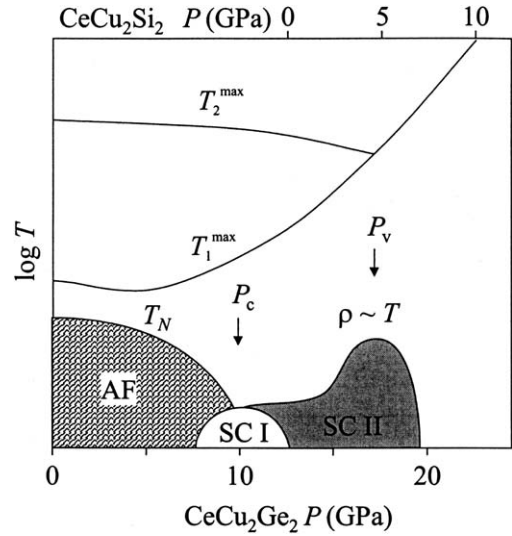

Fig. 3. Schematic $P–T$ phase diagram of CeCu$_2$(Si/Ge)$_2$ showing the two critical pressures P_C and P_V. Near P_C, where the antiferromagnetic ordering temperature $T_N \rightarrow 0$, superconductivity in region SC I is governed by antiferromagnetic spin fluctuations. Around P_V, in the region SC II, valence fluctuations provide the pairing mechanism and the resistivity is linear in temperature. The temperatures T_1^{max} and T_2^{max} of the temperature of the maxima of the resistivity merge at a pressure coinciding with P_V [14].

or Heisenberg local spin, H_C will collapse at P_C and thus there will be a large field range above P_C from $H = 0$ to H_K where AF and FM fluctuations complete. By contrast in the Ising case, both interactions will interfere in a narrow field window around $H_m \approx H_K$ [17].

3. The superconducting magnetic boundaries

The thermodynamics of the interplay between magnetism and superconductivity was often neglected for the debate on the mechanism for superconducting pairing and on the prediction and observation of the order parameter. Very often, the superconducting boundary in (T, P) phase diagram is mainly determined by resistivity measurements. However, recent specific heat [18] and NMR experiments under pressure [19] show clearly that the coexistence of superconductivity and antiferromagnetism is not a general rule whatever are the values of T_N or T_C. As it was done in the past [20] and recently [21], the simplest approach is to consider two order parameters for AF and S via a coupled term of strength g for the Landau free energy. If $g \geqslant 0$, superconductivity and AF compete. As indicated in Fig. 4, with the intensive P variable, a bicritical point exists with a first order transition from AF to S phases. If $g \leqslant 0$, a tetracritical point will occurs (Fig. 5) and each phase enhances the other. A so called SO5 theory has the aim of unifying these two basic states by a symmetry principle [22]. Of course, the constant g may depend on pressure. Thus a Ginzburg–Landau approach is a first step to underline basic possibilities.

In Ce heavy fermion compounds at least for three-dimensional Fermi surface, T_C^{max} is one order of magnitude smaller than the corresponding maxima T_N^{max} observed for AF. The coexistence of S and AF has been observed below P_C but, on the other hand, no example has been reported with $T_N \leqslant T_C$ in a sharp contrast with the conventional case of REMo$_6$S$_8$. The intuitive idea is that if superconductivity appears first on cooling, a large gap will be open in the main part of the FS and the drop of the density of states at the Fermi level is disadvantaging for AF. In HFC, as the characteristic energies are low and the corresponding magnetic field (H_C, H_K, H_{C2}) in the 10 T range, it may be possible to move the domain of the stability of one phase for $g \geqslant 0$.

To illustrate the physics of HFC superconductors we have selected two examples of cerium AF HFC which become superconductors at $P \approx P_C$: CeIn$_3$ and CeRhIn$_5$, and one example of ferromagnetic superconductors, UGe$_2$. Before their presentation let us stress the key role played of the discovery of new materials.
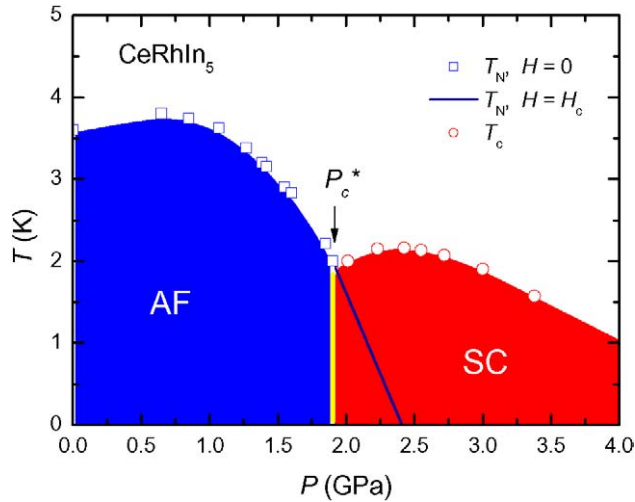
Fig. 4. Schematic (T, P) phase diagram of CeRhIn$_5$. The points observed by resistivity, susceptibility and specific heat below P_C^* characteristic of an extra inhomogeneous media have been removed (see Fig. 9). For $H \geqslant H_{C2}(0)$ and $P_C^* \leqslant P \leqslant P_C$, AF will continuously reappear up to reach $T_N \to 0$ K near P_C (see [20,21]).
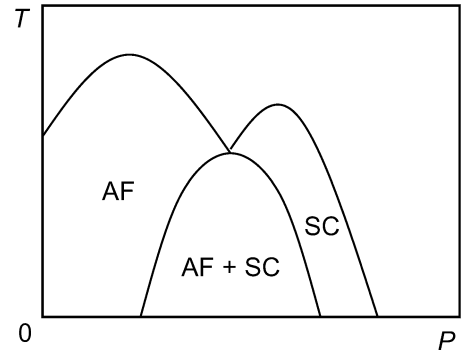

Fig. 5. Schematic (T, P) phase diagram of the interplay between AF and S when a coexistence domain exists as it seems to occur for different HFC. However T_C^{Max} occurs often close to P_C when $T_N^{\text{Max}} \approx 10 T_C^{\text{Max}}$ [21,22].

4. Materials

Examples of superconductor HFC of 4f electrons exist mainly for cerium compounds where also large FS with 4f itinerant electrons have been observed. The simplicity of Ce HFC is that in the $4f^1$ configuration of the trivalent state, it is a Kramer's ion with a total angular momentum $J = 5/2$. For $P \leqslant P_V$, the crystal field leads to a doublet ground state. The formation of a single ground state can only be due to a Kondo mechanism or more generally to the Fermi statistics. After the unexpected discovery of superconductivity in CeCu$_2$Si$_2$ at ambient pressure with $T_C \approx 0.6$ K [3], the main steps were:

- the unusual P dependence of T_C [23,24] in CeCu$_2$Si$_2$ followed by the clear evidence in CeCu$_2$Ge$_2$ that the superconductivity appearance is coupled to P_C [25];
- the discovery of the superconducting domain in CePd$_2$Si$_2$ and CeIn$_3$ centered on P_C [26];
- the high T_C reached in 115 Ce compounds which have a low dimensional character [27,28]. This enhances T_C and its maxima T_C^{max} becomes comparable to T_N^{max};
- recently, a supplementary perspective was given by the appearance of S in the non centrosymmetric crystal of CePt$_3$Si [29].

Despite Yb HFC being often described as the hole analog of the Ce cases, no superconductivity has yet been reported. For Pr HFC where the valence fluctuation will occur between the $4f^2$ and $4f^1$ configuration, superconductivity has been detected in the PrOs$_4$Sb$_{12}$ skutterudite [30], however, the pairing may be due to quadrupolar excitons created by the large dispersion of the crystal field excitation between singlet and excited crystal field levels [31]. In 5f HFC (mainly U or Pu), the 5f electrons can overlap. So the coexistence of magnetism (AF or F) with unconventional superconductivity can occur even for $P \leqslant P_C$ since large magnetic fluctuations may exist already. Highly documented cases are UPd$_2$Al$_3$ for AF [5] and UGe$_2$ for FM [4]. UBe$_{13}$ [32] looks like a dense Kondo lattice rather similar to CeCoIn$_5$ described later. URu$_2$Si$_2$ ($T_N \approx 17$ K and $T_C = 6$ K) and UPt$_3$ ($T_N = 6$ K and $T_C = 0.6$ K) exhibit the coexistence of exotic magnetism with tiny ordered magnetic moments and superconductivity [4]. The double superconducting transition of UPt$_3$ at ambient pressure and $H = 0$ was one of the first macroscopic evidence that the order parameter cannot be a simple scalar in SCES [33]. In many cases, excellent crystals of HFC were grown with:

(i) large electronic mean free path ℓ for the observation of quantum oscillations and for the achievement of the required clean limit ($\ell \geqslant \xi_0$) for the existence of unconventional superconductivity;

(ii) large size to allow complementary experiments such as inelastic neutron scattering, NMR or sensitive macroscopic measurements as thermal expansion or magnetostriction;

(iii) nice shiny surface to realise good thermal contact and thus excellent thermalisation to the low temperature bath and precise thermal transport data. The HFC physics is complex with the interplay of different couplings but clear situations are now well identified.

5. Antiferromagnetism and superconductivity: CeIn₃ and CeRhIn₅

At $P = 0$, the cubic lattice CeIn₃ is an AF HFC with $T_N = 10$ K, a sublattice magnetisation $M_0 = 0.5\mu_B$ at $T \to 0$ K and a $k_0 = 1/2, 1/2, 1/2$ propagation vector [34,35]. The crystal field ground state is the doublet Γ_7. The spin dynamic observed by neutron scattering shows a $T_K \approx 10$ K at low temperature, a crystal field splitting $C_{CF} \approx 10$ meV and below T_N a quasi-elastic line and damped spin wave [36]. Neutron diffraction experiments under pressure suggest that AF may collapse for $P_C = 2.6$ GPa [37]. The analysis of the resistivity shows that at P_C, $k_B T_K \approx C_{CF}$, i.e., P_C and P_V coincide [38].

Experiments on a high quality crystal in Cambridge (residual resistivity $\rho_0 \approx 1$ μΩ cm) [26] shows that the superconductivity occurs in a narrow P range around P_C with $T_C^{max} = 200$ mK (Fig. 6). Confirmation was found in Osaka [39] and Grenoble [38]. The large initial slope of $H_{C2}(T)$ at T_C proves that the heavy particles themselves condensate in Cooper pairs in agreement with the first observation made for CeCu₂Si₂ ($T_C \approx 0.6$ K) at $P = 0$ two decades ago [3]. Nuclear quadrupolar resonance (NQR) on the In site were very successful to study the spin dynamics notably in the assumed AF and S coexisting regime [40,41]. Recent experiments indicate [42] that the second order nature of the QCP must be questioned as two NQR signals (AF and PM) appears just below P_C (Fig. 7). Evidence for the unconventional nature of the superconductivity in both phases is given by the temperature variation of the nuclear relaxation time T_1 which follows the $1/T_1 \approx T^3$ law reported for many unconventional exotic superconductors with line of zeros.
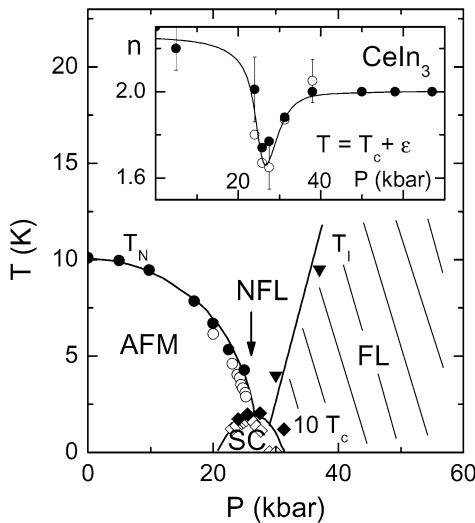

Fig. 6. Phase diagram of CeIn₃. T_N indicates the Néel temperature, T_I the crossover temperature to the Fermi liquid regime. The superconducting transition temperature T_C is scaled by a factor 10. The exponent n of the pressure dependence of the resistivity ($\rho \approx T^n$) is shown in the insert. The minimum of the exponent n in the temperature dependence T^n of the resistivity occurs close to the critical pressure P_C [38]. The Fermi liquid in the PM state corresponds to $n = 2$.
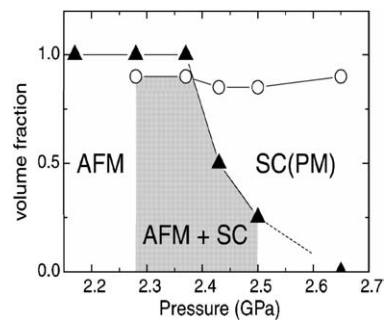
Fig. 7. NQR data of Kawasaki et al. on CeIn₃ [42]: volume fraction of AF and S states as a function of P.

The link between S and AF was recently boosted with the Los Alamos discovery of superconductivity in the so called 115 tetragonal cerium compounds like $CeRhIn_5$, $CeIrIn_5$, $CeCoIn_5$ [28]. A planar anisotropy is induced by inserting in $CeIn_3$ a single layer of MIn_5. The local magnetic anisotropy is weak. The Fermi surface is dominated by slightly warped cylindrical sheets whatever is the localisation of the 4f electrons [43]. The gold mine of these compounds are that they cover all the possibilities of interplay between AF and S: $CeRhIn_5$ which is an AF at $P = 0$ with $T_N = 3.8$ K, becomes PM at $P_C^* \approx 1.9$ GPa [44]. The two others ($CeIrIn_5$, $CeCoIn_5$) are already on the PM side ($P_C \leqslant 0$) and superconductors at $T_C = 0.4$ K and 2.3 K [28].

As for the other Ce HFC, in $CeRhIn_5$ superconductivity emerges near P_C^*; its maxima $T_C^{max} = 2$ K is not too far $T_N^{max} = 3.8$ K. We will focus here on the coexistence of S and AF near P_C^*. Extensive works can be found either under pressure [44] or by alloying, i.e., studies on $CeRh_{1-x}Co_xIn_5$ and $CeRh_{1-x}Ir_xIn_5$ [45,46].

To clarify the situation, careful ac calorimetric measurements to detect T_N and T_C in excellent hydrostatic conditions (Argon pressure transmitting medium) with in situ P tuning at low temperature have been performed [18]. Qualitatively, the important feature is that clear AF specific heat anomalies are observed below $P_C^* \approx 1.9$ GPa and a pronounced signatures of superconductivity one just above P_C (Fig. 8). Thus AF and superconductivity seems here to repel each other. However, tiny AF or superconductivity anomalies are detected just below P_C. The domain of homogeneous coexistence of AF and gapped superconducting phases may not exist. Indeed, ac susceptibility experiments on a sample coming from the same batch show only a broadened diamagnetism below P_C^*; but at higher temperatures than the superconducting specific heat anomaly (Fig. 9). A sharp diamagnetic transition occurs for $P \geqslant P_C$ in coincidence with the superconducting specific heat anomaly. It was proposed from NQR measurements that the observation of the inhomogeneity may not be a parasitic effect but an intrinsic property of a new gapless superconducting phase of parity and odd frequency pairing [47,48]. At least in the NQR studies, simultaneous measurements of ac susceptibility show that its temperature derivative has its maxima at T_C far lower than the previous determination of T_C (ρ) by resistivity. No track of AF has been detected above P_C but let us stress that its detection is difficult: in resistivity by the short circuit of the superconducting component and in calorimetry by the collapse of the specific heat magnetic anomaly with the sublattice magnetisation. The observation of an extra inhomogeneous component is yet not resolved above P_C^*. For an intensive variable as the pressure and a single type of particle, only a phase separation is predicted (Fig. 4). In the complex HFC matter extra effects can occur. Furthermore, an important experimental point is that
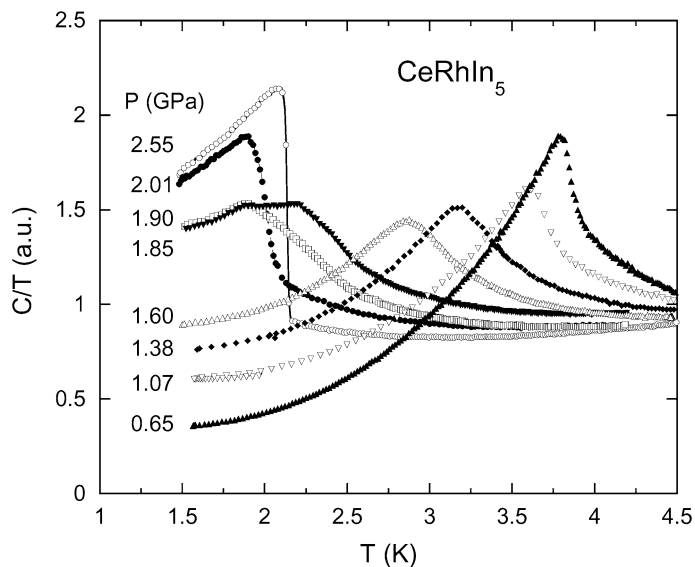

Fig. 8. Specific heat anomalies of $CeRhIn_5$ at different pressures. At $P \approx 1.9$ GPa, there is a superposition of tiny superconducting and magnetic anomalies (Knebel et al. [18]).
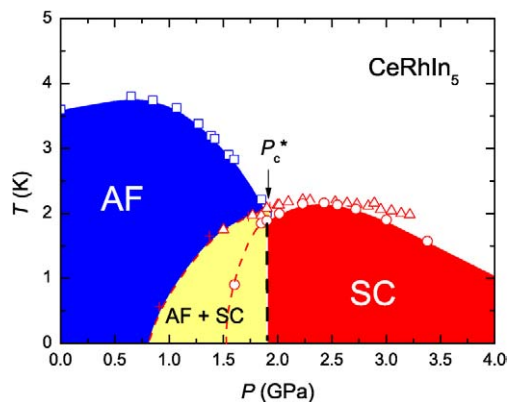
Fig. 9. (T, P) phase diagram of $CeRhIn_5$. Squares and circles correspond to the specific heat anomalies at T_N and T_C; triangles to T_C in susceptibility. The AF anomaly disappears suddenly at $P_C \approx 1.9$ GPa. Gapped superconductivity is observed above P_C. Inhomogeneous ungapped superconductivity may occur below P_C (white domain) [18].

in the high pressure diamond anvil as in the pressure clamp, the condition to work at constant pressure cannot be certified.

We conclude that homogeneous AF and gapped S appear here antagonist. AF collapses through a first order transition at P_C^* due to the appearance of gapped S. The new phenomena is that under magnetic field so far $H_C \geqslant H_{C2}(0)$, AF will shift to higher pressure as indicated in Fig. 4. Basically at $H_{C2}(0, P_C)$, $T_N(P_C)$ will reach zero. Extrapolating from other HFC examples (see CeIn$_3$), $T_N(P_C) = 0$ corresponds roughly to the linear extrapolation of T_N i.e., here to $P_C = 2.4$ GPa. The amazing features are that it corresponds to the maxima of T_C, to the pressure where in de Haas van Alphen experiment a drastic change of the FS occurs with a localisation ($P \leqslant P_C$) and delocalisation ($P \geqslant P_C$) of the 4f electrons [49] and to the maximum of the jump in the specific heat $\Delta C/C$ at T_C (see insert in Fig. 10). We suspect that the field change of the (T, P) phase diagram AF–S is the origin of the new induced superconducting phase of CeCoIn$_5$.

Fig. 10 represents the pressure variation of T_C of CeCoIn$_5$ and of the specific jump $\Delta_C/C(T_C)$ up to 3 GPa. $T_C(P)$ reaches its maximum for $P = 1.5$ GPa while the specific jump at T_C continuously decreases under P. Neglecting strong coupling effects, the jump normalised to the value of the effective mass at $T = 0$ K must be universal, i.e., related to the strength of $m^* T_C$. Thus the effective mass decreases gradually under pressure. In CeRhIn$_5$ the maximum of m^* seems to occur at P_c.

In magnetic field (Fig. 11) the new features are: (i) a crossover from second order to first order in $H_{C2}(T)$ at T_0; (ii) a new high field phase in a restricted low temperature domain [50,51]. Conservative explanations come from predictions made three decades ago: change from 2nd order to 1st order if $H_{C2}(T)$ is dominated by the Pauli limit at low temperature [52] as well as appearance of a new modulated S phase referred as the FFLO state from the work of Fulde Ferrel [53] and Larkin Ovchinnichov [54] below $T_{FFLO} \approx 0.56 T_C$.

An alternative explanation is that at ambient pressure, CeCoIn$_5$ is located just above P_C^* but below P_C where T_C may reach its maxima and T_N a vanishing value if the superconductivity will not appear. Applying a magnetic field will lead, at T_0, to recover the condition $T_C(H) = T_0 = T_N$ $(P = 0, H)$ value of T_N without superconductivity equal basically to the fictitious value at $H = 0$ since $H_C(T = 0) \geqslant H_{C2}(0)$ so far T_N has not collapsed.

A strong support for this picture is that, crossing through H_{C2}, the properties near a magnetic QCP are recovered [55,56]. The Fermi liquid regime is restored continuously to high temperatures with increasing H as observed in CeNi$_2$Ge$_2$ [57] and in YbRh$_2$Si$_2$ [58] HFC considered to be almost right at QCP for $P = 0$.

The new superconducting matter at high magnetic field and very low temperature (the hatched domain of Fig. 11) implies a fancy coherence between the superconducting and normal components (maybe AF or F). Its narrow domain
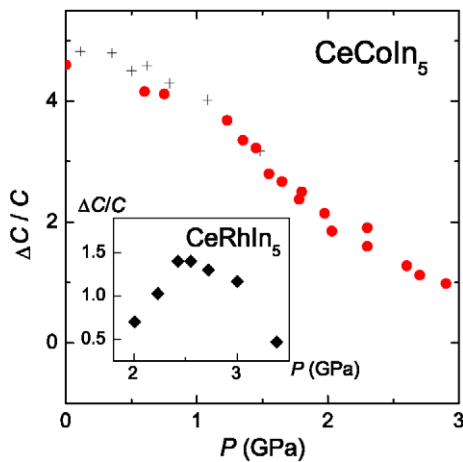

Fig. 10. Jump of the superconducting specific heat anomaly of CeCoIn$_5$ normalised to the value just above T_C (Knebel et al. [18]). The insert shows the variation observed in CeRhIn$_5$.
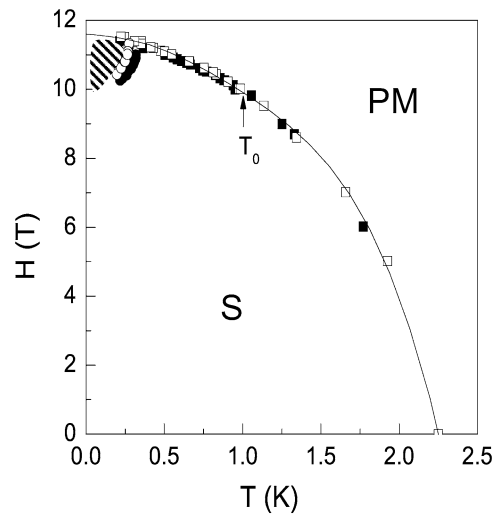
Fig. 11. H–T phase diagram of CeCoIn$_5$ with both $H \parallel [110]$ (filled symbols) and $H \parallel [100]$ (open symbols). (Circles) and (full squares) indicate the assumed T_{FFLO} anomaly for $H \parallel [110]$ and $H \parallel [100]$, respectively [50]. The hatched domain is the new mixed superconducting phase which may be not a FFLO state.

needs further microscopic investigation or analysis. The underlining possibility will be if the magnetic interaction is also modified by the magnetic field (change of ordered wavevector and/or switch from dominant AF to FM correlations). As already pointed out, for weak local magnetic anisotropy as happens for CeCoIn$_5$, ferromagnetic and antiferromagnetic fluctuations will compete above P_C, i.e., near $H_{C2}(0)$. Recent Nernst and dHvA experiments show that the crossover Kondo field $H_K \approx 23$ T occurs far above $H_{C2}(0)$ [59]. Let us also stress that, as the disorder will change the first order nature of the AF–S boundary, it will add extra effects than those predicted for unconventional superconductivity (see recently [60]).

6. UGe$_2$: a ferromagnetic superconductor

The appearance of superconductivity in UGe$_2$ [61] was a surprise. The relevance of ferromagnetic fluctuations [62,63] for anisotropic BCS states was illustrated by the p wave superfluidity of liquid ^{3}He [64]. The p wave T_C in nearly ferromagnetic metals was first calculated in 1971 [65] and in both FM and PM phases in 1980 [66].

At $P = 0$, UGe$_2$ is a ferromagnet with Curie temperature $T_{\text{Curie}} = 54$ K, $M_0 = 1.48$ μ_B/U atom, far lower than the full moment near $3\mu_B$ of the free trivalent or tetravalent uranium configuration [67]. Its residual γ linear temperature term of C is 35 mJ mole^{-1} K^{-2}. Under pressure, T_{Curie} decreases as M_0. However, as reported for many itinerant ferromagnets, FM disappears via a first order transition with a jump $\Delta M_0 = 0.8$ μ_B/U [67,68].

The assertion that even at $P = 0$, UGe$_2$ is itinerant was based on the already described P collapse of T_{Curie} and M_0 [68], on band calculations with their success in explaining dHvA oscillations [70,71], and on the spin dynamics determined by neutrons scattering with a finite magnetic coherence length ξ_m ($T \to O$ K) = 24 Å larger than the typical value found in localised system restricted to atomic distances (6 Å) [69].

Fig. 12 shows the temperature dependence of the ferromagnetic intensity measured by neutron scattering (i.e., the square of the ordered moment $M(T)$ at different pressures). Above a critical pressure $P_X = 1.2$ GPa no structure appears in the temperature variation of $M^2(T)$ while, below P_X, at a characteristic temperature T_X, a jump appears on cooling. Magnetisation experiments under pressure indicate that a discontinuity in M_0 appears at P_X at $T \to 0$ K. Through a first order transition, FM2 transits to FM1 under pressure. The transition FM1 $\to$ FM2 are easily observed in resistivity measurements when P approaches P_X [67]. The competition between two FM phases can be explained in a band theory picture with two phases which differ only by a smooth difference in orbital momentum on the uranium site [73]. Specific heat measurements analysed via γT contribution plus a βT^3 one show a strong increase of γ and a maximum of β at P_X [74,4]. Large changes of the FS have been observed between FM2 ($P \leqslant P_X$) and PM ($P \geqslant P_C$), dHvA in FM1 ($P_X \leqslant P \leqslant P_C$) are controversial [70,71].

Correlatively to the P induced transition from FM2 to FM1, the magnetic field restores FM2 for $P \geqslant P_X$ via a metamagnetic transition at H_X and leads also to the cascade PM $\to$ FM1 at H_m as indicated (Fig. 13) [67,68].

The discovery of superconductivity [61] just above 1.0 GPa close to P_X and below P_C inside the ferromagnetic domain is remarkable, as superconductivity occurs when T_{Curie} is still high and M_0 large: $T_C^{\text{max}} \approx 700$ mK at P_X when $T_{\text{Curie}} = 35$ K and $M_0 = 1.2\mu_B$ (Fig. 13). The fact that the superconductivity is not filamentary was first suggested in flux flow experiments and established without ambiguity by the observation of a nearly 30 per cent specific heat jump at T_C^{max} [75]. Experiments on single crystal achieved in Grenoble [64,67], Cambridge [61], Osaka [75] and Nagoya [76] confirm the S domain, at least on materials respecting the condition of a clean limit for superconductivity ($\ell \geqslant \xi_0$). The (T, P) phase diagram of UGe$_2$ is shown (Fig. 13). Applying a magnetic field in the FM1–S phase lead to enter in the FM2–S state for $H = H_X \leqslant H_{C2}$ for $P \approx P_X + \epsilon$. The H_{C2} curve can be analysed with equal spin pairing triplet order parameter in good agreement with the large estimation of the exchange field ($M_0 H_{\text{ex}} = k_B T_{\text{Curie}}) \approx 100$ T while the Pauli limit will be 1 T at $T_C^{\text{max}} = 0.7$ K.

Coexistence of superconductivity and ferromagnetism was first verified by neutron scattering [67,72] and more recently by NQR experiments on Ge sites [75]. In NQR, $1/T_1$ exhibits a peak at T_{Curie} and a change of slope at T_C from a Korringa law to a T^3 law characteristic of unconventional superconductors with line of zeros (Fig. 15).

Considering the mechanism of superconductivity, obviously the superconducting domain is not centered on P_C but at P_X. Specific heat measurements suggest two mechanisms as the γT and βT^3 terms have quite different P dependences. An interesting proposal is that a charge density wave may occur below T_X [78]. The drop of the resistivity at T_X as well as the coincidence of T_C^{max} when T_X collapses is reminiscent of the paramagnet α uranium where T_X is identified as the charge density wave temperature T_{CDW} [79,80]. Furthermore, its T_C is also maxima when $T_{\text{CDW}} \to 0$ K [81]. In UGe$_2$ as in α uranium, the U atoms are arranged as zigzag chains of nearest neighbours
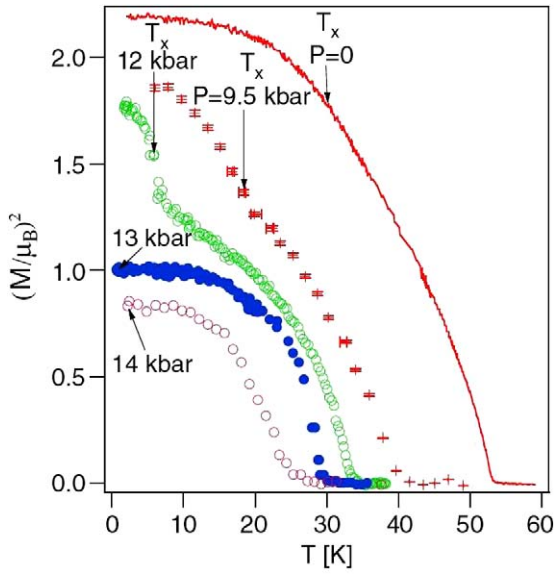
Fig. 12. The temperature dependence of the ordered moment squared at different pressure deduced from neutron scattering measurements [72].
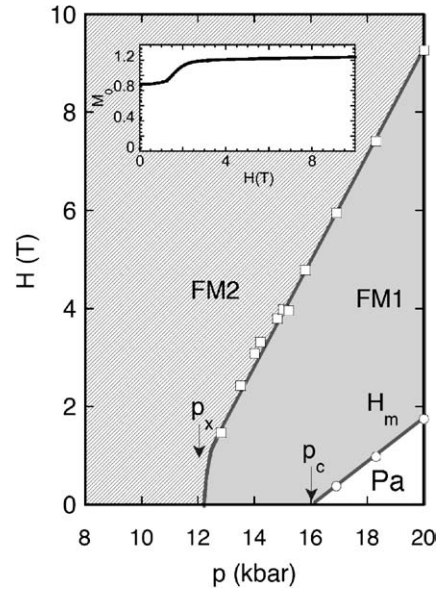

Fig. 13. (H, P) phase diagram of UGe$_2$ the insert show the jump of M_0 in μ_B at the transition FM$_1 \rightarrow$ FM$_2$ at P_X for $T = 2.3$ K [68].
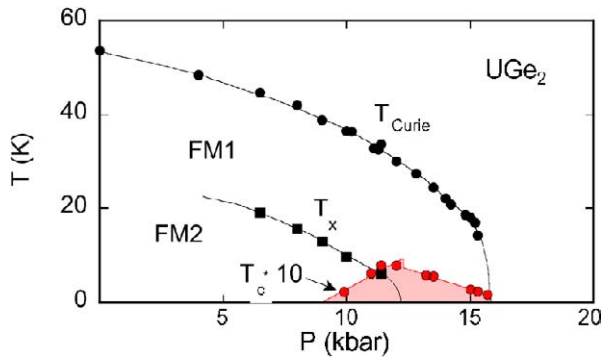

Fig. 14. (T, P) phase diagram of UGe$_2$. The Curie temperature T_{Curie}, the supplementary characteristic temperature T_X which leads to first order transition at $T \rightarrow 0$ K and the superconducting temperature T_C are shown. (T_C scale has been multiplied by 10.)
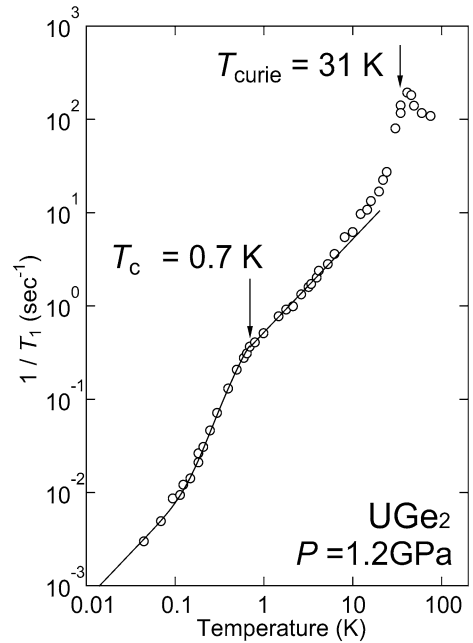

Fig. 15. At $P = 1.2$ GPa, temperature variation of $1/T_1$ with the clear signature of ferromagnetism and superconductivity. The solid line is a calculation assuming an unconventional line node gap [77].

that run along the crystallographic a-axis which is the easy magnetisation. The chains are stacked to from corrugated sheets as in α uranium but with Ge atoms inserted along the b axis. Up to now, no superstructure has been detected below P_X. Now that superconductivity is well established, the superconducting states on both side of P_X deserves special attention notably to determine the nature of unpaired electrons (residual γT in the specific heat).

To realise precise measurements as performed on the unconventional superconductor UPt$_3$, the discovery of a FM superconductors at $P = 0$ is an important step. The condition is realised in the orthorhombic URhGe: $T_C = 300$ mK for $T_{Curie} = 10$ K, $\gamma = 160$ mJ mole^{-1} K^{-2} [82]. Here again the T_C strength appears not correlated with P_C as, under P, T_C collapses already near 4 GPa while T_{Curie} continues to increase linearly with P at least up to 12 GPa (where $T_{Curie} = 18$ K) [83]. The recent success in the growth of single crystals allows one to measure $H_{C2}(T)$ along the three main axis. $H_{C2}(0)$ exceeds the Pauli limitation for fields applied along all three crystal axis. Its temperature variation cannot be reconciled with opposite spin pairing, but is well described by a single component odd parity polar parameter with a maximum gap parallel to the a-axis [84]. In low field, the easy axis of magnetisation is c. The recent new feature is the field re-entrance of superconductivity associated with a field re-orientation of the magnetisation from c to b for $H = 12$ T [85].

Despite different attempts, no superconductivity has been reported for ferromagnetic Ce HFC close to P_C [4]. It was claimed that ZrZn$_2$ [86] will be an ideal ferromagnetic superconductor with $T_C = 0.2$ K. The reproducibility of the effect as its link with the sample quality was rapidly controversial [4]. Recently, it was accepted even by the majority of the discoverers that ZrZn$_2$ superconductivity is not intrinsic [87]. Finally, it is amazing that ϵ Fe, the high pressure of iron ($P \geqslant 10$ GPa), may be a triplet superconductor in its PM phase [88,89].

7. Conclusion

Heavy fermion materials give the opportunity to study deeply S phases in an interplay with AF or F. When $T_C \geqslant T_N$, S and AF appear antagonistic. For $T_C \leqslant T_N$, evidence has been given of the coexistence of either AF and un-gapped S (CeRhIn$_5$) or a phase separation between AF and PM states, both superconducting (CeIn$_3$). In FM materials, superconductivity was discovered only in the FM phase with rather large T_{Curie} but presumably in the vicinity of an incipient first order transition which may induce favourable soft modes for S pairing.

Regarding (T, P) phase diagram, an interesting extension is its magnetic field evolution and complementary studies with a weak disorder. In the vicinity of the first order transition at P_C^* or P_x, the inhomogeneous behaviour must be elucidated. For AF systems, the confirmation that a symmetric situation for superconductivity in CeRhIn$_5$ does not occur between AF and PM phases has been recently verified with new experiments realized down to $T = 0.3$ K. Furthermore in magnetic field, a new superconducting phase (presumably associated with long range magnetism) is detected just below P_C [90] on PM side needs to be carefully verified. These studies enter in the conjecture of quantum first order transitions at low temperature which up to now have been neglected. As just underlined in the introduction, the accepted consensus of a second order magnetic QCP in HFC may be often not realised [4].

The superconductivity of HFC has played also an important role in the understanding of unconventional superconductivity: evidence of point and line nodes [5], consequence with the magnetic field Doppler shift of the excitations [91]; proof that any impurity must be treated by the unitary limit [92]; observation of universal law for thermal conductivity [93,94]; possible occurrence of new mixed state with the possible recovery of exotic cores.

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