Uranium-based heavy-fermion superconductors: an experimental survey

A. de Visser and J.J.M. Franse

Van der Waals - Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, Netherlands

The uranium-based heavy-fermion superconductors were discovered almost one decade ago. Here, we present an experimental survey of their interesting normal and superconducting state properties. It appears that most of the unusual normal-state properties can be attributed to the proximity of an antiferromagnetic instability and the presence of competing electronic interactions. The discovery of a superconducting instability in these strongly-correlated electron systems came totally unexpected. The parameters describing the superconducting state yield strong deviations from the standard BCS behaviour. Accumulating evidence has been gathered for a nontrivial superconducting pair function ($L \neq 0$). We illustrate recent developments by a number of prime studies, like high-field measurements and alloying experiments, and give special attention to multicomponent superconductivity in UPt$_3$ and (U, Th)Be$_3$.

1. Introduction

In the past decade a new research area in solid-state physics has received much attention: heavy-fermion physics. As a matter of fact, heavy-fermion systems have been around from the very beginning of the Journal of Magnetism and Magnetic Materials. In 1975, Andres, Graeber and Ott [1] reported the anomalous low-temperature specific heat of CeAl$_3$, with an extremely large electronic specific-heat coefficient: $\gamma = 1630 \text{ mJ/mol K}^2$. In the case of nontransition metals, $\gamma$ attains values of the order of 1 mJ/mol K$^2$, whereas in the transition metals this coefficient can reach values about ten times as high. The anomalously large $\gamma$-value observed for CeAl$_3$ is ascribed to the low-temperature ($T < 10$ K) formation of a highly-correlated electron band close to the Fermi level, due to the hybridization of the $4f$ (Ce) electrons with the s and p electrons of the Al atoms. The partial delocalization of the f electrons gives rise to a description of the low-temperature properties in the Fermi-liquid model [2], with quasiparticles with an effective mass, $m_{\text{eff}}$, of the order of 100 times the free electron mass, $m_e$. Several other systems with high $\gamma$-values have been discovered after 1975, primarily Ce (4f) and U (5f) intermetallic compounds. Among them: CeCu$_2$Si$_2$ [3], CeCu$_6$ [4], CeRu$_2$Si$_2$ [5], UBe$_{13}$ [6], UPt$_3$ [7], UCD$_{11}$ [8] and U$_2$Zn$_{17}$ [9]. These compounds are nowadays known as the heavy-fermion compounds.

The discovery in 1979 of heavy-fermion superconductivity in CeCu$_2$Si$_2$ by Steglich and co-workers [5], later followed by the discovery of superconductivity in UBe$_{13}$ [6] and UPt$_3$ [10], came as a big surprise. The hallmark of heavy-fermion superconductivity is that the very quasiparticles that form the heavy-electron bands take part in the superconducting condensate. The mass renormalization of a factor 100 implies that the Fermi-velocity of the superconducting quasiparticles is of the order of the sound velocity in the solid. This remarkable renormalization is not easily reconciled within the standard BCS theory. However, decisive proof for it is provided by the large anomaly observed in the electronic specific heat at the superconducting phase transition, indicating that virtually all the heavy-electrons become superconducting. The unexpected superconducting instability in a strongly correlated electron gas, where the interactions are princi-
particularly magnetic in nature, has attracted much attention to the heavy-fermion superconductors. It has been clear from the very beginning, that the superconducting properties of these compounds deviate from standard BCS behaviour, thereby giving rise to speculations upon nontrivial pairing ($L \neq 0$) [11].

Other heavy-fermion compounds remain in a Pauli paramagnetic ground state (CeCu$_6$ [12] and CeRu$_2$Si$_2$ [13]), as has been investigated for temperatures as low as 10 mK, or exhibit some type of antiferromagnetism (CeAl$_3$ [14], UCd$_{11}$ [8] and U$_2$Zn$_{17}$ [9]). The (normal-state) properties of most of the heavy-fermion systems indicate the proximity of an antiferromagnetic instability. The large effective mass is built up by a wealth of (competing) electronic interactions and excitations, among which the on-site Kondo (lattice) effect and the inter-site Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction are thought to play the major roles [15].

The heavy-fermion systems are not only of interest from the experimentalists point of view, but also form a challenge for theoretical physicists. An adequate description of strongly correlated electron systems, that focuses on the superconducting and antiferromagnetic instability, is still lacking (see refs. [15–17] for an introduction to the theoretical aspects of heavy-fermion systems). In this article we discuss the main issues that have emerged after one decade of uranium-based heavy-fermion superconductivity. We survey normal and superconducting state properties of UBe$_{13}$, UPt$_3$ and URu$_2$Si$_2$, concentrating on the experimental aspects. We illustrate the unusual properties by a number of prime experiments reported in the literature.

2. Heavy-fermion superconductivity in UBe$_{13}$

The discovery of UBe$_{13}$ as the second heavy-fermion superconductor was reported in 1983 by Ott and co-workers [6]. Resistivity, susceptibility and specific heat data taken on unannealed single-crystalline samples revealed an enormous specific heat coefficient ($\gamma = 1100 \text{ mJ/mol K}^2$) and a superconducting transition at $T_c = 0.85$ K. The large discontinuity observed in the specific heat at $T_c$ (fig. 1) showed convincingly that superconductivity in UBe$_{13}$ is a bulk property. It is interesting to note that superconductivity in UBe$_{13}$ had already been reported in 1973 [18], but at that time was ascribed to precipitated superconducting U filaments in the polycrystalline samples.

The anomalous low-temperature properties of UBe$_{13}$ are clearly demonstrated by the specific heat [19] (fig. 1) and the electrical resistivity [19] (see fig. 2). The steady rise of $\rho(T)$ with decreasing temperature indicates the presence of Kondo-phenomena. Below $\sim 20$ K, $\rho(T)$ levels...
off, but then starts to rise again and a maximum $(\rho_{\text{max}} = 250 \mu \Omega \text{cm})$ appears at $T_{\text{max}} = 2.5 \text{ K}$. The electrical resistivity of UBe$_{13}$ is rather similar to $\rho(T)$ of CeCu$_2$Si$_2$ [20]. At high temperatures, contributions from the single-ion Kondo and crystalline electric field are present, while at very low temperatures a coherent Kondo-lattice is formed, as evidenced by the resistance drop below $T_{\text{max}}$. From the high-temperature susceptibility [19] an effective moment $p_{\text{eff}} = 3.08\mu_B$ is deduced, which falls in between the free-ion values for one f electron (2.54$\mu_B$) and two (3.58$\mu_B$) or three (3.62$\mu_B$) f electrons. Deviations from the Curie–Weiss behaviour appear in the high-temperature susceptibility below $\sim 150 \text{ K}$. The negative Curie–Weiss constant ($\theta = -53$) points to the presence of antiferromagnetic correlations. The low-temperature susceptibility [19] is enhanced, $\chi(T = 1.5 \text{ K}) = 1.5 \times 10^{-2} \text{ emu/mole}$, indicating strong Pauli-paramagnetism, however, the ratio $\chi(T = 1.5 \text{ K}) / \gamma$ is close to 1, as $\gamma$ is enhanced accordingly. Inelastic neutron-scattering experiments performed at 10 K on polycrystalline samples [21], yield a broad quasi-elastic contribution with a width of $13 \pm 2 \text{ meV}$. This energy scale is close to the temperature where deviations from the Curie–Weiss behaviour appear. The high-field magnetization [22] is nearly linear up to 24 T at 4.2 K, while a small increase in the differential susceptibility, $\chi_{\text{diff}} = \Delta \sigma / \Delta H$, is observed above 12 T at 1.25 K. As most of the heavy-fermion compounds exhibit some type of antiferromagnetic order, this might also be expected for UBe$_{13}$. However, sensitive $\mu$SR studies [23] and neutron-scattering experiments yield thus far negative results. Recently, anomalies observed in the low-temperature magnetostriction [24] were taken as evidence for antiferromagnetic order below $T_N = 8.8 \text{ K}$. However, this was not confirmed by a more recent magneto-volume study [25]. An additional anomaly observed in the specific heat at high magnetic field [26] possibly indicates antiferromagnetic order below $\sim 100 \text{ mK}$. Measurements of the thermoelectric power at very high pressures (67 kbar) [27] might indicate pressure induced long-range order at a temperature of a few kelvin. It is obvious that these claims need verification.

2.1. Unconventional superconducting properties of UBe$_{13}$

The superconducting properties of UBe$_{13}$ are quite unusual [6]. First of all a remarkably large jump in the electronic specific heat is observed at $T_c: \Delta C / C \approx 2.5$ (the standard BCS-value is 1.43). Furthermore, the temperature dependence of the specific heat in the superconducting state deviates strongly from the usual exponential behaviour. Instead it was noticed that $C(T)$ varies approximately as $T^3$, suggesting (strong coupling) p-wave superconductivity (point nodes in the gap) [28]. However, subsequent specific-heat data revealed significant deviations from the $T^3$ dependence, indicating the importance of impurity scattering [29,30]. The London penetration depth [31], investigated for several single- and polycrystalline samples, shows also a power law temperature dependence, $\lambda_1 \sim T^2$, which is primarily attributed to impurity scattering. NMR measurements [32] yield a spin-lattice relaxation rate $1/T_1 \sim T^3$, suggesting a gap that vanishes along lines on the Fermi surface. Obviously, the analyses of the different power-law temperature dependencies are at variance with each other. Therefore, the power-law behaviour cannot be

![Fig. 3. The upper critical field of UBe$_{13}$ determined resistively (after Brison et al. [33]). Note the unusual upwards curvature and the quasi-linear behaviour below 450 mK.](image-url)
used at present for the definite determination of the symmetry of the order parameter. The upper-critical field for $T \to 0$, $B_{c2}(0)$, amounts to 13 T [33], an extremely large value for a low-$T_c$ superconductor (see fig. 3). The initial slope, $dB_{c2}/dT \big|_{T \to T_c}$, is nearly vertical which hampers a correct experimental determination. Estimates vary from $-26$ [6] to $-200$ [29] T/K. $B_{c2}$ has an unusual upwards curvature near $T/T_c = 0.5$, and a quasi-linear behaviour below this value, possibly indicating the presence of two different regimes in the superconducting phase.

It is undoubtedly clear that the superconducting properties of UBe$_{13}$ are unconventional. Nevertheless, decisive proof for a nontrivial pairing state cannot be deduced from the experiments discussed above. However, impurity studies have revealed several other remarkable features, yielding further convincing evidence for unconventional superconductivity.

2.2. The superconducting phase diagram of (U, Th)Be$_{13}$

The influence of substitution on the uranium sites of a few percent of several impurity elements on the superconducting transition temperature of UBe$_{13}$ has been studied by Smith and co-workers [34]. Most impurities tested, i.e. Sc, Ce, Lu, Y, Zr, Gd and La cause a monotonic suppression of $T_c$. Also a few percent of Cu or Ga, substituted on the Be sites, suppresses $T_c$, particularly rapidly in the case of Cu [35]. However, most remarkable effects occur for a few percent of Th substituted for U [36]. Specific-heat measurements by Ott and co-workers [37] revealed a new phase transition in the superconducting state for concentrations between $\sim 2$ and $\sim 4$ at% Th (see fig. 4). Tracing $T_c = T_{c1}$ and the temperature, $T_{c2}$ where the second anomaly in $C(T)$ is observed, as function of Th content results in a remarkable phase diagram (fig. 5) [38]. Resistivity and susceptibility measurements prove that the upper transition in the concentration range $0.019 < x < 0.042$ is to the superconducting state. The second phase transition also turns up in the lower critical field $B_{c1}$ [38]. Below $T_{c2}$, $B_{c1}$ rises more rapidly, which can be explained as an
increase of the superfluid density (or a decrease of the effective mass). μSR measurements [38] have revealed that the phase below $T_{c2}$ possesses some magnetic moment (fig. 6). The nature of the low-temperature state is rather puzzling. Several scenarios have been proposed in order to explain the transition at $T_{c2}$ (see ref. [38] and references therein), among which: i) a combined antiferromagnetic and superconducting transition; ii) a transition to a magnetic (time-reversal-violating) superconducting phase; and iii) an antiferromagnetic spin-density wave transition. The first two proposals require a multicomponent (vector) order parameter. It has been argued that the large size of the jump in the specific heat at $T_{c2}$ (see fig. 4) discards the spin-density wave scenario, as the Fermi-surface is already largely consumed by the superconducting transition. The complex superconducting phase diagram (fig. 5) would therefore provide strong evidence for a multicomponent order parameter in UBe$_{13}$. It is clear that the anomalous superconducting and normal state properties of UBe$_{13}$ are still rather puzzling, and that further studies might yield more surprising results. In this respect, we mention the unexpected observation, made recently, for B doping, where for polycrystalline UBe$_{12.97}$B$_{0.03}$ a specific heat jump at $T_c$ is measured, that is almost twice as large as for pure UBe$_{13}$ [39].

3. Spin fluctuations and superconductivity in UPt$_3$

The first detailed investigation of the low-temperature properties of UPt$_3$ was reported by Frings et al. [7] in 1983. Specific-heat measurements revealed an anomalous upturn at low-temperatures, yielding an enhanced $\gamma$-value of 420 mJ/mol K$^2$. The upturn could be described with an additional $T^3 \ln(T/T^*)$-term suggesting the presence of pronounced spin-fluctuation phenomena [40,41]. Measurements on single-crystalline samples showed that the magnetic properties of UPt$_3$ are strongly anisotropic, with the (hexagonal) basal plane as the easy-plane for magnetization. The susceptibility, $\chi(T)$, has a pronounced maximum at $T_{\text{max}} = 18$ K, for a field direction in the basal plane, while no anomaly is observed for a field along the hexagonal (c) axis [7]. For temperatures $T < T_{\text{max}}$, the high-field magnetization [7] shows a metamagnetic transition at $B^* = 20$ T for a field in the basal plane, while a linear behaviour is observed along the c-axis (see fig. 7).
The transition at 20 T is not a metamagnetic transition in the classical sense, because UPt$_3$ does not exhibit long-range order with large moments, as is evidenced by the absence of anomalies in the thermodynamic and transport properties. Therefore, it is often referred to as a pseudometamagnetic or metamagnetic-like. The maximum in the susceptibility is likely related with the stabilization of intersite antiferromagnetic (Ruderman–Kittel–Kasuya–Yosida) interactions that give rise to deviations from the Curie–Weiss law below $\sim$ 50 K. The metamagnetic-like transition is explained by a quenching of the antiferromagnetic spin fluctuations above $B^*$ (the total increase in magnetization at the metamagnetic transition is roughly 0.5$\mu_B$/U-atom). The high-field magnetoresistance $\rho(B)$ reveals a sharp maximum at $B^*$ which is consistent with such a picture [42]. Solid evidence for antiferromagnetic spin-fluctuation phenomena comes from inelastic-neutron scattering experiments [43]. The fluctuation spectrum is quite complex, as different energy scales, are present. Experiments on polycrystalline samples yield a quasi-elastic contribution centered at 10 meV, that is related to the fluctuating local f-moment. The size of the fluctuating moment is of the order of 2$\mu_B$/U-atom, which is of the same order as the effective moment deduced from the high-temperature Curie constant. Experiments on single-crystalline samples reveal a response centered at 6–8 meV, that evidences antiferromagnetic short-range order between nearest neighbour uranium atoms located in adjacent planes. The antiferromagnetic correlations disappear above $T_{\text{max}}$, whereas in-plane ferromagnetic correlations are present till about 150 K. At yet a lower energy (0.5 meV), a second type of antiferromagnetic (in-plane) correlations is found and, surprisingly, also a very weak long-range magnetic order appears with a Neél temperature $T_N = 5$ K [44]. The ordered moment equals $(0.02 \pm 0.01)\mu_B$/U-atom, and is directed along the $b$-axis. The order parameter has an unusual temperature dependence, it continues to grow linearly till far below $T_N$ (see fig. 8). Note that the magnetic diffraction peaks are not resolution limited, indicating that some disorder must be present in the sample. Therefore, one cannot rule out completely that the appearance of the small-moment magnetism is related to crystallographic imperfections.

The discovery of superconductivity below 0.5 K by Stewart et al. [10] in 1984 brought UPt$_3$ into the select class of heavy-fermion superconductors. The unusual combination of superconductivity and strong spin-fluctuation phenomena immediately led to speculations upon a nontrivial pairing state, mediated by an electron–electron interaction. Since then an enormous experimental and theoretical effort had been made to unravel the intriguing aspects of heavy-fermion superconductivity in UPt$_3$ [45]. The most convincing evidence

---

Fig. 7. High-field magnetization of single-crystalline U(Pt$_{1-x}$Pd$_x$)$_3$ at 4.2 K (after Franse et al. [53]). For $x = 0.00$ and 0.05 a metamagnetic-like transition appears for a field in the hexagonal plane.

Fig. 8. Temperature dependence of the elastic peak intensity of $Q = (0.5, 0, 1)$ for UPt$_3$ (after Aeppli et al. [44]). Below $T_N = 5$ K, antiferromagnetic order is observed with a weak ordered moment $(0.02 \pm 0.01)\mu_B$ along the $b$-axis.
for unconventional superconductivity in UPt$_3$ stems from the observation of a multi-component superconducting phase diagram (see section 3.2). Superconductivity in UPt$_3$ is rapidly lost by doping with Pd [46] or Th [47]. Surprisingly, at increasing the Pd or Th concentration, long-range antiferromagnetic order appears [46,48]. The ordered moment amounts to 0.6$\mu_B$ (see fig. 9) for 5 at% Pd [49] and Th [43] alloys, indicating that only part of the fluctuating moment orders. Note that the size of the ordered moment is roughly equal to the increase of the magnetization in pure UPt$_3$ at the metamagnetic-like transition, which suggests a common origin of the field induced moment and the moment stabilized by alloying. The ordering vector is the same as for the small-moment magnetism observed in pure UPt$_3$. The antiferromagnetic order, with a maximum Neél temperature of 5.8 K, is only found in a rather small concentration range. The magnetic and superconducting phase diagram for the U(Pt, Pd)$_3$ [50] and (U, Th)Pt$_3$ [51] compounds is shown in fig. 10. The stabilisation of part of the U moment by alloying does, however, not remove the anomalous behaviour of the low-temperature specific heat, i.e. the contribution from the antiferromagnetic order is superimposed on the large heavy-fermion background. This is likely related to the competition of the RKKY and the Kondo effect, as will be discussed in the next section.

3.1. Competition between RKKY and Kondo-effect in U(Pt, Pd)$_3$

Evidence for competing electronic interactions in heavy-fermion systems has for the greater part been gathered by alloying studies, i.e. by progressive replacements of one of the constituents. In this respect U(Pt$_{1-x}$Pd$_x$)$_3$ is an exemplary system. In pure UPt$_3$ the low-temperature properties are dominated by antiferromagnetic interactions, while by substituting small amounts of Pt by isoelectronic Pd, a crossover to a regime dominated by Kondo interactions is observed. This change in regime is most clearly demonstrated by the electrical resistivity, $\rho(T)$ (see fig. 11) [52]. For pure UPt$_3$, the gradual drop of $\rho(T)$ with decreasing temperature is ascribed to the stabilization of antiferromagnetic correlations, while for a Pd content of only 10 at%, a Kondo-like upturn is observed. The maximum in the susceptibility, $\chi(T)$, at $T_{\text{max}} = 18$ K, and the metamagnetic-like transition at a field of 20 T ($T < T_{\text{max}}$), characteristic of pure UPt$_3$, gradually decrease on alloying and are no longer observed for $x = 0.10$ (see fig. 7) [46,53], lending further support for a suppression of the antiferromagnetic correlations. The $\gamma$-value initially increases with Pd content and passes through a maximum near $x = 0.10$, evidencing that the heavy-fermion properties are preserved. However, $\partial\gamma/\partial B$ changes sign between $x = 0.07$ and $x = 0.10$, (as $\rho(B)$ does at low temperatures [54]), consistent with a crossover...
3.2. Multicomponent superconductivity in UPt$_3$

The unusual combination of strong spin-fluctuation phenomena and superconductivity in UPt$_3$ attracts ample attention, in particular because of the speculations upon electron–electron mediated Cooper pairing. The observation of a power law temperature dependence for the electronic excitation spectrum below $T_c$ is strongly suggestive for an anisotropic gap function and unconventional $L \neq 0$ paring. In particular, detailed measurements of the acoustic attenuation [57] and the penetration depth [31,58] along different crystallographic directions, indicate a so-called hybrid gap function, i.e. a line of zeros at the equator and nodes at the poles. However, the temperature range where the validity of the power laws should be tested ($T \ll T_c$) has not been probed reliably yet. Furthermore, the contribution of impurity scattering might also give rise to deviations from the standard exponential BCS behaviour. Studies of the upper-critical field revealed several unusual features, in particular a kink for a field direction in the basal plane, first observed by Rauchschwalbe et al. [59], and a crossing of the $B_{c2}(T)$ curves for the different crystallographic directions at 200 mK [60]. It has been suggested that the latter feature provides strong evidence for odd-parity superconductivity [61]. Recently, another type of evidence for unconventional superconductivity in UPt$_3$ has come to light, namely the observation by Fisher et al. [62] of a double anomaly in the specific heat at the transition to the superconducting state (see fig. 12). The double transition has now been confirmed by several groups by specific-heat measurements on polycrystalline and single-crystaline samples prepared in different ways [63,64], and has further been observed in other thermodynamic properties, like the thermal expansion [65] and the sound velocity [66,67]. Studies of the effect of a magnetic field on the double transition reveal a phase diagram in the temperature-field plane with three (superconducting) phases, that meet at a tetra-critical point (see fig. 13). The phase diagrams recently determined from specific-heat [63,65], thermal expansion [65] and sound velocity [66,67] measurements, give rather consistent results. The thermodynamic studies essentially confirm the change in slope (at the tetra-critical point) of $B_{c2}(T)$ for fields in the hexagonal plane, as first reported by Rauchschwalbe et al. [59].

From group-theoretical work [68–71] it has been inferred that the double-peak structure in
the specific heat at the superconducting transition might be ascribed to the lifting of the degeneracy of the superconducting vector order parameter by a symmetry breaking field. An appealing speculation is that the symmetry breaking field is provided by the weak antiferromagnetic moment that lies in the basal plane. Neutron-scattering experiments provide some evidence for a coupling of the superconducting and magnetic order parameter [72]. Applying phenomenological Ginzburg–Landau theory, the different order parameters that might describe the unusual superconducting state can be investigated. A comparison with the experimental results indicates that the order parameter belongs to the $E_{1g}$ representation of the hexagonal group (d-wave pairing), however, this is still controversial. Also the existence of a tetra-critical point in the phase diagram is controversial according to thermodynamic constraints [73]. In order to further investigate the multicomponent superconducting phase diagram, alloying experiments have been performed, with U substituted by Y and Pt substituted by Pd [74]. These two impurities behave differently as far as the effect on the distance in temperature between the two peaks in the $C/T$ versus $T$ curve is concerned. In the case of Y this distance remains about the same, whereas for Pd doping up to 0.2 at% this distance is increased. In view of the stabilisation of the uranium moment with

Fig. 12. The double superconducting transition in the specific heat for two polycrystalline UPt$_3$ samples, plotted as $C/T$ versus $T$ (after Fisher et al. [62]). The dashed (solid) lines represent two (one) ideally sharp transition(s), taking into account entropy conservation.

Fig. 13. Phase diagrams of superconducting UPt$_3$ for $H/c$ and $H \perp c$ obtained from sound velocity measurements (after Adenwalla et al. [67]). The insets show a comparison of the phase boundaries determined by sound velocity (▲) and specific heat (+) measurements [63,65].
increasing Pd content (see section 3.1, note that for a 5 at% Y alloy no long-range ordered state has been observed [75]), the increased distance between the two specific-heat peaks could point to a strengthening of the symmetry-breaking field (the uranium magnetic moment), proving in that way the origin of the symmetry-breaking field. These suggestions have to be verified by neutron studies of the uranium moment in these doped UPt₃ compound. Also systematic metallurgical studies on the effect of heat treatment and/or defect structures have not been performed so far. Therefore, definite conclusions as to the interplay of superconductivity and weak antiferromagnetic order can not be drawn at present.

4. Antiferromagnetism and superconductivity in URu₂Si₂

In 1985, Schlabitz et al. [76], Palstra et al. [77] and Maple et al. [78] reported the existence of both an antiferromagnetic and a superconducting transition in the ternary compound URu₂Si₂. The anomalous properties of URu₂Si₂ are clearly illustrated by the electrical resistivity [79], as shown in fig. 14 for current directions along the tetragonal (c) axis and in the basal plane (a axis). On cooling, ρ(T) first increases, passes through a maximum near 70 K, and then drops rapidly, due to the formation of a coherent state. Such a high-temperature behaviour is normally ascribed to the Kondo(-lattice) effect. At 17.5 K a Cr-like anomaly evidences the antiferromagnetic transition. In the specific-heat data, the transition at 17.5 K turns up as a λ peak [76–78]. The exponential temperature dependence of C(T) below T_N suggests that the magnetic order is accompanied by the opening of an energy gap over a part of the Fermi surface (Δ = 100 K), indicating the presence of a spin-density wave. The Cr-like anomaly observed in the resistivity, and the strong increase in the Hall resistance below 17.5 K [80], are in accordance with such an interpretation. Superconductivity occurs below ~ 1.2 K. A large anomaly in the specific heat is observed at the superconducting transition (fig. 15) [76–78,81]. The upper-critical field, B_c2(T), has an unusual shape (see fig. 16) [77]. Although B_c2 is initially isotropic, a large anisotropy appears just below T_c. For a field directed along the c-axis B_c2(0) = 1.8 T, while for a field in the tetragonal plane B_c2(0) has not been determined yet, but is probably of the order of 8 T. The γ-value of URu₂Si₂ is small when compared to UBe₁₃ and UPt₃, however, an analysis of the initial slope of the upper critical field, yields an effective mass in the order of 50mₑ [76], which justifies the classifica-
tion of URu$_2$Si$_2$ as a moderate heavy-fermion superconductor.

Neutron-scattering measurements performed by Broholm et al. [82] confirm the antiferromagnetic order below $T_N = 17.5$ K. As in the case for UPt$_3$, the ordered moment is extremely small: $(0.03 \pm 0.01)\mu_B/\text{U-atom}$. A simple antiferromagnetic structure results, with the moments aligned along the tetragonal axis. However, because of the broad gradual increase of the magnetic moment, as follows from the unusual temperature dependence of the integrated elastic Bragg scattering, and the rather small magnetic coherence length, i.e. in the order of several hundredth Ångström, these results were rather controversial. Recently, neutron-scattering [83] and magnetic X-ray scattering [84] on samples grown with higher-purity uranium, have removed this controversy (see fig. 17). It is remarkable, that the anomalies in the thermodynamic properties at 17.5 K are rather pronounced, while the ordered moments that have been deduced from the neutron studies are not more than a few hundredths of a Bohr magneton. This has led to speculations that the transition at 17.5 K has primarily an electronic nature and that magnetic order is a second order effect.

In order to shed more light on the electronic properties, high-field magnetization and magnetoresistance measurements have been performed [85,86]. Surprisingly, three sharp transitions at 35.8, 37.3 and 39.4 T have been observed (at 1.5 K), for a field directed along the tetragonal axis (see fig. 18). For fields above the three-step magnetization process an uranium moment of the order of $1.5\mu_B$ results. The accompanying large jumps observed in the magnetoresistance point to complex electronic processes (fig. 19). Several mechanisms have been put forward in order to explain this intriguing high-field behaviour: (magnetic) crystal field levels that cross the Fermi level, a reconstruction of the Fermi surface and competing antiferromagnetic interactions. An analysis of the specific-heat and thermal-expansion data [87] above 17.5 K, and the high-temperature susceptibility data [77], point indeed to the presence of crystal-field effects [88]. The low-temperature specific heat, with the enhanced $\gamma$-value of 70 mJ/mol K$^2$, and the transition at 17.5 K, however, indicate that other processes must be taken into account.
The superconducting transition is rather sample dependent, with values for $T_c$ that vary between 0.8 and 1.4 K depending on the quality of starting materials and preparation methods. The earlier specific-heat data showed a rather broad transition or even in some cases, a double transition [89]. However, nowadays, samples prepared with high-purity uranium show one single sharp peak at the superconducting transition (see fig. 17) [81]. Below $T_c$, $C/T$ follows a power law temperature dependence, like observed for UPt$_3$ and UBe$_{13}$, in contrast to the standard BCS exponential temperature dependence. The large anisotropy observed in the upper critical field (fig. 16) points to a strong coupling between the superconducting order parameter and the antiferromagnetic moment along the $c$-axis. The tetragonal symmetry, however, is not removed by this coupling and no splitting of the superconducting transition is expected, contrary to UPt$_3$. The power-law behaviour of the specific heat in the superconducting state with linear and quadratic terms in temperature points to a polar-like state with lines of zero-gap in the tetragonal plane.

5. Concluding remarks

The experimental results reviewed here clearly demonstrate the unequalled anomalous properties of the uranium-based heavy-fermion superconductors. Although many attempts to analyse the anomalous properties within current models have been undertaken, it appears that a satisfying description is in most cases still lacking. In the past years much insight has been gained from phenomenological models. However, we stress the need for microscopic models, that incorporate both superconductivity and antiferromagnetic interactions. We hope that this experimental review will further challenge theoretical physicists to develop such models. Most experiments have been performed on good-quality single-crystalline material. It appears, however, that metallurgical aspects are extremely important, in particular as to the small-moment antiferromagnetism and the (double) superconducting transition. Therefore, improved sample preparation techniques must be among the main goals, before a next series of detailing experiments is started. For experimentalists it will be a challenge to perform measure-
ments at still higher-magnetic fields in order to investigate the suppression of the heavy-fermion state. Also neutron-scattering studies, in order to elucidate the competing electronic interactions will be very helpful. Only very few alloying studies have been performed thus far, often with remarkable results. New alloying studies will be necessary to further unravel the heavy-fermion properties. The unconventional superconducting properties of UBe$_3$, UPt$_3$, and URu$_2$Si$_2$ yield strong evidence for nontrivial ($L \neq 0$) pairing. Therefore, we believe that a wealth of exotic physics waits to be unveiled in the next decade.

Acknowledgement

The work of one of us (AdV) has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences.

References
