Non-fermi liquid behaviour in uranium-based heavy-fermion compounds

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In this chapter, the results are presented of the measurements of the thermal, magnetic and transport properties of a few other uranium intermetallic compounds, which show non-Fermi liquid behaviour (NFL) and/or quantum critical points.

The first compound is a stoichiometric one: $\text{U}_3\text{Ni}_3\text{Sn}_4$. NFL behaviour is observed for $0.5 \text{ K} < T < 5 \text{ K}$ [1], while at lower temperatures the Fermi liquid (FL) state is attained [2]. Upon applying pressure, the FL regime becomes more robust, as it is observed up to higher temperatures [3]. As it will be shown, the data are consistent with the location of $\text{U}_3\text{Ni}_3\text{Sn}_4$ close to (but not at) an antiferromagnetic quantum critical point (QCP).

The second system is the pseudobinary series $\text{U}(\text{Pt}, \text{Pd})_3$. Pure $\text{UPt}_3$ is an unconventional superconductor. Upon alloying with Pd, superconductivity is suppressed and an antiferromagnetic phase with "large" ordered moments is found for $0.006 < x < 0.1$. At the critical concentration $x_c = 0.006$, both the superconducting and antiferromagnetic phase lines meet at a ($T = 0 \text{ K}$) QCP [4].

The last material is the system $\text{URh}_{1-x}\text{Ni}_x\text{Al}$. On the Ni-rich side of the magnetic phase diagram antiferromagnetism exists, while the compounds with a low Ni content order ferromagnetically. The antiferromagnetic and ferromagnetic phases meet at $x = 2/3$, where magnetism vanishes and NFL properties are observed [5].

The experiments, of which the results are presented in this chapter, include:
- specific-heat measurements on \( \text{U}_{3}\text{Ni}_3\text{Sn}_4 \) single crystals at \( 0.1 \text{ K} \leq T \leq 5 \text{ K} \);
- muon spin relaxation experiments on \( \text{U}_{3}\text{Ni}_3\text{Sn}_4 \) single crystals at \( 2 \text{ K} \leq T \leq 10 \text{ K} \);
- resistivity measurements under hydrostatic pressures up to 1.8 GPa on \( \text{U}_{3}\text{Ni}_3\text{Sn}_4 \) single crystals at \( 0.3 \text{ K} \leq T \leq 300 \text{ K} \);
- muon spin rotation experiments on polycrystalline samples of \( \text{U} (\text{Pt}_{1-x}\text{Pd}_x) \) with \( x = 0.007, 0.008 \) and \( 0.009 \) in a transverse field of 0.01 T at \( 0.04 \text{ K} \leq T \leq 2 \text{ K} \);
- resistivity measurements on a polycrystalline sample of \( \text{URh}_{1/3}\text{Ni}_{2/3}\text{Al} \) at \( 0.05 \text{ K} \leq T \leq 300 \text{ K} \).

These results have been published [1.2.5] or are submitted for publication [3.4]. In this chapter, these papers are partially reproduced.

### 7.1. \( \text{U}_3\text{Ni}_3\text{Sn}_4 \)

#### 7.1.1. Non-Fermi liquid behaviour in \( \text{U}_3\text{Ni}_3\text{Sn}_4 \)

The ternary \( \text{U}_3\text{T}_3\text{Sn}_4 \) compounds (where \( \text{T} = \text{Ni}, \text{Cu}, \text{Pt}, \text{Au} \)) crystallize in the cubic \( \text{Y}_3\text{Au}_3\text{Sb}_2 \)-type structure (space group \( I4_3d \)) which is a filled variant of the \( \text{Th}_3\text{P}_4 \)-type [6]. The key feature of this system is that the 5f-hybridization of the \( \text{U} \) atoms can be systematically increased by adding relatively small transition element atoms into voids in the \( \text{Th}_3\text{P}_4 \)-type structure [6]. Indeed, different magnetic ground states (paramagnetism and weak magnetic order) can be found in the \( \text{U}_3\text{T}_3\text{Sn}_4 \) family of compounds, including several that exhibit heavy-fermion (HF) behaviour. Only the \( \text{Cu} \) variant orders magnetically (antiferromagnet at \( T_N = 12 \text{ K} \)) while the other analogues are paramagnetic [7]. Of special interest are the striking departures from the standard FL theory of metals observed in nominally stoichiometric \( \text{U}_3\text{Ni}_3\text{Sn}_4 \) single crystals [1]. The magnetic, transport and specific-heat properties of \( \text{U}_3\text{Ni}_3\text{Sn}_4 \) are consistent with recent theoretical models based upon classical fluctuations near an antiferromagnetic QCP.

Single crystals of \( \text{U}_3\text{Ni}_3\text{Sn}_4 \) and \( \text{U}_3\text{Cu}_3\text{Sn}_4 \) were grown by the Kyropoulos technique from the top of the melt by means of a cooled-seed crystal holder. Bulk charges were first prepared by induction melting with 3:3:4 atomic ratios of pure \( \text{U} \) (depleted), \( \text{Ni} \) or \( \text{Cu} \) and \( \text{Sn} \) respectively, each of at least 99.9% purity. Finally single-crystalline samples of \( \text{U}_3\text{Ni}_3\text{Sn}_4 \) and \( \text{U}_3\text{Cu}_3\text{Sn}_4 \) were
grown by slowly cooling a semi-levitated melt of the bulk charges in a cold crucible using an induction furnace. The rate of cooling was approximately 40 °C/h between 1600-1400°C and 50 °C/h between 1400-800°C. The obtained solid products were about 2-2.5 cm in diameter, and consisted of many crystalline grains, from which single-crystals with dimensions ranging from 0.5 to 2 mm were extracted.

Single-crystal X-ray diffraction (XRD) data, collected at room temperature, are consistent with the cubic space-group $I\bar{4}3d$. The unit-cell parameters of U$_3$Ni$_3$Sn$_4$ and U$_3$Cu$_3$Sn$_4$ are 9.3524(5) Å and 9.4956(5) Å, respectively.

Previously the heat capacity of a U$_3$Ni$_3$Sn$_4$ single crystal [1] in the temperature interval 0.3-5 K was described using the expression:

$$c = (\gamma_0 - \alpha\sqrt{T})T + \beta T^\lambda + D/T^2,$$

(7.1)

where $c_L = (\gamma_0 - \alpha\sqrt{T})T$ is the electronic contribution, $c_L = \beta T^\lambda$ the lattice contribution, and $c_N = D/T^2$ represents the high-temperature form of a nuclear Schottky term [10]. The best-fit coefficients obtained were $\gamma_0 = 0.124$ J/mol K$^{1.5}$, $\alpha = 0.0151$ J/mol K$^{2.5}$, $\beta = 2.07 \times 10^3$ J/mol K$^4$ and $D = 4.62 \times 10^4$ JK/mol$^4$. From the value of $\beta$ we estimated a Debye temperature $\Theta_D = 210$ K [1]. This description is in agreement with a renormalization group theory [8], which predicts $\gamma - \gamma_0 - \alpha\sqrt{T}$ near a zero-temperature antiferromagnetic instability (NFL behaviour). A non-universal scale factor $T_0 = 10$ K was estimated using the fitted value of $\alpha = (15/64)k_B\zeta N(2/\pi\Theta_D)^{3/2}(5/2)$ [11]. This value of $T_0$ corresponds very well with the onset temperature of the non-analytic behaviour of the magnetic susceptibility and resistivity.

Alternatively, recent experimental [12] and theoretical [13] work proposes that NFL behaviour might be caused by a competition between RKKY and Kondo interactions in the presence of atomic disorder leading to a Griffiths phase (large magnetic clusters) close to a QCP. We found that the NFL behaviour of nominally stoichiometric U$_3$Ni$_3$Sn$_4$ single-crystals can also be described by a divergent power law predicted by this model, i.e., $\alpha(T)/T \propto \chi(T) \propto T^{1+\lambda}$ with $\lambda = 0.7$ [1]. The best-fit coefficients yielded electronic, lattice and nuclear contributions that differ by only a few percent from those obtained using the renormalization group theory form of Equation 7.1.

New heat capacity data spanning the temperature interval 0.1-300 K for a U$_3$Ni$_3$Sn$_4$ single-crystal are presented in Figure 7.1. A $^3$He/$^4$He dilution refrigerator was used for attaining temperatures down to 0.1 K, while the high temperature data were obtained in a standard $^4$He
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cryostat using a semi-adiabatic method. The phononic contribution to the high temperature specific heat can be properly estimated for comparison to previous results. Fitting the high temperature data with a Debye function [14] we obtain the value $\theta_D = 208$ K. The solid line in Figure 7.1 is the sum of the numerical solution of the Debye integral and linear electronic contribution.

![Graph of U$_3$Ni$_3$Sn$_4$](image)

**Figure 7.1** - Temperature dependence of the specific heat of single-crystalline U$_3$Ni$_3$Sn$_4$. The solid line is a fit to the data with the sum of the Debye approximation of the phonon contribution and the linear electronic term to the specific heat.

Data for $c/T$ over the temperature range 0.1-5 K are plotted versus the logarithm of temperature in Figure 7.2. The lower temperature data make it clear that the previously calculated nuclear contribution to the specific heat was overestimated [1], since the specific heat data below 0.4 K exhibit a tendency toward saturation, in contrast with what would be expected from an important nuclear contribution to the specific heat, unless a Schottky anomaly (maximum) takes place in the temperature range 0.1-0.2 K. However, this would be very unlikely considering that: i) although quadrupolar interactions from $^{235}$U and $^{62}$Ni could yield a specific heat Schottky anomaly in the measured temperature range, the fact that these isotopes form very small quantities of U$_3$Ni$_3$Sn$_4$ (<1 at.% for the formula unit) makes it difficult to conceive that such contribution would be observable with the relatively large electronic background in U$_3$Ni$_3$Sn$_4$:
ii) the $I = 1/2$ Sn isotopes (that have no quadrupolar interactions) would be expected to give rise to a Schottky maximum only at much lower temperatures.

\[ c = \gamma T + \delta T^{-1} \ln(T/T^*) + c_L + c_N \]

where $T^*$ is a characteristic spin fluctuation temperature [15-16]. The lattice contribution can be fixed using our high temperature Debye fit, while for the nuclear contribution we used $D = 6.45 \times 10^8$ J/K/mol, which corresponds to a typical hyperfine field of $B_{hf} = 0.5$ T for the Sn isotopes with $I = 1/2$, consistent with preliminary Mössbauer experiments on $U_3\text{Ni}_3\text{Sn}_4$ single crystals [17]. Using this expression we obtain a characteristic spin fluctuation temperature $T^*$ of the order of $T_0$ and a Sommerfeld coefficient $\gamma = 0.130$ J/mol$_U$K$^2$. In Figure 7.2, we present the fits to the data using the form of Equation 7.1 for $T > 0.5$ K, and Equation 7.2 for $T < 0.4$ K, considering the same values of $c_L$ and $c_N$ for both temperature ranges. The saturation behaviour of the heat capacity can be interpreted as the onset of a degenerate Fermi liquid regime for

**Figure 7.2** - $U_3\text{Ni}_3\text{Sn}_4$ low temperature specific heat divided by temperature versus log$T$. The lines are fits to the data with Equations 7.1 and 7.2 (see text).
Defining $T_c$, as a crossover temperature to a Fermi liquid state, i.e. the temperature below which Equation 7.2 applies, we obtain $T_c = 0.40(2) \text{ K}$. With this reduced nuclear contribution Equation 7.1 only holds down to $T \approx 0.5 \text{ K}$, which means that there is a crossover region in the temperature range 0.4-0.5 K separating a non-Fermi liquid to a Fermi liquid regime.

An assessment of the potential existence of a Schottky term in the specific heat can only be made by studying the effect of a magnetic field, or the acquisition of data for $T < 0.1 \text{ K}$.

We have characterized the heat capacity, microstructure and crystal structure of $\text{U}_3\text{Ni}_3\text{Sn}_4$ and $\text{U}_3\text{Cu}_3\text{Sn}_4$ single-crystals. $\text{U}_3\text{Cu}_3\text{Sn}_4$ is a heavy-fermion antiferromagnet while nominally stoichiometric $\text{U}_3\text{Ni}_3\text{Sn}_4$ is a nearly magnetic NFL compound.

We find that satisfactory fits of the heat capacity data for $\text{U}_3\text{Ni}_3\text{Sn}_4$ in the temperature range 0.5-5 K always require a dominant electronic term which exhibits a near-square-root temperature dependence, consistent with a theoretical model for NFL systems near a zero-temperature quantum transition from magnetic to non-magnetic states [8] or an alternative Griffiths phase model [13]. It should be noted that the renormalization group theory treatment does not include the effects of disorder, which must be present in real systems to some degree, while the Griffiths phase model includes disorder as a crucial ingredient.

Previously we have undertaken a thorough analysis of the heat capacity and susceptibility of nominally stoichiometric $\text{U}_3\text{Ni}_3\text{Sn}_4$ [1], and conclude that several NFL models (e.g. multichannel Kondo [18] and Kondo disorder [19]) commonly considered in the contemporary literature do not describe the entire data set known for this material. All attempts to include a logarithmic heat capacity term resulted in an unphysically high characteristic temperature scale $T_0$ [1]. On the other hand, the scaling temperature $T_0 = 10 \text{ K}$, obtained from low temperature analysis based on renormalization group theory, is consistent with the onset of the non-analytic behaviour of physical properties in this material. Having extended heat capacity measurements to the lower temperatures we found a crossover to a Fermi liquid state below 0.4 K described by a $T^{-1}\ln T$ term to the specific heat, characteristic of spin fluctuation phenomena. The crossover to a Fermi liquid state is a characteristic of NFL materials that are imprecisely tuned to a QCP [8], due to unfavourable conditions of a control parameter such as pressure, magnetic field, composition or atomic disorder. In the case of nominally stoichiometric $\text{U}_3\text{Ni}_3\text{Sn}_4$, such a non-thermal critical parameter might be vacancy doping which governs the degree of $spdf$ hybridization leading to competition between NFL-FL states. On the other hand, a possible marginal Fermi liquid ground state can not be ruled out. The precise role of small amounts of
disorder detected by XRD analysis in nominally stoichiometric U$_3$Ni$_3$Sn$_4$ single crystals [1] must be investigated by further studies of carefully characterized samples.

The moderate size of the Sommerfeld coefficient $\gamma \sim 0.130$ J/mol K$^2$ and reduction of $\mu_{\text{eff}} = 2.0 \mu_B/U$ [1] from 3.62 or 3.58 $\mu_B$ expected for U$^{3+}$ or U$^{4+}$ free ions, respectively suggest significant hybridization between 5f and itinerant electron states takes place in U$_3$Ni$_3$Sn$_4$. The replacement of the Ni atoms by Cu gives rise to an increase in the number of 3d electrons, leading to a dehybridization of the 5f states with the 3d band. This is consistent with the observed lattice expansion on replacing Ni ($a = 9.3524(5)$ Å) with Cu ($a = 9.4956(5)$ Å), the increase of $\gamma$ by a factor of about 3, and development of antiferromagnetism below 14 K in U$_3$Cu$_3$Sn$_4$ with an effective magnetic moment $\mu_{\text{eff}} = 3.3 \mu_B/U$, corresponding to either a 5f$^2$ or 5f$^3$ uranium configuration. The apparent variation in 5f hybridization with transition element substitution, the crossover from a Fermi liquid ground state in U$_3$Ni$_3$Sn$_4$ to weak antiferromagnetism with $T_N = 14$ K in U$_3$Cu$_3$Sn$_4$, and the observation of NFL properties in U$_3$Ni$_3$Sn$_4$ for the temperature range 0.5-5 K, imply that a QCP should exist in this series of materials over some range of composition and/or pressure in the vicinity of stoichiometric U$_3$Ni$_3$Sn$_4$.

7.1.2. Recovery of the Fermi liquid state in U$_3$Ni$_3$Sn$_4$ under pressure

The specific heat of single-crystalline U$_3$Ni$_3$Sn$_4$ shows a temperature dependence of the type $c/T \sim \gamma^0 T^{\alpha}$ in the temperature interval 0.5-5 K [1,2]. This is consistent with theoretical models for NFL systems near a zero-temperature antiferromagnetic (AF) QCP [8,9]. Below about 0.4 K, there is a crossover to a FL state [2]. It is interesting to compare U$_3$Ni$_3$Sn$_4$ with U$_3$Cu$_3$Sn$_4$. The latter compound is an antiferromagnet with $T_N = 14$ K [2]. Replacement of Ni by Cu results in an increase of the number of 3d electrons, leading to a decrease of the hybridization of the 5f-states with the 3d-band. The hybridization change across the U$_3$(Ni,Cu)$_3$Sn$_4$ series, namely the crossover from a FL ground state in U$_3$Ni$_3$Sn$_4$ to weak antiferromagnetism in U$_3$Cu$_3$Sn$_4$, together with the observation of a NFL region in U$_3$Ni$_3$Sn$_4$ suggests that a QCP may exist in this series of compounds.

In order to confirm the absence of magnetic order in U$_3$Ni$_3$Sn$_4$, zero-field muon spin relaxation ($\mu$SR) experiments were carried out on single-crystalline samples at 2 K and 10 K in the general purpose spectrometer (GPS) of the Paul Scherrer Institute (Switzerland). Best fits to
the spectra were obtained by a depolarization function consisting of a single Gaussian component. The depolarization rate obtained at 10 K is $\Delta = 0.044(3) \, \mu s^{-1}$. This small value of $\Delta$ can be attributed to a random distribution of the Sn nuclei with spin $I = \frac{1}{2}$ and magnetic moment $\mu = 1.0 \mu_N$. At 2 K, the depolarization rate slightly increases to $\Delta = 0.061(2) \, \mu s^{-1}$. This small increase, if significant, could be attributed to the presence of spin fluctuations in the system associated with the NFL behaviour observed in the specific heat below 5 K. No static magnetic order has been detected in these $\mu$SR experiments.

Resistivity measurements were performed on a bar-shaped single crystal of $U_3Ni_3Sn_4$ under hydrostatic pressures up to 1.8 GPa in the temperature range 0.3-300 K. A CuBe piston clamp cell was used with Fluorinert acting as pressure transmitting medium. The pressure values here presented were corrected for an empirical efficiency of 80%. The resistivity was measured using a standard a.c. 4-probe method. Since the crystallographic structure of $U_3Ni_3Sn_4$ is cubic, the resistivity should be isotropic. Therefore, the current was applied along an arbitrary direction.

The low-temperature ($T < 10$ K) resistivity curves at $p = 0$, 0.6 GPa and 1.8 GPa are shown in Figure 7.3. At ambient pressure, the resistivity increases slowly as temperature is decreased below room temperature (RT), reaching a maximum value at $T_{\text{max}} \sim 240$ K. Below this temperature the resistivity decreases and coherent scattering sets in at lower temperatures. A low residual-resistivity value of $\rho_0 = 6 \, \mu \Omega \text{cm}$ is attained, indicating that the single crystal is relatively clean ($\text{RRR} = \rho_{RT}/\rho_0 = 60$).

In order to account for possible changes in the distance between the voltage contacts upon applying pressure, $\rho_{RT}$ was assumed to be pressure independent. This assumption is supported by the resulting negligible pressure dependence of $\rho_0$. Pressure has the effect of reducing the resistivity values. At the lowest temperatures, a tendency to FL-like behaviour $\rho \sim T^2$ is clearly observed (Figure 7.3)
The pressure dependence of the temperature $T_{\text{pFL}}$ below which the resistivity follows the relationship $\rho = \rho_0 + AT^2$ is shown in Figure 7.4. $T_{\text{pFL}}$ follows the pressure dependence $T_{\text{pFL}} = a (p-p_c)^\nu$, with $p_c = -0.04(2)$ GPa, $\nu = 0.50(7)$ and $a = 2.0(1) \text{ K GPa}^\nu$ (Figure 7.4).

At the proximity to an AF QCP, $T_{\text{pFL}}$ is predicted within the theory of Millis [8] to vary as $T_{\text{pFL}} \sim (p-p_c)$, where $p_c$ is the critical pressure (i.e. the pressure value at which the QCP occurs). However, according to the theory of Rosch [20] for the resistivity of HF compounds close to an AF QCP, the linear behaviour of $T_{\text{pFL}} (p)$ depends on the amount of disorder in the system. The less disordered the material is, the narrower the region $T_{\text{pFL}} \sim (p-p_c)$. Above this region, $T_{\text{pFL}} = a (p-p_c)^{1/2}$. In the very clean limit, the linear behaviour of $T_{\text{pFL}} (p)$ is not observed.

The RRR value of 60 of $\text{U}_3\text{Ni}_3\text{Sn}_4$ implies that the range where $T_{\text{pFL}} \sim (p-p_c)$ should be narrow. Due to the limited number of data points at low pressures, it is not possible to clearly distinguish the range in which this linear behaviour is observed. The location of a QCP at $p_c = -0.04(2)$ GPa is in agreement with the observed NFL behaviour in the specific heat of $\text{U}_3\text{Ni}_3\text{Sn}_4$ for $0.5 < T < 5$ K.
The FL resistivity coefficient $A$ is related to the coherence temperature $T_{coh}$. In the FL regime and close to a QCP, $T_{coh}$ is related to the electronic specific-heat coefficient $\gamma$ by $\gamma \propto T_{coh}^{-1}$ [21]. On the other hand, $A \propto \gamma^2$ according to the Kadowaki-Woods relation for HF compounds [22]. The volume dependence of $T_{coh}$ is given by the Grüneisen parameter $\Gamma_{coh}$ defined as

$$\Gamma_{coh} = -\left. \frac{\partial \ln T_{coh}}{\partial \ln V} \right|_{V=V_0} = -\left( \frac{\Delta V}{V_0} \right)^{-1} \ln \frac{T_{coh}}{T_{coh,0}} .$$

where $V_0 \equiv V(p=0)$ and $T_{coh,0} \equiv T_K(p=0)$. Using $\Delta V/V_0 = -\kappa p$, where $\kappa$ is the compressibility, the pressure dependence of $A$ can be written as

$$A(p) = A(p = 0) \exp(-2\kappa \Gamma_{coh} p) .$$

The pressure dependence of $A$ is shown in Figure 7.5. Due to the limited temperature range where $p = p_0 + AT^2$ at ambient pressure, $A(p=0)$ cannot be reliably determined. Fitting the data with Equation 7.4 yields $\kappa \Gamma_{coh} = 0.29(5)$ GPa$^{-1}$ and $A(p=0) = 0.43(4)$ $\mu$ΩcmK$^{-2}$. This value of $\kappa \Gamma_{coh}$ is similar to the value of 0.26 GPa$^{-1}$ obtained for UPt$_3$ [23] from measurements of $\gamma$ and $A$ under pressure (see references cited in Ref. 21).
Since $\gamma \sim A^{1/2}$ and $\gamma(p=0) = 0.13 \text{ J/mol K}^2$ [2], a value of $\gamma(p = 1.8 \text{ GPa})$ of about 0.08 J/mol K$^2$ can be predicted. The reduction of $\gamma$ reflects the fact that, upon pressure, the compound is driven away from the magnetic instability and that the interactions between the quasiparticles are reduced.

![Figure 7.5](image)

Figure 7.5 - Pressure dependence of the resistivity coefficient $A$ of U$_3$Ni$_3$Sn$_4$. The line represents a fit to Equation 7.4.

At high temperatures, a weak maximum in $\rho(T)$ is observed at $T = T_{\text{max}}$, which is attributed to the Kondo effect. $T_{\text{max}}$ increases almost linearly from 240 K at $p=0$ to 265 K at $p = 1.8 \text{ GPa}$. Taking $T_{\text{max}}$ roughly proportional to $T_K$ [24], the increase of $T_{\text{max}}$ reflects the increase of the characteristic temperature of the Kondo effect. Because the observed maximum is weak and the phonon contribution to the resistivity has not been determined, an analysis of $T_{\text{max}}(p)$ in terms of the Grüneisen parameter $\Gamma_K$ is not possible.

In conclusion, upon application of pressure, a FL behaviour is restored in the resistivity of U$_3$Ni$_3$Sn$_4$ at temperatures below $T_{\rho,\text{FL}}$, which increases with increasing $p$. The pressure dependence of $T_{\rho,\text{FL}}$ is consistent with the presence of an AF QCP at $p_c = -0.04(2) \text{ GPa}$. The pressure dependence of the resistivity coefficient $A$ can be analysed in terms of the Grüneisen parameter for the coherence temperature $T_{\text{coh}}$. Upon pressure, the compound is driven away from
the QCP and the increase of $T_{coh}$ is reflected in a decrease of $A$. Also $T_K$, being related to $T_{coh}$, increases upon pressure. The increase of $T_K$ is seen in the increase of the temperature at which $p(T)$ reaches a maximum. The NFL behaviour observed at ambient pressure at temperatures above the FL regime in $U_3Ni_2Sn_2$ is a direct consequence of its proximity to a QCP.

7.2. Magnetic quantum critical point and superconductivity in $U(Pt_{1-x}Pd_x)_3$

For more than a decade now it has been recognized that superconductivity (SC) and magnetism are intimately related in strongly correlated systems, such as the high-$T_c$ cuprates, heavy-fermion materials and organic superconductors [25]. One of the key issues is to identify the nature of the attractive interaction for Cooper pairing. In conventional s-wave superconductors Cooper pairing is mediated by phonons. In strongly correlated electron systems magnetic interactions suppress s-wave SC, and therefore it has been proposed that SC is unconventional and mediated by spin fluctuations [26,27]. Compelling evidence for spin-fluctuation mediated SC [28] has recently been obtained for the magnetically ordered heavy-fermion materials CePd$_2$Si$_2$ and CeIn$_3$. By tuning these materials towards a magnetic quantum critical point (the Néel temperature $T_N \rightarrow 0$ K), by the application of mechanical pressure, a SC phase appeared.

The heavy-fermion superconductor $UPt_3$ ($T_c \sim 0.5$ K) has become an exemplary system to study unconventional SC [25,29]. Because of the unusual coexistence of SC and ferromagnetic (FM) spin fluctuations, the latter signalled by a pronounced $T^3lnT$ contribution to the low-temperature specific heat [30,31], it has been argued that $UPt_3$ is an odd-parity spin-fluctuation mediated superconductor [31,32], in close analogy with superfluidity in $^3$He. The thermodynamic properties and multicomponent SC phase diagram can only be explained by Ginzburg-Landau models, based on an unconventional SC order parameter [29,33-35]. Much attention has been devoted to models where a symmetry-breaking field (SBF) lifts the (spin) degeneracy of the 2D (or 1D) order parameter, which results in a splitting $\Delta T_c = T_c^\ast - T_c$ of the SC phase transition [33-35]. Experimental evidence [36] has been put forward that the SBF is provided by small-
moment antiferromagnetism (SMAF) which sets in at $T_{N,SMAF} \approx 6$ K [37]. This established a clear coupling between magnetism and SC in UPt$_3$.

The nature of the SMAF state itself is the subject of lively debate. It has been observed convincingly through neutron [36,37] and magnetic x-ray [38] scattering only. The ordered moment, $m = 0.02 \mu_B/U$-atom ($T \to 0$), is extremely small, which hampers its detection by standard bulk probes. However, NMR [39] and zero-field muon spin relaxation ($\mu$SR) experiments [40,41] also do not signal the small moment (the early $\mu$SR results of Ref. 42 have not been reproduced thereafter), which strongly suggests that the moment fluctuates at a rate larger than 10 MHz, but on a time scale which appears static to neutrons and X-rays. Therefore, $T_{N,SMAF}$ may be considered to represent a cross-over temperature, rather than being connected to a true phase transition. This is in line with the unusual quasi-linear increase of $m^2(T)$ below $T_{N,SMAF}$ [37].

One of the hallmarks of heavy-fermion materials is the proximity to a magnetic quantum critical point (QCP). In the case of UPt$_3$ pronounced antiferromagnetic (AF) phase transitions can readily be induced by chemical alloying, e.g. by substituting small amounts of Pt by Pd [43] or U by Th [44]. In the U(Pt$_{1-x}$Pd$_x$)$_3$ pseudobinaries, AF order of the spin-density wave type has been observed in the thermal, magnetic and transport properties in the concentration range $0.02 \leq x \leq 0.08$ (see Figure 7.6). Neutron-diffraction experiments [45,46] show that at optimal doping ($x = 0.05$, $T_N = 6$ K) the ordered moment of the so-called large-moment antiferromagnetic phase (LMAF) is substantial, $m = 0.63\pm0.05 \mu_B/U$-atom, and that the magnetic order parameter is conventional. The magnetic structure consists of a doubling of the nuclear unit cell (space group $P6_3/mmc$) along the $a^*-axis$, with the moments pointing along $a^*$. LMAF is also detected by local probe techniques, such as $\mu$SR [41] and NMR [47]. $T_N(x)$ follows a rather conventional Doniach-type phase diagram [48] (see Figure 7.6).

The SMAF phase has clearly a different signature, although the magnetic structure is identical to the one of the LMAF phase. Neutron-diffraction experiments [46] show that SMAF is robust upon alloying with Pd and persists till at least $x = 0.005$. The ordered moment grows upon alloying, but $T_{N,SMAF}(x)$ remains $\sim 6$ K and does not vary at these small Pd concentrations (see Figure 7.6). Notice that $T_{N,SMAF}$ is also insensitive to the application of pressure [36], unlike the LMAF $T_N$ [49].

All these results strongly suggest that SMAF and LMAF are different phases with a distinctly different nature. As a consequence they might also couple differently to SC. Pressure
and alloying experiments [50] are consistent with SMAF acting as SBF. In order to fully understand the nature of the SC phase, it is important to examine the relation (coexistence or competition) between LMAF and SC as well. Therefore, it is crucial to determine the critical Pd concentration for the emergence of the LMAF phase. In this Letter we present μSR experiments carried out on U(Pt$_{1-x}$Pd$_x$)$_3$ samples (x = 0.007, 0.008 and 0.009), which show that the Néel temperature $T_N$ for the LMAF phase is suppressed to 0 K at a Pd concentration $x_{caf} \approx 0.006$. Combined with our earlier results on the suppression of SC by Pd substitution [50-52], we find that $x_{caf} \approx x_{c,sc}$ and that unconventional SC is replaced by LMAF. As we will show, these results provide strong evidence for SC mediated by *ferromagnetic* spin fluctuations.

![Figure 7.6 - Magnetic and superconducting phase diagram for U(Pt$_{1-x}$Pd$_x$)$_3$ alloys. SMAF = small-moment antiferromagnetic phase, LMAF = large-moment antiferromagnetic phase, SC = superconducting phase. Néel temperatures $T_N$ are measured by neutron-diffraction (o and ▲) [46], specific heat (•) [43,46] and μSR (○) (Ref. 41 and this work). Resistively determined superconducting transition temperatures $T_c$ (○) are taken from Refs. 51 and 52. The solid lines are to guide the eye.](image_url)

Polycrystalline U(Pt$_{1-x}$Pd$_x$)$_3$ samples were prepared in a two-step process. First, master alloys of UPt$_3$ and U(Pt$_{0.95}$Pd$_{0.05}$)$_3$ were prepared by arc-melting stoichiometric amounts U (purity 99.98%), Pt and Pd (both with purity 99.999%) on a water-cooled copper crucible in a high-purity argon atmosphere (0.5 bar). Next samples with x = 0.007, 0.008 and 0.009 were
Non-Fermi liquid behavior in other uranium compounds

Prepared by arc-melting together appropriate amounts of the master alloys. After an annealing procedure (see Ref. 41), four thin platelets (thickness 0.8 mm, area 6x10 mm²) were prepared by spark-erosion and glued with General Electric varnish on a silver support, in order to cover an area of 12x20 mm², which corresponds to the total cross-section of the muon beam. Measurements of the residual resistivity on pieces cut from the annealed buttons are consistent with previous results [51,52], which ensures that Pd dissolves homogeneously in the UPt₃ matrix.

Measurements of the positive muon (μ⁺) precession in an applied transverse field of 100 G were conducted at the low temperature μSR facility (LTF) on the πM3 beam line at the Paul Scherrer Institute. The samples were mounted on the cold-finger of a top-loading dilution refrigerator with a base temperature of 0.025 K. As we shall see, the muon spin depolarization rates are very small. Accurate determination of the rates for the samples with x = 0.007 and 0.008 was made possible by the use of a kicker device, which ensures that only one muon at a time is present in the sample and that no other muons are present in the spectrometer [53]. This so-called MORE (Muons On REquest) mode allows to extend the μSR time window to 20 μs, with virtually no accidental background, making it possible to measure relaxation rates as small as 0.001 μs⁻¹.

When positive muons come to rest in the sample they start to precess around the local field, $B_{\text{loc}}$, with a precession frequency $\nu_{\mu} = \gamma_{\mu} B_{\text{loc}}$ ($\gamma_{\mu}/2\pi = 135.5$ MHz/T is the muon gyromagnetic ratio). The internal dipolar magnetic field distribution in general leads to de-phasing of the precession frequency and consequently the signal is damped. As a first step, we have analyzed the μSR spectra using a Gaussian-damped depolarization function $P_{1}(t) = A_{ci} \cos(\omega t) \exp(-\Delta^2 t^2/2)$, where $A_{ci}$ is the asymmetry, $\omega = 2\pi v_{\mu}$ and $\Delta$ is the Gaussian damping rate. At the highest temperatures, $\Delta$ attains a temperature-independent value of $\sim 0.06 \mu$s⁻¹, which is consistent with depolarization due to static $^{195}$Pt nuclear moments [41]. Upon lowering the temperature, $\Delta$ rises progressively, which points to the presence of an additional source of internal dipolar magnetic fields. Improved fit results were obtained using the damped-Gauss muon spin depolarization function

$$P_{1}(t) = A_{1D} \cos(\omega t) \exp(-\Delta_{1} t - \Delta^2 t^2/2)$$ (7.5)

with $\Delta$ fixed at the observed Pt nuclear depolarization rate $\sim 0.06 \mu$s⁻¹. In Equation 7.5 the factor $\exp(-\Delta_{1} t)$ accounts for damping due to the additional magnetic signal. Because of the low damping rates and the large sample size, the asymmetry $A_{1D}$ is close to the maximum value $\sim 0.3$. 
In Figure 7.7 the temperature dependence of $\lambda_E$ is shown for all three samples. At the highest temperatures, $\lambda_E$ is very small (about 0.003 $\mu s^{-1}$) and essentially temperature independent. Upon lowering the temperature, $\lambda_E$ increases, as the additional source of magnetism emerges. The additional source of magnetism becomes stronger when the Pd concentration increases, and we associate its onset temperature with the Néel temperature $T_N$ for LMAF.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure7.7}
\caption{Temperature variation of the exponential relaxation rate, extracted from transverse field (100 G) $\mu$SR spectra using Equation 7.5, for $U(Pt_{1-x}Pd_x)_3$ with $x = 0.007$, 0.008 and 0.009. The solid lines show the quasi-logarithmic increase of $\lambda_{LMAF}$ below $T_N$ and the temperature independent background $\lambda_{BG}$ above $T_N$.}
\end{figure}

In order to extract $T_N$, we write the observed exponential damping rate as $\lambda_E = \lambda_{BG} + \lambda_{LMAF}$, where $\lambda_{BG}$ and $\lambda_{LMAF}$ are due to the background and the LMAF phase, respectively. $\lambda_{BG}$ may account for small variations of the actual depolarization rate due to Pt nuclear moments, as in the fitting procedure we used the fixed value $\Delta = 0.06 \mu s^{-1}$. The super-linear increase of $\lambda_{LMAF}$ is unusual, and can be described phenomenologically, in this limited
temperature interval, by a quasi-logarithmic increase $\lambda_{\text{LMAF}} \sim \ln (T/T_N)$. Making use of this functional dependence and imposing $\lambda_{\text{LMAF}} = 0$ for $T > T_N$, we obtain $T_N$ values of 1.23±0.10 K, 0.78±0.10 K and 0.45±0.15 K for $x = 0.009$, 0.008 and 0.007, respectively.

The assignment of the increase of $\lambda_t$ to the onset of LMAF ordering is based on an analogy with the analysis of the zero-field µSR spectra obtained in the LMAF phase for samples with higher Pd concentrations [41]. For $x \geq 0.01$ the spectra are well described by a two-component depolarization function, consisting of the standard depolarization function of a polycrystalline antiferromagnet and a Kubo-Lorentzian (KL) term, accounting for the spectral distribution of internal fields. Within this phenomenological approach it was observed that the depolarization rate of the KL function, $\lambda_{\text{KL}}$, scales with the ordered moment as determined by neutron diffraction. Our new results indicate that below $x = 0.01$ the LMAF state rapidly weakens. The quasi-logarithmic temperature dependence of $\lambda_{\text{LMAF}}$ below $T_N$ shows that the internal magnetic dipolar fields measured at the $\mu^+$ localization site [54] grow only slowly with decreasing temperature.

In Figure 7.8 we show the magnetic and SC phase diagram for $x < 0.012$, highlighting our new µSR results. For $x = 0.01$, a $T_N$ value of 1.6±0.1 K has been extracted from zero-field µSR data taken on a polycrystal [41], while $T_N = 1.7±0.1$ K was obtained by single-crystal neutron-diffraction [46]. The SC ($T_\text{c}^\text{+}$) phase transition temperatures have been taken from Ref. 51. Our new data for $T_N$ nicely follow the Doniach-diagram type behaviour. From the data in Figure 7.6 and in Figure 7.8, we can safely conclude that the LMAF phase line smoothly extrapolates to $T_N = 0$ at $x_{\text{c,af}} = 0.006$. Locating the magnetic QCP near $x = 0.006$ is consistent with the absence of any signal of the LMAF phase for $x = 0.005$, as was concluded from zero-field µSR measurements on a polycrystal down to 0.04 K [41], as well as from single-crystal neutron-diffraction data down to 0.1 K [46].

Our results show that it is the LMAF phase which presents the magnetic instability in $\text{U(Pt,Pd)}_{1-x}$ and not SMAF. This is consistent with recent transport measurements on polycrystalline $\text{U(Pt,Pd)}_{1-x}$ [55], which show clear deviations from Fermi-liquid behaviour in the vicinity of $x_{\text{c,af}}$, as predicted for a QCP [56].

Inspecting the phase lines $T_\text{c}(x)$ and $T_\text{c}^\text{+}(x)$ plotted in Figure 7.8, we arrive at a most important conclusion, namely the phase diagram two quantum critical points coincide, i.e. the critical concentration for the suppression of SC coincides with the critical concentration for the
emergence of LMAF, $x_{c,s} = x_{c,af} = 0.006$. The fact that Pd substitution results in an anomalously high rate of suppression of $T_c^+$ [51,52], as well as in the onset of the LMAF phase, indicates that this relationship is not coincidental. Stabilization of the LMAF phase completely suppresses unconventional SC. Recent NMR measurements [39], as well as alloying experiments [57,58], provide strong evidence that the SC wave function has odd parity. This in turn implies that Cooper pairing is driven by FM spin fluctuations, rather than by AF fluctuations [26,32]. Therefore, our experiments indicate that doping $UPt_3$ with Pd leads to a shift of the spectral weight from FM to AF fluctuations. This is not uncommon near a QCP, where the many energy scales become comparable and competition between various phases becomes important. Indeed, inelastic neutron scattering experiments carried out on pure $UPt_3$ [59] show that the magnetic fluctuation spectrum is complex and has both AF and FM components.

![Figure 7.8](image)

**Figure 7.8** - Magnetic and superconducting phase diagram for $U(Pt_1-xPd_x)_3$ alloys with $x < 0.012$. The meaning of the symbols is the same as in Figure 7.6. The solid lines serve to guide the eye.

The phase diagram shown in Figure 7.6, differs from the generic phase diagram, proposed for magnetically ordered pure heavy-fermion materials under pressure [28]. In these materials, the approach to the magnetic QCP at $T=0$ is circumvented by the occurrence of a SC ground state. $T_c$ is maximum near the critical pressure $p_{c,af}$, which has been interpreted as evidence for
SC mediated by AF fluctuations. In the case of \( \text{U(Pt.Pd)}_3 \), however, \( T_c \rightarrow 0 \) at the QCP. This is naturally explained if \( \text{SC in U(Pt)} \) is mediated by \( \text{FM spin fluctuations} \), which cannot coexist at any non-zero temperature with an ordered AF state. This is consistent with the notion that the SMAF state is fluctuating in time.

In conclusion, we have shown that the magnetic instability in \( \text{U(Pt.Pd)}_3 \) is due to the LMAF phase rather than SMAF. The \( \text{U(Pt}_{1-x} \text{Pd}_x)_3 \) phase diagram has a critical point at \( x = 0.006 \) where unconventional SC is suppressed and LMAF emerges. The existence of this critical point provides strong evidence for SC mediated by FM spin fluctuations. A complete understanding of the phase diagram and its quantum critical point might prove to be essential in further specifying the SC pairing mechanism. Measurements of the critical exponents of the thermal, magnetic and transport properties in the concomitant non-Fermi liquid regime are needed to identify the character of the magnetic fluctuations [56]. Moreover, the results may be relevant [60] to other strongly correlated systems, such as the high temperature superconductors, which have phase diagrams that exhibit a similar competition between SC and static AF order.

### 7.3. Possible non-Fermi liquid behaviour in \( \text{URh}_{1/3}\text{Ni}_{2/3}\text{Al} \)

Ternary intermetallic compounds with the general formula \( \text{UTX} \) (\( T = \text{late transition metal}, \quad X = p\)-element) crystallizing in the hexagonal \( \text{ZrNiAl}-\text{type of structure} \) exhibit a large variety of magnetic properties [61]. This structure consists of two basal planes, one containing \( \text{U} \) and \( 1/3 \) of \( T \) atoms and the other the remaining \( T \) atoms and \( \text{Al} \). It is well established that the magnetism, which is mainly due to \( \text{U} \) moments, is controlled by the strength of the hybridization between the \( 5f \)- and the ligand-electronic states. On one hand, hybridization delocalizes the \( 5f \)-states and inhibits magnetic ordering, on the other hand, however, it mediates interaction between them and promotes magnetic ordering. It is therefore not surprising that the magnetic properties of these compounds vary as a function of the constituents, which change the hybridization. Recently, we have started a systematic study of quasiternary compounds with substitutions on the transition-metal sites [62]. Here, we report on the magnetic, thermal and transport properties of \( \text{URh}_{1/3}\text{Ni}_{2/3}\text{Al} \), which appears to show anomalous low-temperature behaviour.
URh\(_{1/3}\)Ni\(_{2/3}\)Al was prepared in polycrystalline form by arc melting stoichiometric amounts of the constituting elements (the purity of U was 99.8\%, of the other elements 99.99\%). After remelting and reversing the ingot several times to ensure homogeneity, the resulting ingot was annealed for one week at 700°C in a vacuum-sealed quartz ampoule. After crushing the annealed material under protective atmosphere, X-ray powder diffraction was carried out to verify the structure and lattice parameters. The magnetic susceptibility \(\chi(T) = M/H\) was measured between 1.7 and 320 K in fields up to 5 T on a sample consisting of powder that was fixed in random orientation in a SQUID magnetometer (Quantum Design). Electrical-resistivity measurements were performed in the temperature range 0.05-300 K on a bar-shaped sample by means of a standard four-probe method. The temperature dependence of the specific heat was measured between 0.4 and 40 K by means of a semi-adiabatic heat-pulse method.

In Figure 7.9 we show the temperature dependence of (a) the magnetic susceptibility measured in 0.1 T both in zero-field cooled (ZFC) and field-cooled (FC) modes, (b) the specific heat in the absence of a magnetic field and (c) of the electrical resistivity. It is clearly seen that all the three physical properties deviate from the temperature dependencies expected for Fermi-liquid systems. At low temperatures, the FC susceptibility diverges and the ZFC curve exhibits a clear maximum at 10 K above which the FC and ZFC curves coincide. The maximum suggests the presence of AF correlations and the difference between the FC and ZFC curves reminds one of a spin-glass system (SG). For a SG system, some type of disorder in the compound is required. Indeed, recent X-ray and neutron-diffraction studies suggest a random occupation of Rh and Ni atoms of sites in the plane that does not contain U atoms [63].

The specific heat shown in Figure 7.9b exhibits a low-temperature dependence that can be described by a \(-\ln(T/T_0)\) dependence with \(T_0 = 10\) K \(-\approx -0.9\) (dashed line in Figure 7.9b), suggesting non-Fermi-liquid (NFL) behaviour. However, the data are equally well described by the expression \(c/T = T^{-\lambda}\) with \(\lambda = 0.94\) (solid line in Figure 7.9b). To discriminate between the two descriptions, measurements at even lower temperatures would be required.

At high temperatures, as in normal metals, the electrical resistivity decreases with decreasing temperature. However in URh\(_{1/3}\)Ni\(_{2/3}\)Al, it exhibits a minimum near 10 K and a pronounced increase below this temperature. In other words, the \(aT^2\) term is absent or it is very weak. The resistivity can be fitted to a \(\rho_0 + a(T/T_0)^\alpha\) dependence with a negative \(a\) and \(\alpha = 0.96\). The best fit is shown in Figure 7.9c by the full line. At an even lower temperature of 0.33 mK, a distinct step-like decrease of the resistivity is found (see inset of Figure 7.9) which we tentatively
attribute to a small amount of UNi$_2$Al$_3$ which may be present as impurity phase and which exhibits superconductivity around this temperature [64].

![Figure 7.9](image)

Figure 7.9 - The temperature dependence of the magnetic susceptibility (a), the specific heat (b) and the electrical resistivity of URh$_{1/3}$Ni$_{2/3}$Al (c). The curves through the symbols denote the best fits to the expressions given in the text. The inset of (c) shows the low-temperature detail of the electrical resistivity.

In the limit $T \rightarrow 0$, the Fermi-liquid theory (FL) predicts a temperature-independent contribution to the specific heat, an $aT^2$-type of behaviour of the electrical resistivity and a substantial temperature-independent contribution to the magnetic susceptibility. Deviations from the behaviour predicted by FL theory are referred to as NFL behaviour. One of the hallmarks of NFL is divergence at low temperature of the specific heat divided by temperature, $C/T$, which behaves as $-\ln(T/T_0)$ or as $T^{1/2}$ as found in URh$_{1/3}$Ni$_{2/3}$Al. It is also clear that the magnetic and transport properties of the URh$_{1/3}$Ni$_{2/3}$Al compound cannot be explained solely within the FL theory.

1 A possible off-stoichiometry of an impurity phase of UNi$_2$Al$_3$ ($T_c = 1.2$ K) might reduce its superconducting transition temperature.
References

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