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

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Citation for published version (APA):
4. Non-Fermi liquid behaviour in \( \text{U}_2\text{Pt}_2\text{In} \)

4.1. The \( \text{U}_2\text{T}_2\text{X} \) family of compounds

The family of \( \text{U}_2\text{T}_2\text{X} \) (where T is a transition metal and X is In or Sn) intermetallic compounds has attracted much interest in the past years [1-4], because it may serve as an exemplary system to study hybridization phenomena in 5f-electron compounds. The hybridization strength can be tuned by varying the T and X elements and as a result various magnetic ground states are observed, notably Pauli paramagnetism, spin-fluctuation phenomena and antiferromagnetism. The shortest U-U distance in these tetragonal 2:2:1 compounds is close to the Hill limit (~ 3.5 Å) and is found either along the c-axis or within the ab-plane, depending on the T and X elements. Therefore, this family of compounds may be used to study the influence of the direct \( f-f \) coupling on the magnetic \( f \)-moment direction. On the other hand, it is the strength of the 5f-\( d \)-ligand hybridization that controls the evolution of magnetism across the 2:2:1 series.
4.1.1. Crystallographic structure and overview

In order to carry out a systematic study of the structural and physical properties of the An-T-X series (where An is an actinide), single crystals of several uranium 2:2:1 compounds were grown by L.C.J. Pereira at the Institute for Transuranium Elements (Karlsruhe, Germany) [4].

The compounds were prepared in a polycrystalline form by arc melting together the stoichiometric amounts of the elements (U with a purity better than 99.9% and T and X with a purity 99.999%) in a water-cooled copper crucible under a purified argon atmosphere. Small excess amounts of the X element were added in order to compensate for evaporation losses. The mass losses after arc melting were less than 0.5% of the total mass. The single-phase character of the ingots was checked by means of X-ray analysis, optical microscopy and secondary electron microscopy (SEM).

The polycrystalline batches (mass about 20 g) were then encapsulated in tungsten crucibles and sealed by electron-beam welding under vacuum. Single crystals were grown by a modified mineralization technique [4] using radiofrequency heating with an in situ temperature reading in order to control the melting temperature plateau. The in situ temperature reading made it possible to reduce the mineralization time significantly, from typically 1 week to 5 hours only. The single-phase character of the grown materials was checked by means of X-ray diffraction, optical microscopy and SEM. The single-crystallinity was checked by the X-ray back-reflection Laue method (or by neutron diffraction in the case of some of the compounds).

On several pieces of the single-crystalline materials, a complete structural analysis was carried out on a four-circle diffractometer. The U$_2$T$_2$X compounds crystallize in the ordered tetragonal U$_3$Si$_2$-type of structure (space group $P4/mnbm$) [1], except for U$_2$Ir$_5$Sn, U$_2$Pt$_5$Sn and U$_2$Pt$_5$In, which crystallize in the Zr$_3$Al$_2$-type of structure (space group $P4_2/mmm$) [5,6]. The Zr$_3$Al$_2$-type of structure is a superstructure (doubling of the c-axis) of the U$_3$Si$_2$-type. The U$_3$Si$_2$-type of structure was also reported for the Np [1.4], Pu and Am [7] 2:2:1 compounds and for the rare-earth based ones [8,9].

In the U$_3$Si$_2$-type of structure (Figure 4.1), the U atoms occupy the 4h ($x_1$, $x_1$ +1/2, 1/2) positions, while the T and X atoms occupy the 4g ($y_1$, $y_1$ +1/2, 0) and 2a (0,0,0) positions, respectively, where $x_1 = 0.17$ and $y_1 = 0.37$. The point symmetries of the 4h, 4g and 2a positions are $m2m$, $m2m$ and $4/m$, respectively. On the other hand, the U atoms in the Zr$_3$Al$_2$-type of
structure (Figure 4.2) occupy two different crystallographic positions: 4f \((x_1,x_1,0)\) and 4g \((x_2,x_2,0)\). The X atoms are on the 4d \((0.1/2,1/4)\) positions and the T atoms on the 8j \((x_T,x_T,z_T)\) positions \((x_1 = 0.31, x_2 = 0.16, x_T = 0.13\) and \(z_T = 0.28\)). The point symmetries of the 4f, 4g, 8j and 4d positions are \(m2m, m2m, m\) and \(-4\), respectively.

Figure 4.1 - Unit cell of the \(U_3Si_2\)-type of structure. Each unit cell contains 2 formula units.

Figure 4.2 - Unit cell of the \(Zr_3Al_2\)-type of structure. Each unit cell contains 4 formula units.
In the Zr$_3$Al$_2$-type of structure, the U atoms do not form linear chains as is the case for the U$_3$Si$_2$-type of structure, but form zig-zag chains along the c-axis. This leads to a reduction of the shortest U-U spacing within the basal plane. Close scrutiny of Figure 4.1 and Figure 4.2 reveals that a transition between the two structures involves only minor shifts in the positions of the atoms.

From the structural point of view, U$_2$Pt$_2$In is a special case within the 2:2:1 family of compounds, as poly- and single-crystalline materials form in different structures [10]. The X-ray powder diffraction data taken on polycrystalline U$_2$Pt$_2$In confirm the U$_3$Si$_2$-type of structure with lattice parameters $a = 7.654$ Å and $c = 3.725$ Å. However, U$_2$Pt$_2$In single crystals form in the superstructure of the Zr$_3$Al$_2$-type with lattice parameters $a = 7.695$ Å and $c = 7.368$ Å.

This polymorphism of U$_2$Pt$_2$In shows that the stability of the crystallographic structure depends on the experimental conditions, like pressure and temperature, during the sample preparation process. While preparing the arc-melted polycrystalline sample, the temperatures attained are well above the melting point of U$_2$Pt$_2$In and the cooling process is rather fast. This leads to the formation of the U$_3$Si$_2$-type of structure. During the single crystal growth, i.e., the mineralization process, the temperature range is much reduced (up to $20^\circ$C above the melting point) and the cooling takes place very slowly. Under these conditions, which are closer to equilibrium, the preferred structure is the tetragonal Zr$_3$Al$_2$-type of structure.

The interatomic distances and near-neighbour ($d < 4.2$ Å) positions, calculated for the U$_2$Pt$_2$In single- and polycrystals, are listed in Table 4.1. The number of nearest neighbours for each atom is the same in both structures (since the main effect is the doubling of the c-axis). The average interatomic distances do not change significantly. For the U atoms, the in-plane U(4f)-U(4f) distance decreases, while the in-plane U(4g)-U(4g) increases when moving from polycrystals to single crystals.

As mentioned before, several magnetic ground states are found in the 2:2:1 family of compounds. A review of the properties of the U$_2$T$_2$X compounds has been given in Ref. 11 and some of the results are summarized in Table 4.2. Among these compounds, U$_2$Pt$_2$In and U$_2$Pd$_2$In present heavy-fermion behaviour, as can be concluded from the large value of the linear coefficient of the low-temperature specific heat, which is indicative of an enhanced effective mass.
The electronic structure and related properties of the $U_2T_2X$ compounds mainly originate from the band filling of the transition-metal $d$-states and from the $5f$-moments of the U atoms. A decrease of the $f$-$d$ hybridization strength occurs when the $d$-band is gradually filled, as evidenced by theoretical calculations based on the local density approximation (LDA) [12,13]. Also the evolution of magnetism across the 2:2:1 series (for In and Sn compounds) is shown to be related to the strength of the $5f$-$d$-ligand hybridization [14].

As shown in Table 4.2, in the $U_2T_2In$ series, $U_2Pd_2In$ and $U_2Ni_2In$ order antiferromagnetically with Néel temperatures of 37 and 14 K, respectively, while in the $U_2T_2Sn$ series, the compounds with Pd, Rh, Ni and Pt have antiferromagnetic transitions at $T_N = 41, 28, 26$ and 15 K, respectively.

In all other $U_2T_2X$ compounds, no anomalies have been found in the temperature dependence of the magnetic susceptibility, resistivity and specific heat down to 1.2 K, suggesting paramagnetic ground states. The strong hybridization effects are reflected in reduced effective-moment values with respect to the $U^{3+}$ and $U^{4+}$ free-ion values, as calculated from the Curie-Weiss behaviour of the magnetic susceptibility.

The transition elements in the $U_2T_2X$ compounds do not carry magnetic moments, except for the cases $T = Co$ and $Fe$. Detailed LDA band-structure calculations on $U_2T_2Sn$ ($T = Fe, Co, Ni$) compounds [15] show an hybridization-induced magnetic polarization on the transition-metal atoms in both $U_2Fe_2Sn$ and $U_2Co_2Sn$ (with a magnitude that is almost twice as large for the former). This is considered as indicative of a strong covalent interaction between Fe and U and, to a lesser extent, between Co and U. The polarization of Ni in $U_2Ni_2Sn$ is found to be very small. A negligible polarization characterizes the Sn atoms.

### Table 4.1 - Interatomic distances and near-neighbours numbers (NN) in poly- and single-crystalline $U_2PtIn$

<table>
<thead>
<tr>
<th>Bond (polycrystal)</th>
<th>$U_2S_U$-type</th>
<th>$Zr_2Al$-type (single crystal)</th>
<th>$d$ (Å)</th>
<th>$U_2-U_1$</th>
<th>$U_2-U_2$</th>
<th>$3.583$</th>
<th>$3.925$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U-U$</td>
<td>1</td>
<td></td>
<td>3.725</td>
<td>$U_2-U_1$</td>
<td>$U_2-U_2$</td>
<td>3.687</td>
<td></td>
</tr>
<tr>
<td>$U-U$</td>
<td>4</td>
<td></td>
<td>4.006</td>
<td>$U_2-U_1$</td>
<td>$U_2-U_2$</td>
<td>3.913</td>
<td>4.144</td>
</tr>
<tr>
<td>$U-Pt$</td>
<td>2</td>
<td></td>
<td>2.835</td>
<td>$U_2-Pt$</td>
<td>$U_2-Pt$</td>
<td>2.838</td>
<td></td>
</tr>
<tr>
<td>$U-Pt$</td>
<td>4</td>
<td></td>
<td>2.990</td>
<td>$U_2-Pt$</td>
<td>$U_2-Pt$</td>
<td>3.013</td>
<td>2.975</td>
</tr>
<tr>
<td>$U-X$</td>
<td>4</td>
<td></td>
<td>3.390</td>
<td>$U_2-X$</td>
<td>$U_2-X$</td>
<td>3.414</td>
<td>3.372</td>
</tr>
</tbody>
</table>

$U_1=U(4f), U_2=U(4g)$
**Table 4.2** - Magnetic ground states in the U:Ti:X family of compounds.

<table>
<thead>
<tr>
<th>ground state</th>
<th>$T_N$ (K)</th>
<th>$\mu_{eff}$ (µB/µ)</th>
<th>$\gamma$ (mJ/mol K²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂FeSn</td>
<td>PP</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>U₂CoSn</td>
<td>SF</td>
<td>-</td>
<td>130</td>
</tr>
<tr>
<td>U₂NiSn</td>
<td>AF</td>
<td>26</td>
<td>1.05</td>
</tr>
<tr>
<td>U₂RuSn</td>
<td>PP</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>U₂RhSn</td>
<td>AF</td>
<td>28</td>
<td>0.53</td>
</tr>
<tr>
<td>U₂PdSn</td>
<td>AF</td>
<td>41</td>
<td>1.89</td>
</tr>
<tr>
<td>U₂IrSn</td>
<td>SF</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>U₂PtSn</td>
<td>AF</td>
<td>15</td>
<td>n.d.</td>
</tr>
<tr>
<td>U₂Co-In</td>
<td>PP</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>U₂Ni-In</td>
<td>AF</td>
<td>15</td>
<td>0.92</td>
</tr>
<tr>
<td>U₂Ru-In</td>
<td>PP</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>U₂Rh-In</td>
<td>SF</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>U₂Pd-In</td>
<td>AF</td>
<td>37</td>
<td>1.40</td>
</tr>
<tr>
<td>U₂Ir-In</td>
<td>PP</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>U₂Pt-In</td>
<td>NFL</td>
<td>-</td>
<td>410 *</td>
</tr>
</tbody>
</table>

AF=antiferromagnet, PP=Pauli paramagnet, SF=spin fluctuator, NFL=non-Fermi liquid
n.d.=not determined. * value of $c/T$ at $T=1$ K.

**Table 4.3** - Lattice parameters of the U:Ti:X family of compounds.

<table>
<thead>
<tr>
<th>U₂Si₂-type</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂Fe₂Sn</td>
<td>7.296</td>
<td>3.446</td>
<td>0.472</td>
<td>183.436</td>
</tr>
<tr>
<td>U₂Co₂Sn</td>
<td>7.208</td>
<td>3.606</td>
<td>0.500</td>
<td>187.351</td>
</tr>
<tr>
<td>U₂Ni₂Sn</td>
<td>7.263</td>
<td>3.691</td>
<td>0.508</td>
<td>194.705</td>
</tr>
<tr>
<td>U₂Ru₂Sn</td>
<td>7.482</td>
<td>3.558</td>
<td>0.476</td>
<td>199.178</td>
</tr>
<tr>
<td>U₂Rh₂Sn</td>
<td>7.534</td>
<td>3.625</td>
<td>0.481</td>
<td>205.759</td>
</tr>
<tr>
<td>U₂Pd₂Sn</td>
<td>7.603</td>
<td>3.785</td>
<td>0.498</td>
<td>218.794</td>
</tr>
<tr>
<td>U₂Co-In</td>
<td>7.361</td>
<td>3.431</td>
<td>0.466</td>
<td>185.906</td>
</tr>
<tr>
<td>U₂Ni-In</td>
<td>7.374</td>
<td>3.572</td>
<td>0.484</td>
<td>194.231</td>
</tr>
<tr>
<td>U₂Ru-In</td>
<td>7.505</td>
<td>3.545</td>
<td>0.472</td>
<td>199.672</td>
</tr>
<tr>
<td>U₂Rh-In</td>
<td>7.553</td>
<td>3.605</td>
<td>0.477</td>
<td>205.657</td>
</tr>
<tr>
<td>U₂Pd-In</td>
<td>7.637</td>
<td>3.752</td>
<td>0.491</td>
<td>218.831</td>
</tr>
<tr>
<td>U₂Ir-In</td>
<td>7.596</td>
<td>3.582</td>
<td>0.472</td>
<td>206.679</td>
</tr>
<tr>
<td>U₂Pt-In</td>
<td>7.654</td>
<td>3.725</td>
<td>0.487</td>
<td>218.224</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zr:Al₂-type</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂Ir₂Sn</td>
<td>7.557</td>
<td>7.195</td>
<td>0.952</td>
<td>410.894</td>
</tr>
<tr>
<td>U₂Pt₂Sn</td>
<td>7.668</td>
<td>7.389</td>
<td>0.964</td>
<td>434.460</td>
</tr>
<tr>
<td>U₂Pt₂-In</td>
<td>7.695</td>
<td>7.368</td>
<td>0.958</td>
<td>436.282</td>
</tr>
</tbody>
</table>

When comparing the magnetic properties of the 2:2:1 compounds (Table 4.2) with their lattice parameters (Table 4.3), the following trends are noticeable: i) the ordering temperature increases within each T series (from Fe to Ni, Ru to Pd and Ir to Pt), together with the volume...
and the c/a ratio; ii) the In compounds have less tendency to magnetic order than the Sn compounds, which may be related to the corresponding decrease of the c/a ratio since the volume remains the same in both series.

High-field magnetization studies have been carried out on several polycrystalline samples [16] in order to study the evolution of the magnetocrystalline anisotropy in the U₂T₂X series. In all cases, the magnetization at 4.2 K does not saturate, not even at the highest fields (quasi-static fields up to 38 T [17] and/or pulse fields up to 57 T [18]), which makes it difficult to determine the type of magnetic anisotropy by comparing values of the saturation magnetization for free- and fixed-powder samples. This lack of saturation and the large high-field magnetization values observed in the paramagnetic U₂T₂X compounds may be an indication of field-induced moments on the U or transition-metal sites. At relatively high magnetic fields, the antiferromagnetically ordered compounds undergo metamagnetic transitions. However, the magnetization steps corresponding to these transitions are small and therefore other metamagnetic transitions at even higher fields can not be excluded (e.g. U₂Ni₂Sn has 3 metamagnetic transitions at 30, 39 and 51 T).

4.1.2. Doniach diagram

A quantitative estimate of the importance of f-ligand hybridization in complicated structures can be obtained by means of a tight-binding approximation. The tight-binding approximation has been frequently used to calculate e.g. structural properties, structural stability and the electronic structure of ionic, covalent and metallic systems.

A generalized method based on a muffin-tin orbital model with transition metal pseudopotential model can be applied to calculate the coupling between atomic orbitals of s, p, d or f symmetry, mediated by the free-electron states [19,20]. The parameters are the atomic radii of the respective atoms $r$, the interatomic distance $d$, the angular momentum $l$ ($l = 0, 1, 2$ and $3$ for s, p, d and f orbitals, respectively) and the symmetry of the bond $m$ ($m = 0, 1, 2$ and $3$ for $\sigma$, $\pi$, $\delta$ and $\varphi$ bonds, respectively). The general hybridization-matrix element $V_{\nu\mu}$ is written as [21]

$$V_{\nu\mu} = \frac{\eta_{\nu\mu} \hbar^2}{m_e} \sqrt{\frac{r^{2l+1} r^{2l+1}}{d^{l+1}}}$$

where the coefficients $\eta_{\nu\mu}$ [22] are given by the expression (see Table 4.4)
\[ \eta_{\mu,m} = \frac{(-1)^{l' + m}(l + l')!(2l)!(2l')!}{6\pi \, 2^{-l'/2} \, l'!} \sqrt{\frac{(2l + 1)(2l' + 1)}{((l + m)!(l - m)!(l' + m)!(l' - m)!}}. \quad (4.2) \]

<table>
<thead>
<tr>
<th>( m )</th>
<th>( \sigma )</th>
<th>( \pi )</th>
<th>( \delta )</th>
<th>( \varphi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta )</td>
<td>10 \sqrt{21}/\pi</td>
<td>75 \sqrt{35}/\pi</td>
<td>20(525/2\pi)</td>
<td></td>
</tr>
<tr>
<td>( \mu )</td>
<td>-15 \sqrt{7}/2/\pi</td>
<td>-75 \sqrt{35}/2/\pi</td>
<td>-15(525/2\pi)</td>
<td></td>
</tr>
<tr>
<td>( \mu' )</td>
<td>( \eta' )</td>
<td>( \mu' )</td>
<td>( \mu' )</td>
<td>( \eta' )</td>
</tr>
<tr>
<td>|</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The covalent energy of the coupling between the \( l \) and \( l' \) states is related to the trace of the hybridization matrices \([23]\)

\[ V_{\eta} = \left[ \frac{N_{\eta}}{2l + 1} \sum_{l = -l} V_{\mu,m}^{\ast} \right]^{1/2} = \left[ \frac{N_{\eta}}{2l + 1} \left( V_{\eta,\sigma}^{2} + 2V_{\eta,\pi}^{2} + 2V_{\eta,\delta}^{2} + 2V_{\eta,\varphi}^{2} \right) \right]^{1/2}. \quad (4.3) \]

where \( N_{\eta} \) is the number of nearest neighbours between the atoms with angular momenta \( l \) and \( l' \).

An estimate of the total conduction electron hybridization on the \( f \)-atom, \( V_{\eta,f} \), is then given by

\[ V_{\eta,f} = \left[ V_{\eta,f}^{2} + V_{\rho,f}^{2} + V_{\theta,f}^{2} \right]^{1/2}. \quad (4.4) \]

In Table 4.5, average interatomic distances are given for several compounds of the U\(_2\)T\(_2\)X family. The averages were calculated by considering the number of nearest neighbours for each bond (each U atom has 4 X, 6 T and 7 U nearest neighbours). In the case of the compounds with the Zr\(_3\)Al\(_2\)-type of structure, the mean value was taken as the average distances to the U(4f) and U(4g) atoms. In order to calculate the hybridization for each compound of the 2:2:1 family, a consistent set of atomic radii was taken from bandwidth calculations in an atomic-surface method \([24]\), based on free-atom wave functions evaluated at the Wigner-Seitz atomic-sphere radius (Table 4.6).
Table 4.5 - Average distances ($d_{\sigma}$, $d_{\pi}$, $d_{\sigma^{*}}$), hybridization traces ($V_{\sigma}$, $V_{\pi}$, $V_{\sigma^{*}}$) and total hybridization ($V_{t}$) for the $\text{U}_{2}T_{2}X$ ($X=$In or Sn) family of compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{\sigma}$ (Å)</th>
<th>$d_{\pi}$ (Å)</th>
<th>$d_{\sigma^{*}}$ (Å)</th>
<th>$V_{\sigma}$ (eV)</th>
<th>$V_{\pi}$ (eV)</th>
<th>$V_{\sigma^{*}}$ (eV)</th>
<th>$V_{t}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}<em>{2}\text{Fe}</em>{2}\text{Sn}$</td>
<td>3.211</td>
<td>2.764</td>
<td>3.674</td>
<td>0.178</td>
<td>0.657</td>
<td>0.235</td>
<td>0.720</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Co}</em>{2}\text{Sn}$</td>
<td>3.220</td>
<td>2.782</td>
<td>3.689</td>
<td>0.176</td>
<td>0.572</td>
<td>0.228</td>
<td>0.640</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Ni}</em>{2}\text{Sn}$</td>
<td>3.256</td>
<td>2.838</td>
<td>3.734</td>
<td>0.166</td>
<td>0.460</td>
<td>0.210</td>
<td>0.532</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Ru}</em>{2}\text{Sn}$</td>
<td>3.303</td>
<td>2.842</td>
<td>3.775</td>
<td>0.155</td>
<td>0.977</td>
<td>0.194</td>
<td>1.008</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Rh}</em>{2}\text{Sn}$</td>
<td>3.320</td>
<td>2.880</td>
<td>3.813</td>
<td>0.151</td>
<td>0.825</td>
<td>0.181</td>
<td>0.858</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Pd}</em>{2}\text{Sn}$</td>
<td>3.383</td>
<td>2.949</td>
<td>3.887</td>
<td>0.137</td>
<td>0.703</td>
<td>0.158</td>
<td>0.733</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Ir}</em>{2}\text{Sn}^{*}$</td>
<td>3.323</td>
<td>2.816</td>
<td>3.818</td>
<td>0.150</td>
<td>1.036</td>
<td>0.180</td>
<td>1.062</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Pt}</em>{2}\text{Sn}^{*}$</td>
<td>3.391</td>
<td>2.894</td>
<td>3.887</td>
<td>0.136</td>
<td>0.860</td>
<td>0.159</td>
<td>0.885</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Co}</em>{2}\text{In}$</td>
<td>3.228</td>
<td>2.773</td>
<td>3.694</td>
<td>0.180</td>
<td>0.583</td>
<td>0.226</td>
<td>0.651</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Ni}</em>{2}\text{In}$</td>
<td>3.361</td>
<td>2.822</td>
<td>3.740</td>
<td>0.147</td>
<td>0.476</td>
<td>0.207</td>
<td>0.539</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Rh}</em>{2}\text{In}$</td>
<td>3.331</td>
<td>2.876</td>
<td>3.815</td>
<td>0.154</td>
<td>0.832</td>
<td>0.181</td>
<td>0.865</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Pd}</em>{2}\text{In}$</td>
<td>3.388</td>
<td>2.945</td>
<td>3.889</td>
<td>0.141</td>
<td>0.709</td>
<td>0.158</td>
<td>0.740</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Ir}</em>{2}\text{In}$</td>
<td>3.390</td>
<td>2.938</td>
<td>3.887</td>
<td>0.141</td>
<td>0.785</td>
<td>0.158</td>
<td>0.813</td>
</tr>
<tr>
<td>$\text{U}<em>{2}\text{Pt}</em>{2}\text{In}^{*}$</td>
<td>3.393</td>
<td>2.940</td>
<td>3.892</td>
<td>0.140</td>
<td>0.781</td>
<td>0.157</td>
<td>0.809</td>
</tr>
</tbody>
</table>

*ZrAl$_2$-type structure

Table 4.6 - Atomic radii $r$ (in Å) of the various constituting elements of the compounds in Table 4.5. Taken after Ref. 24.

<table>
<thead>
<tr>
<th>Element</th>
<th>$r$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.744</td>
</tr>
<tr>
<td>Co</td>
<td>0.696</td>
</tr>
<tr>
<td>Ni</td>
<td>0.652</td>
</tr>
<tr>
<td>Ru</td>
<td>1.083</td>
</tr>
<tr>
<td>Ir</td>
<td>1.085</td>
</tr>
<tr>
<td>In</td>
<td>1.930</td>
</tr>
<tr>
<td>U</td>
<td>0.590</td>
</tr>
<tr>
<td>Rh</td>
<td>1.020</td>
</tr>
<tr>
<td>Pt</td>
<td>1.069</td>
</tr>
<tr>
<td>Sn</td>
<td>1.800</td>
</tr>
<tr>
<td>Pd</td>
<td>1.008</td>
</tr>
</tbody>
</table>

The Doniach phase diagram (see Section 2.1) can be constructed by comparing the binding energy of a Kondo singlet

$$k_{B}T_{K} \propto \frac{1}{N(0)} e^{-\frac{1}{2} \lambda_{0} |J|}$$  \hspace{1cm} (4.5a)

with that of a RKKY antiferromagnetic state

$$k_{B}T_{RKKY} \propto J^{3}N(0)$$  \hspace{1cm} (4.5b)

where $N(0)$ is the conduction-electron density of states at the Fermi level and $J$ the exchange-coupling constant. One can estimate a conduction-electron - $f$-electron exchange-interaction parameter $J_{f}$ by assuming a hybridization-mediated mechanism, as treated in the Schrieffer-Wolff [25] and Coqblin-Schrieffer [26] models, according to the proportionality

$$J_{f} \propto \frac{V^{2}_{f}}{E_{f} - E_{s}}$$  \hspace{1cm} (4.6)
where $V_{cf}$ is the hybridization-matrix element for conduction-electron - $f$-electron hybridization and the denominator gives the position of the $f$-level energy $E_f$ relative to the Fermi energy $E_F$. Within a transition-metal series, the distance $E_F - E_f$ can be taken constant since the $f$-level is stable with respect to the Fermi energy [20]. The evolution of $J_{cf}$ can then be traced by calculation of the conduction-electron - $f$-electron hybridization of the compounds. Using the hybridization values calculated for the $U_2T_2In$ and $U_2T_2Sn$ series (Table 4.5), the Doniach-type phase diagram depicted in Figure 4.3 emerges by plotting $T_N$ versus $V_{cf}^2$.

It should be noted that a comparison between the $d_f$ distances in polycrystalline $U_2PtIn$ ($U_3Si_2$-type of structure) and single-crystalline $U_2PtIn$ ($Zr_3Al_2$-type of structure) clearly shows that there is no significant difference between the hybridization effects in the two structures (Table 4.5). Therefore the compounds forming in the $Zr_3Al_2$-type of structure can be included in the overall Doniach diagram.

![Doniach-type diagram for the $U_2T_2X$ ($X = In, Sn$) family of compounds. The dotted lines are guides to the eye.](image)

**Figure 4.3** - Doniach-type of diagram for the $U_2T_2X$ ($X = In, Sn$) family of compounds. The dotted lines are guides to the eye.

The compounds with Fe and Co do not fit in the general trend of the diagram (not shown in Figure 4.3). However, as discussed in the previous section, these compounds may present hybridization-induced magnetic polarization of the transition-metal atoms, and therefore should
be treated separately from the other $U_2T_2X$ compounds when discussing the evolution of magnetism within a Dokiach-type of diagram.

An important point to extract from this diagram is the location of $U_2Pt_2In$ at the border line between magnetic and non-magnetic compounds. This strongly suggests that $U_2Pt_2In$ is close to a magnetic instability and explains its heavy-fermion behaviour.

### 4.2. $U_2Pt_2In$

$U_2Pt_2In$ has a number of unrivalled properties. The heavy-electron properties of $U_2Pt_2In$ were first reported by Havela et al. [2]. Specific-heat experiments carried out on a polycrystalline sample [2.3] in the temperature range 1.3-40 K revealed the presence of a pronounced upturn of the electronic specific heat divided by temperature ($c/T$) below about 8 K, insensitive to an applied field of 5 T. The $c(T)$ data could be fitted with a $T^3InT$ term below 5 K, providing evidence for spin-fluctuation phenomena. The resulting linear coefficient of the electronic specific heat $\gamma(T\rightarrow0\,K)$ amounted to 415 mJ/molK², which classifies $U_2Pt_2In$ as a heavy-electron compound. In line with this, the electrical resistivity, $\rho(T)$, of $U_2Pt_2In$ was found to show a weak maximum around 80 K and coherence effects at low temperatures [3], which could be attributed to the Kondo-lattice effect. The magnetic susceptibility, $\chi(T)$, shows deviations from the Curie-Weiss behaviour below about 150 K [2]. In the limit $T\rightarrow1.2\,K$, $\chi$ is enhanced and continues to rise. No sign of magnetic ordering has been observed.

More recently, data taken on a polycrystalline sample [27] showed that $\rho(T) = \rho_o + AT$ in the temperature range 1.4-6 K. This led to the suggestion that $U_2Pt_2In$ might be a good candidate to study non-Fermi liquid (NFL) phenomena.

In order to probe and investigate the NFL behaviour in $U_2Pt_2In$, it is of interest to study the thermal, transport and magnetic properties of single crystals at lower temperatures ($T < 1.2\,K$). As discussed in Section 2.5, only a few stoichiometric compounds (like e.g. CeNi$_2$Ge$_2$) show NFL properties at ambient pressure. $U_2Pt_2In$ is the first U compound exhibiting NFL behaviour without chemical substitution, pressure or magnetic field as a control parameter. In this section, results of magnetization ($2\,K \leq T \leq 350\,K$, $B \leq 35\,T$), resistivity ($0.3\,K \leq T \leq 300\,K$),
magnetoresistance \((B \leq 38 \text{ T})\), specific-heat \((0.1 \text{ K} \leq T \leq 180 \text{ K})\), specific-heat in field \((B \leq 8 \text{ T})\) and thermal-expansion \((0.35 \text{ K} \leq T \leq 200 \text{ K})\) experiments carried out on \(\text{U}_2\text{Pt}_2\text{In}\) single crystals are presented (for details on the preparation and characterization of the single crystals see Section 4.1.1 and Ref. 10).

**4.2.1. Magnetization**

Magnetization measurements were performed on several single crystals (with a mass of 10-50 mg) using a SQUID magnetometer (Quantum Design) in the temperature range 2-350 K and in applied fields up to 5.5 T. In addition, magnetization measurements were carried out in high magnetic fields up to 35 T at 4.2 K in the Amsterdam High-Field Facility.

The magnetizations \(M_a(B)\) and \(M_c(B)\) at some selected temperatures are shown in Figure 4.4a, where \(a\) and \(c\) refer to the crystallographic direction along which the magnetic field is applied. In both cases, the magnetization is linear in fields up to 5.5 T. The slope \(dM/dB\) is always higher for \(B \parallel c\) than for \(B \parallel a\), though the anisotropy is not substantial. \(M(T = 2 \text{ K})\) reaches the value of 0.25 \((0.21) \mu_\text{B} / \text{f.u.}\) in a field of 5.5 T applied along the \(c\)- (\(a\)-) axis. No hysteresis in \(M_a\) and \(M_c\) was observed. Magnetization measurements for \(B \parallel c\) at 4.2 K were carried out up to 35 T (Figure 4.4b). No significant deviation from a linear behaviour was observed. In the maximum field, \(M_c(35 \text{ T}) = 1.48 \mu_\text{B} / \text{f.u.}\). These results are similar to the ones obtained on polycrystalline samples up to 35 T [17] and 57 T [18]. In the polycrystalline data, a weak non-linearity was observed, which was not found in the single-crystal data. This non-linearity is due to the saturation of magnetic impurities in the polycrystalline sample (about 2% of ferromagnetic \(\text{UPt}\) was present as a second phase [3]). The data taken on free and fixed powder are identical, which is another indication that the magnetic anisotropy is rather weak in this compound.

The temperature variation of the d.c. susceptibility \((M/H)\), \(\chi_a(T)\) and \(\chi_c(T)\), is presented in Figure 4.5 for \(B = 0.1 \text{ T}\). The susceptibility is anisotropic, with the \(c\)-axis as the easy axis of the magnetization. This anisotropy persists in the whole temperature range (up to 350 K).

At low temperatures, a clear difference between \(\chi_a\) and \(\chi_c\) is observed. \(\chi_a\) continues to increase as the temperature is lowered down to 2 K, while \(\chi_c\) displays a broad maximum (Figure 4.5). Tracing the derivatives, \(d\chi/dT\), shows that the maximum occurs at \(T_{\text{max}} = 7.9(3) \text{ K}\). The
Non-Fermi liquid behaviour in $U_2$Pt$_2$In

relative height and width of the maximum do not change significantly with the applied field strength (from 0.005 to 5.5 T). This type of behaviour is frequently observed in systems which exhibit exchange-enhanced Pauli paramagnetism. The maximum in $\chi_c$ is indicative of the stabilization of short-range antiferromagnetic correlations along the c-axis [28,29].

Above 10 K, the susceptibility follows a modified Curie-Weiss law, $\chi = \chi_0 + C/(T-\theta)$. For $B \parallel c$, the parameters obtained are $\chi_0 = 1.1 \times 10^{-8} \text{m}^3/\text{mol}_U$, $\theta = -62 \text{K}$ and $\mu_{\text{eff}} = 2.6 \mu_B/\text{U}$, while for $B \parallel a$, $\chi_0 = 1.1 \times 10^{-8} \text{m}^3/\text{mol}_U$, $\theta = -63 \text{K}$ and $\mu_{\text{eff}} = 2.2 \mu_B/\text{U}$. The fitted Curie-Weiss behaviour is represented by the lines in Figure 4.5. The near-equality of the paramagnetic Pauli temperatures $\theta$ reflects the weak magnetic anisotropy in this system. The $\mu_{\text{eff}}$ values are considerably reduced with respect to the free-ion values for $U^{3+}$ and $U^{4+}$ of 3.62 $\mu_B$ and 3.58 $\mu_B$, respectively, which points to a strong $V_{cf}$ hybridization.

The magnetization data do not show any sign of long-range magnetic order down to 2 K. In order to investigate the presence of possible spin-glass effects, magnetization measurements were performed after zero-field cooling and field cooling to 2 K. However, no difference was observed for $0.01 \text{T} \leq B \leq 5.5 \text{T}$, indicating the absence of a spin-glass ground state.

![Figure 4.4](image)

**Figure 4.4** - a) Field dependence of the magnetizations $M_a$ and $M_c$ of $U_2$Pt$_2$In for several temperatures and b) high-field magnetization at 4.2 K for $B \parallel c$ (different symbols represent different field pulses). The lines are linear fits through the data points.
4.2.2. Resistivity

Resistivity measurements were carried out on bar-shaped crystals with typical dimensions 3×1×1 mm$^3$, for electrical currents along the a- and c-axis, in the temperature range 0.3-300 K using a $^3$He system. A standard a.c. four-point method was used with an excitation current of the order of 300 μA. The excitation current was varied in order to check for Joule-heating effects.

The resistance curves for $I \parallel a$ and $I \parallel c$ are shown in Figure 4.6a for temperatures below 10 K and in Figure 4.6b for temperatures below 300 K. The $R(T)$ values are normalized to the room temperature values $R_{RT}$. For both $I \parallel a$ and $I \parallel c$, the resistivity $\rho_{RT}$ amounts to 220 ± 20 μΩcm. The experimental error in $\rho_{RT}$ is mainly due to the uncertainty in the determination of the distance between the voltage contacts. Upon cooling, $\rho_{ac}(T)$ starts to rise and a weak broad maximum is observed at about 80 K followed by a relatively sharp decrease at
lower temperatures, typical of coherence effects in heavy-fermion compounds. As shown in Figure 4.6, the resistivity is anisotropic: $\rho_c > \rho_a$ for $T < 150$ K.

![Figure 4.6 - Resistivity (normalized to the room temperature values) of U$_2$Pt$_2$In for $I\parallel a$ and $I\parallel c$ for $T < 10$ K (a) and $T < 300$ K (b).](image)

Clearly, the resistivity curves do not obey the Fermi-liquid expression $\rho \sim T^2$ at low temperatures. Instead, as shown below, $\rho \sim T^\alpha$ with $\alpha < 2$.

If the resistivity below a certain temperature $T^*$ can be expressed by

$$\rho = \rho_0 + aT^\alpha,$$

then the exponent $\alpha$ can be calculated by

$$\alpha = \frac{d\ln(\rho - \rho_0)}{d\ln T}.$$  \hspace{1cm} (4.8a)

However, using Equation 4.8a may result in significant errors in $\alpha$ due to the uncertainty in evaluating the residual resistivity $\rho_0$, especially when $\alpha$ is small. Alternatively, the following expression can be used:

$$\alpha = 1 + \frac{d\ln \rho}{d\ln T}.$$  \hspace{1cm} (4.8b)
One can define an effective temperature-dependent exponent $\alpha_{\text{eff}}(T)$ by applying equation 4.8b at all temperatures. The effective exponent can be identified with $\alpha$ if $\alpha_{\text{eff}}(T) = \text{constant}$ in a certain temperature range.

Figure 4.7 shows $\alpha_{\text{eff}}(T)$ computed from the derivative of the smoothed low-temperature resistivity curves. For $I \parallel a$, one obtains $\alpha_{a} = 1.25(5)$ below about 1 K. For $I \parallel c$, $\alpha_{\text{eff}}(T)$ does not attain a constant value and thus $\rho_{c}$ does not follow a clear $T^{n}$ law down to 0.3 K. Assuming that $\alpha_{\text{eff},c}(T)$ levels off below 0.3 K in a way similar to $\alpha_{\text{eff},a}(T)$, the rough estimate $\alpha_{c} \approx 0.9(1)$ can be made.

![Graph](image)

**Figure 4.7** - Effective exponent $\alpha_{\text{eff}}$ of the resistivity of U$_{3}$Pt$_{2}$In for $I \parallel a$ and $I \parallel c$.

With these $\alpha$-values the following residual resistivities result: $\rho_{0,a} = 0.53 \rho_{RT}$ and $\rho_{0,c} = 0.95 \rho_{RT}$, i.e. $\rho_{0} \approx 115 \mu \Omega \text{cm}$ for $I \parallel a$ and $\rho_{0} = 210 \mu \Omega \text{cm}$ for $I \parallel c$. The residual resistivity values are large, which is normally taken as evidence that some disorder is present in the crystals. However, this has not been confirmed by single-crystal X-ray [10] and neutron-diffraction [30] experiments. The structure refinement confirms the high crystalline quality. The possibility of site inversion (e.g. Pt and In inversion) is also excluded by the neutron-diffraction refinement. Moreover, because the residual resistivity depends strongly on the direction of the applied...
current, it is clear that besides impurities other scattering mechanisms contribute to \( \rho_0 \). It should be noted that the low-temperature resistivity data were taken on several single crystals, all showing the same behaviour.

### 4.2.2.1. Magnetoresistance

Transport properties in a magnetic field provide an important tool to investigate the non-Fermi liquid state. In general, a magnetic field is expected to restore the Fermi liquid state, as for the case of a proximity to a quantum critical point. If a compound is driven away from the magnetic instability, the suppression of magnetic correlations should be observable in the resistivity.

In Figure 4.8, the temperature dependence of the resistivity is shown in a field of 8 T applied along the different crystallographic directions. Below 4.2 K the magnetoresistance (MR) for \( I \parallel c \) is negative for both \( B \parallel c \) (longitudinal configuration) and \( B \parallel a \) (transverse configuration). At the lowest temperatures, the \( \rho(T) \) curves show a tendency to level off. For \( I \parallel a \), the curves obtained in the two transverse configurations (\( B \parallel b \) and \( B \parallel c \)) are essentially the same, i.e. a negative MR at high temperatures and a positive MR below 0.8 K. At the lowest temperatures, an approximate \( \rho \sim T^2 \) behaviour is observed in 8 T. In the longitudinal configuration, the magnetoresistance is always positive and shows no tendency to level off at low temperatures.

Assuming that the \( \rho(T) \) curves follow power laws of the type \( \rho \sim T^\alpha \), the exponent \( \alpha \) can be estimated using equation 4.8b. The effective exponent obtained for different magnetic fields is plotted in Figure 4.9 for the transverse configurations (since for \( I \parallel a \) the data for \( B \parallel b \) and \( B \parallel c \) are almost identical, only \( B \parallel c \) is shown). The low-temperature value of \( \alpha \) increases with increasing magnetic-field strength, reaching values close to 2 for 8 T, as expected for a Fermi liquid. The field evolution of the exponent \( \alpha \) is shown in Figure 4.10, which clearly illustrates that there is a tendency towards a Fermi-liquid \( \rho \sim T^2 \) law near 8 T.
Figure 4.8 - Temperature dependence of the resistivity of U$_3$Pt$_2$In in a field of 8 T applied along the main crystallographic directions.

Figure 4.9 - Effective exponent $\alpha$ of the resistivity of U$_3$Pt$_2$In in magnetic fields in the transverse configuration ($B \perp I$).
Non-Fermi liquid behaviour in $U_2Pt_2In$

In Figure 4.10 and Figure 4.12, the magnetoresistance in the longitudinal and transverse configurations is shown at 0.48, 1.3, 4.2 and 10 K. The magnetoresistance curves show several unusual features.

In the longitudinal configuration, a negative MR is obtained when current and field are applied along the c-axis. A weak upward curvature is observed at the lowest temperatures at high fields. On the other hand, when current and field are applied along the a-axis the magnetoresistance is positive and approximately follows a $\Delta \rho/\rho \sim B^2$ law.

In the transverse configuration, the MR obtained for $I \parallel c$ is also negative with $\Delta \rho/\rho$ values higher (in absolute value) than for $B \parallel I \parallel c$. No tendency to upward curvature is visible at the lowest temperatures. In the $B \perp I \parallel a$ case, the MR values are negative at low fields, pass through a minimum and then become positive. The position of the minimum increases with temperature: $B_{\text{min}} \sim 3.5, 5$ and 14 T at $T = 0.48, 1.3$ and 4.2 K, respectively (see Figure 4.13 for the high-field MR at 4.2 K).
Figure 4.11 - Magnetoresistance of U$_3$Pt$_3$In in the longitudinal configuration ($B \parallel I$) at temperatures as indicated.

Figure 4.12 - Magnetoresistance of U$_3$Pt$_3$In in the transverse configuration ($B \perp I$) at temperatures as indicated.
According to Ref. 31, the magnetoresistance of weakly- or non-disordered metals in the NFL regime close to an antiferromagnetic quantum critical point (see Section 2.3) can be separated into spin and orbital effects. For the spin effects, small magnetic fields will suppress the antiferromagnetic fluctuations as the compound is driven away from the QCP. This suppression of the fluctuations will reduce the amount of scattering and the MR will be negative. For localized-moment paramagnets, applying a magnetic field results in a net polarization of the disordered magnetic moments and thus to a reduction of their scattering contribution to the resistivity. The magnetoresistance is related to the correlation function $\langle S_i S_j \rangle$ between the ion spins and therefore to the low-field magnetization $M$ [32]:

$$\frac{\Delta \rho}{\rho} = -a \left( \frac{M}{M_{\text{sat}}} \right)^2,$$

(4.9)

where $\Delta \rho/\rho = [\rho(B,T) - \rho(0,T)]/\rho(0,T)$, $a > 0$ and $M_{\text{sat}}$ is the saturation magnetization obtained at extremely high fields. Since the magnetization of U$_2$Pt$_2$In is proportional to the field, it follows that $\Delta \rho/\rho = -B^2$. 

**Figure 4.13** - High-field magnetoresistance of U$_2$Pt$_2$In at 4.2 K for $I \parallel a$ and $B \parallel c$. The line is a polynomial fit through the data points. Note: the oscillations observed are an artefact of the averaging procedure.
On the other hand, for the orbital effects a positive MR is expected, which varies initially as $B^2$, then crosses over to a linear behaviour in $B$ and finally saturates at high fields [31].

In addition, if the Lorentz force would be responsible for the $B^2$ behaviour observed, then one would expect a weak positive $B^2$ contribution to the transverse MR and, to a lesser extent, to the longitudinal magnetoresistance. A comparison of the MR values obtained for the different configurations (Figure 4.14) shows that this contribution is very weak and not significant. In fact, the opposite effect is observed: for $I \parallel c$, $\Delta \rho/\rho$ is less negative for $B \parallel I$ than for $B \perp I$, while for $I \parallel a$ the positive contribution is clearly stronger in the longitudinal configuration than in the transverse one.

![Figure 4.14](image)

**Figure 4.14** - Magnetoresistance of U$_2$PtIn at $T = 0.48$ K for $B \parallel I$ and $B \perp I$.

When summarizing the magnetoresistance data, a competition of a positive and a negative contribution is clearly found. At low fields, the negative contribution is always dominant, except when $B \parallel I \parallel a$. As the field increases, the positive contribution becomes dominant. The high field experiments show that the MR has a tendency to saturate at extremely high fields (about 100 T). This is also predicted by the theory of magnetotransport in nearly antiferromagnetic metals [31].
A proper analysis of the relative weight of the different contributions is difficult due to their competition, although it is evident that the negative contribution, associated with a polarization of the moments, is stronger when the current is applied along the c-axis.

A closer inspection of the zero-field resistivity curves for $I \parallel c$ reveals the presence of a shoulder in $\rho(T)$ centered at about 7 K. The shoulder becomes more clear in a $\rho$ versus log$T$ plot (Figure 4.15). This anomaly is not observed for $I \parallel a$. It should be noted that $B \parallel c$ is the direction for which a maximum at $T_{\text{max}} = 7.9$ K is observed in the magnetic susceptibility. This suggests that the resistivity shoulder may be related to short-range antiferromagnetic correlations along the c-axis. The field effect ($B \parallel I, B \leq 5$ T) on the shoulder is shown in Figure 4.15. The shoulder is suppressed under the influence of the magnetic field and becomes very faint at 5 T. As antiferromagnetic fluctuations tend to be suppressed by a magnetic field, also the shoulder should be gradually suppressed with field. However, suppression of the magnetic fluctuations was not observed in the susceptibility in fields up to 5.5 T. Since the shoulder in $\rho(T)$ is very faint, it may possibly be more sensitive to this effect than the maximum in $\chi(T)$.

Another important point is that $\rho_0$ varies significantly with the applied magnetic field, which clearly shows that the residual resistivity is not uniquely due to impurity or defect scattering.

![Graph](attachment:image.png)

Figure 4.15 - Temperature dependence ($T \leq 15$ K) of the resistivity of $U_2Pt_2In$ for $B \parallel I \parallel c$. 
4.2.3. Specific heat

The specific heat of U$_3$Pt$_2$In was measured on several single-crystalline samples, using a semi-adiabatic technique in a bath cryostat above 1.5 K, while data below 5 K were taken in a $^3$He system (0.3 K < $T$ < 5 K) and a dilution refrigerator (0.1 K < $T$ < 0.7 K) employing the relaxation method. The results are shown in Figure 4.16 in a plot of $c/T$ versus $\log T$. Below 10 K, $c/T$ shows an upturn and instead of attaining a constant value in the limit $T \rightarrow 0$ K, as expected for a Fermi liquid, $c/T$ diverges logarithmically, which is one of the hallmarks of a non-Fermi-liquid ground state.

![Figure 4.16 - Low-temperature specific heat of U$_3$Pt$_2$In divided by temperature as a function of $\log T$. The line is a $c/T - \ln(T/T_0)$ fit.](image)

The data below 6 K are well described by

$$\frac{c}{T} = \gamma_1 - \delta \ln \left( \frac{T}{T_1} \right) = -\delta \ln \left( \frac{T}{T_0} \right)$$

with $\gamma_1 = 406.8(5)$ mJ/mol$_U$K$^2$ and $\delta = 89.9(5)$ mJ/mol$_U$K$^2$. Here, $T_1 \equiv 1$ K and $T_0 = \exp(\gamma_1/\delta) = 92(1)$ K. In this case, $\gamma_1$ is the value of $c/T$ at 1 K and not the enhanced-Sommerfeld coefficient, as usually observed for heavy-fermion compounds.
Of main importance is that U$_2$Pt$_3$In is one of the few stoichiometric systems exhibiting non-Fermi liquid behaviour with a strong logarithmic divergency of the specific heat. Moreover, this logarithmic divergency has been found in the data over almost 2 decades of temperature.

At higher temperatures, the dominant contribution to the specific heat is the lattice contribution. Since no samples of the non-magnetic compound Th$_2$Pt$_3$In were available, the phonon contribution to the specific heat could not be estimated. However, an approximation can be given by the Debye function

$$c_v = 3R \left[ 12\left(\frac{\theta_D}{T}\right)^3 \int_0^T \frac{x^3}{e^x - 1} dx - \frac{3\theta_D}{T} \right].$$  \hspace{1cm} (4.11)

This expression is valid for the specific heat at constant volume ($c_V$) but, experimentally, the specific heat at constant pressure ($c_p$) is obtained. The difference between $c_V$ and $c_p$ can usually be neglected as it will be shown in Section 4.2.4.

The Debye function has been tabulated in Refs. 33 and 34 and can therefore easily be compared to the experimental data. The high-temperature slope of the specific heat of U$_2$Pt$_3$In can be approximated by a linear electronic term $c_{el} = \gamma T$ with $\gamma = 88$ mJ/molK$^2$. Using this value, $c_{ph} = c - c_{el}$ is in good agreement with the Debye function calculated with $\theta_D = 175$ K (see the line in Figure 4.17a). However, the subtracted linear term has an unusually large coefficient, about 10 times higher than expected, which possibly indicates that the Debye function underestimates the lattice contribution to the specific heat of U$_2$Pt$_3$In.

The electronic contribution obtained after subtracting the Debye function from the total specific heat is plotted in Figure 4.17b. In this contribution, the logarithmic divergency is observed up to about 35 K. However, the high-temperature linear term above 50 K is extremely large. The entropy associated with it is also too large to account for a possible crystalline electric-field effect.

Assuming that the low-temperature phonon contribution to the specific heat is $c_{ph} = \beta T^3$, with $\beta$ obtained from $\theta_D = 175$ K, the low-temperature entropy associated with the electronic specific heat can be determined by the integral of $(c-c_{ph})/T$.

$$S_{el}(T) - S_{el}(T = 0.1K) = \int_{0.1K}^T \frac{c_{el}(T)}{T} dT.$$  \hspace{1cm} (4.12)

The entropy is shown in Figure 4.18. In the $S=\frac{1}{2}$ two-channel Kondo effect, the entropy is predicted to saturate at $\frac{1}{2}R\ln2$ ($= 2.88$ J/molK) before continuing to increase at higher
temperatures (see Section 2.3). For U$_2$Pt$_3$In, there is no clear evidence for this effect.

Figure 4.17 - (a) Lattice specific heat (per mole formula unit) of U$_2$Pt$_3$In. The dashed line is the Debye function with $\theta_D = 175$ K. (b) Lattice ($c_{\text{Debye}}$) and electronic ($c_{\text{el}}$) contributions to the total specific heat $c/T$. Notice the logarithmic $T$ scale. The full line is a guide to the eye.

Figure 4.18 - Entropy (per mole U) derived from the electronic specific heat of U$_2$Pt$_3$In.
4.2.3.1. Specific heat in field

In order to investigate the robustness of the non-Fermi-liquid state in U$_3$Pt$_2$In in an external magnetic field, specific-heat measurements were performed in the temperature range 0.1-1 K with $B \parallel c$ up to field values of 8 T. In Figure 4.19, the results obtained in the dilution refrigerator ($T < 0.7$ K) are shown. The straight line represents the zero-field $c/T = -\delta \ln(T/T_0)$ behaviour taken from Figure 4.16.

![Figure 4.19 - Specific heat divided by temperature versus logT for U$_3$Pt$_2$In under magnetic fields applied along the c-axis. Insert: nuclear specific heat $c_N \equiv c - c_{\text{el}}$ versus $T^2$ for $T < 0.25$ K; the lines are functions $c_N = D_T T^2$ (see text below).](image)

A strong enhancement of the specific heat is observed at low temperatures as the field strength increases. As will be shown below, this enhancement is predominantly due to the specific heat of the In nuclei.

A nuclear contribution to the specific heat arises when an interaction lifts the degeneracy of the states, which are characterized by different orientations of the nuclear moments. This interaction may be provided by an external magnetic field, an effective hyperfine field or an electric field gradient. The energy levels, $e_{mn}$, of a nucleus with spin quantum number $I$ in a magnetic field and in an electrical field gradient with axial symmetry are given by [35,36]
\[ \frac{\varepsilon_m}{k_B} = -\alpha' m + P \left[ m^2 - \frac{I(I+1)}{3} \right] \quad (m = -I, -I+1, \ldots, I) \quad (4.13) \]

with
\[ \alpha' = \frac{\mu B_{\text{eff}}}{k_B I} \quad \text{(magnetic-interaction parameter)} \quad (4.14a) \]
\[ P = \frac{3e^2 qQ}{4k_B I(2I-1)} \quad \text{(quadrupole-coupling constant)} \quad (4.14b) \]

where \( \mu = g_N \mu_N \) is the magnetic moment of the nucleus (\( \mu_N \) is the nuclear magneton and \( g_N \) the nuclear \( g \)-factor) and \( B_{\text{eff}} \) is the effective field at the nucleus arising from the hyperfine field \( B_{hf} \) and/or an external field \( B \). \( eQ \) is the component of the electric-field gradient tensor along the high-symmetry axis and \( Q \) is the nuclear quadrupole moment. One has \( Q = 0 \) for \( I = 1/2 \), while \( Q = 0 \) for nuclei in a cubic environment.

The exact expression for the nuclear specific heat (of the Schottky-anomaly type) is
\[ c_N = \frac{\sum_{m=-I}^{I} \sum_{n=-I}^{I} (\varepsilon_m - \varepsilon_n) \exp \left( -\frac{\varepsilon_m + \varepsilon_n}{k_B T} \right)}{R \left( k_B T \right)^3 \sum_{m=-I}^{I} \sum_{n=-I}^{I} \exp \left( -\frac{\varepsilon_m + \varepsilon_n}{k_B T} \right)} \quad (4.15) \]

From this expression it follows that at low temperatures \( c_N \sim \exp(-1/T) \), while at high temperatures \( c_N \sim T^2 \). A maximum occurs at \( T_{\text{max}} = (\varepsilon_{m+1} - \varepsilon_m)/k_B I \) and the entropy associated with \( c_N \) equals \( R \ln(2I+1) \).

Since the measurements are usually made at temperatures well above \( T_{\text{max}} \) of \( c_N \) (for most metals the maximum is found at \( T \ll 0.1 \) K), one can use a high-temperature expansion of \( c_N \) in a power series of \( 1/T \):
\[ c_N = \sum_{l \geq 2} D_l T^{-l} \quad (4.16) \]

The coefficients \( D_l \) are determined by the various moments of the energy levels. If the magnetic field is parallel to the symmetry axis of an axially symmetric electric-field gradient, the first two coefficients are given by [37]
\[ \frac{D_2}{R} = \frac{1}{4} I(I+1) \alpha' \quad (4.17a) \]
\[ \frac{D_3}{R} = -\frac{1}{4} I(I+1)(2I-1)(2I+3) \alpha'^2 P - \frac{1}{8} I(I+1)(2I-3)(2I+1)(2I+3)(2I+5) P^3 \quad (4.17b) \]
If the quadrupole interaction is zero (P=0), all odd coefficients in Equation 4.16 vanish. In most cases, the first term is sufficient for fitting the experimental data: $c_\infty = D_2 T^{-2}$.

In Table 4.7, the nuclear spin quantum number, magnetic moment and quadrupole moment of the isotopes that may contribute to the nuclear specific heat of U$_2$Pt$_2$In (i.e. the isotopes with $I \neq 0$) are shown. Considering the abundancies and the nuclear moments of these isotopes, one can assume that the origin of the nuclear specific heat shown in Figure 4.19 is mainly due to the nuclei of In ($^{113}$In and $^{115}$In have a nuclear magnetic moment that is one order of magnitude higher than $^{195}$Pt and $^{238}$U). The In nuclei have a spin of 9/2 and the average (taking into account the relative abundancies) magnetic and quadrupole moments are equal to $\mu = 5.5403 \mu_N$ and $Q = 0.81 \times 10^{-21} \text{cm}^2$, respectively.

<table>
<thead>
<tr>
<th>isotope</th>
<th>abundance (%)</th>
<th>$I$</th>
<th>$\mu$ (\mu_N)</th>
<th>$Q$ (10$^{-21}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{113}$In</td>
<td>4.29</td>
<td>9/2</td>
<td>5.5289</td>
<td>0.799</td>
</tr>
<tr>
<td>$^{115}$In</td>
<td>95.71</td>
<td>9/2</td>
<td>5.5408</td>
<td>0.81</td>
</tr>
<tr>
<td>$^{195}$Pt</td>
<td>33.83</td>
<td>1/2</td>
<td>0.60950</td>
<td>0</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>0.72</td>
<td>7/2</td>
<td>-0.35</td>
<td>4.936</td>
</tr>
</tbody>
</table>

The insert in Figure 4.19 shows the field effect on the specific heat, obtained by subtracting the zero-field function. $\Delta c = c - c_{\text{zero-field}} = c - (\gamma_1 - \delta \ln T)$. This figure shows that $\Delta c$ varies approximately linearly with $T^{-2}$. Extracting values of $D_2$ from the $B = 6$ T and 8 T curves (for the lower fields the scatter is rather large after subtracting the zero-field curve), one obtains $B_{\text{hit}} = 51.5$ mT and a quadrupole-coupling constant $P \approx 0.9$ mK. With these parameters, values of $D_2$ can then be calculated for $B = 2$ and 4 T (insert of Figure 4.19).

Although above 0.3 K the nuclear contribution to $c/T$ is small, the data in Figure 4.19 show $c/T$ values a few percent higher than for the zero-field data in this temperature range. There are two possible explanations for this behaviour: i) it can be attributed to small errors in the calibration of the thermometer on the sapphire plate in field. In fact, data taken above 0.4 K in a $^3$He system with another calibrated thermometer did not show this effect. Notice that a small calibration error does not affect significantly the overall $c(T)$ curve; ii) the nuclear contribution might overshadow a decrease of the electronic term at low temperatures. As under influence of a magnetic field, a compound is pushed away from a magnetic instability, the low-temperature $c/T$ will level off in order to recover the Fermi liquid behaviour. A decrease of $c/T$ at low
temperatures has to be accompanied by an increase at higher temperatures because of the conservation of entropy [38].

In zero field, the calculated value of $D_2$ amounts to $4.303 \times 10^{-5} \text{JK/mol}_\text{In}$, which indicates that the nuclear contribution can be neglected with respect to the U electronic specific heat ($T \geq 0.1 \text{K}$). This value of $D_2$ is about 40 times larger than the one calculated for pure In in its tetragonal structure [39]. This is possibly explained by a substantial enhancement of the hyperfine interactions, which is not an unusual phenomenon in intermetallic compounds [40].

This large nuclear contribution hampers the study of the field effect on the non-Fermi liquid contribution. As a result, the proposed scaling properties of the specific heat (see Section 2.3) cannot be investigated. Magnetoresistance measurements showed a recovery of the Fermi liquid behaviour at the lowest temperatures. This seems, however, not to be confirmed by the specific-heat data.

### 4.2.4. Thermal expansion

Thermal-expansion measurements were performed on a single crystal of U$_2$Pt$_2$In in the temperature intervals 0.3-10 K (using a $^4\text{He}$ system) and 1.7-200 K (using a $^3\text{He}$ bath cryostat). Data were taken along the a-axis ($L = 4.478 \text{mm}$) and the c-axis ($L = 1.570 \text{mm}$). The linear thermal-expansion coefficients, $\alpha_a$ and $\alpha_c$, obtained along the a- and c-axis, respectively, are shown in Figure 4.20, together with the temperature dependence of the volume expansion coefficient $\alpha_v = 2\alpha_a + \alpha_c$ (tetragonal structure).

The coefficients $\alpha_a$ and $\alpha_c$ are both positive and show a rapid increase with increasing temperature below 3 K. $\alpha_a$ varies approximately linearly with temperature for $3 \text{K} < T < 60 \text{K}$ and levels off at higher temperatures. $\alpha_c$ is much larger than $\alpha_a$ below 12 K, but $\alpha_c = \alpha_a$ above this temperature. The observed anisotropy in the thermal-expansion coefficients shows that when lowering the temperature below the coherence temperature, the c-axis shrinks more rapidly than the a-axis. The coefficient of the volume expansion shows, besides the heavy-fermion contribution, an unusual quasi-linear temperature dependence between 12 K and 60 K.
Figure 4.20 - Low-temperature ($T \leq 15$ K) linear thermal-expansion coefficient of U$_2$Pt$_3$In along the a- and c-axis. The line corresponds to 1/3 of the derived coefficient of the volume expansion. Insert: $\alpha_v/3$ ($T \leq 200$ K).

Figure 4.21 - Difference between the specific heats of U$_2$Pt$_3$In at constant pressure and volume.

The thermal-expansion data can be used to estimate the specific heat at constant volume. The difference between $c_v$ and $c_p$ can be expressed as
\[ c_\text{V} - c_\text{p} = -\frac{9\alpha V_m T}{\kappa} \quad . \]  

(4.18)

Using the compressibility value of \( \kappa = 0.68 \) Mbar\(^{-1} \) (see Section 6.1), the difference \( c_\text{p} - c_\text{V} \) shown in Figure 4.21 is obtained. The relative value \( (c_\text{p} - c_\text{V})/c_\text{p} \) is limited to \( 3\% \) up to 200 K. Therefore, the specific-heat data presented in the previous section do not need to be corrected for the difference between \( c_\text{p} \) and \( c_\text{V} \).

The thermal expansion can be related to the specific heat by means of a Grüneisen parameter. A physically meaningful Grüneisen parameter emerges when part of the entropy can be written as \( S_i(T/\Gamma_i) \) where \( \Gamma_i \) is a (volume dependent) characteristic temperature of the entropy term. The Grüneisen parameter is defined as \([41]\)

\[ \Gamma_i = \frac{\frac{\partial S_i}{\partial V}}{T \left( \frac{\partial S_i}{\partial T} \right)_V} = -\frac{\partial \ln T_i(V)}{\partial \ln V} \quad . \]  

(4.19)

Taking into account the relations

\[ \alpha_\chi = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \kappa \left( \frac{\partial S}{\partial V} \right)_T \]  

(4.20a)

and

\[ c_\text{V} = T \left( \frac{\partial S}{\partial T} \right)_V \quad . \]  

(4.20b)

where \( \kappa \) is the isothermal compressibility

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad . \]  

(4.20c)

one obtains

\[ \Gamma = \frac{\alpha_\chi V}{\kappa c_\text{V}} \quad . \]  

(4.21)

It is useful to define an effective temperature-dependent Grüneisen parameter

\[ \Gamma_{\text{eff}}(T) = \frac{\alpha_\chi(T) V_m}{\kappa c(T)} \quad . \]  

(4.22)

where \( V_m \) is the molar volume \( (V_m = 6.568\times10^{-5} \) m\(^3\)/mol\(m\) for U\(_3\)Pt\(_2\)In\). The temperature dependencies of \( V_m \) and \( \kappa \) are usually small and can be neglected.
In general, if the effective Grüneisen parameter is constant in a certain temperature interval, one can identify $\Gamma_{\text{eff}}$ with the Grüneisen parameter for the particular mechanism that governs the thermal properties in that temperature range [41,42].

The temperature dependence of the effective Grüneisen parameter of $U_2Pt_3In$ is shown in Figure 4.22. At high temperatures, the Grüneisen parameter amounts to $\Gamma_{\text{ph}} = 3.1$. This value can be compared to the value of 2 normally found for the phonon contribution in metals. $\Gamma_{\text{eff}}$ increases smoothly as the temperature is decreased down to about 40 K, below which a fast increase occurs, reflecting the heavy-fermion character of $U_2Pt_3In$. At the lowest temperature of 0.35 K, $\Gamma_{\text{eff}} = 56$. Similar values have been observed in other heavy-fermion compounds [43]. The small anomaly near 0.5 K is not significant, as it is an artefact of the experiment. The continuous increase of $\Gamma_{\text{eff}}(T)$ at low temperatures hampers the extraction of the bare NFL form from the thermal-expansion data.

![Figure 4.22](image.png)

**Figure 4.22** - Low-temperature ($T \leq 15$ K) dependence of the effective Grüneisen parameter of $U_2Pt_3In$. Insert: $\Gamma_{\text{eff}}$ at temperatures up to 180 K.
4.3. **Discussion**

4.3.1. **Hybridization phenomena and evidence for NFL behaviour**

The inter-uranium distances in U$_3$Pt$_3$In, shown in Table 4.1, are slightly above the Hill limit (∼3.5 Å) for uranium [44]. From this, one may conjecture that U$_3$Pt$_3$In would order magnetically, as it is located on the magnetic side in the Hill plot. However, in the past decade it has become clear that the electronic structure in many U compounds is governed by the 5f-5f-5f-ligand overlap and that the Hill-limit picture is too simple.

If the magnetic ordering temperatures of the In and Sn 2:2:1 compounds are plotted versus the square of the calculated hybridization matrix elements, a Doniach-like phase diagram results (Section 4.1.2 and Ref. [45]). Interestingly, U$_3$Pt$_3$In is close to the border line between magnetic and non-magnetic compounds.

The participation of 5f-electrons in the bonding in light-actinide intermetallics, leads to a compression of the 5f charge densities towards the bonding directions, which are given primarily by the shortest inter-actinide directions [46]. In the UTX (1:1:1) family, it was found as an empirical rule that the magnetic moment is always directed perpendicular to the shortest U-U direction. However, exceptions for this rule have been found in the 2:2:1 family. In U$_3$Rh$_2$Sn [47] the shortest U-U distance is located along the c-axis and yet the U moments are aligned along the c-axis. In the case of U$_3$Pt$_3$In, the shortest U-U distance is located in the tetragonal plane. The susceptibility data show that antiferromagnetic correlations (of the Ising type) are found along the c-axis. This complies with the shortest U-U distance rule, as reported for the 1:1:1 compounds.

The analysis of the resistivity leads to a description with a low-temperature term $T^"(T\rightarrow0\text{K}), with \alpha = 1.2 and 0.9 for the a- and c-axis, respectively. The absence of the usual Fermi-liquid $T^2$ term gives strong support for non-Fermi liquid behaviour in U$_3$Pt$_3$In. The specific-heat measurements on a single crystal down to 0.1 K show a clear logarithmic divergency of $\epsilon/T$ below 6 K, i.e. over almost two decades of temperature. This puts the NFL behaviour in U$_3$Pt$_3$In on firm footing.
Neutron-diffraction studies carried out on single-crystalline U₃Pt₃In [30] confirmed that the crystallographic structure is of the Zr₂Al₂-type. The structure refinement showed a perfect stoichiometry in the sense that no significant improvements in the final refinement factor could be achieved by allowing the occupational parameters to vary (including possibilities of atomic disorder like, e.g., Pt-In site inversion). At 1.5 K, exhaustive scans along different reciprocal lattice lines revealed no evidence of any long- or short-range magnetic ordering.

Polarized neutron-diffraction experiments carried out on the same U₃Pt₃In single crystal [30] probed the local susceptibility at the two U sites: U(4f) and U(4g). The observed magnetization density in the unit cell, constructed using the maximum entropy method, is reproduced in Figure 4.23 for $T = 10$ K and $B = 4.6$ T applied along the [101] direction. The site susceptibility of the U atoms at the 4f positions is almost twice that of U(4g).

![Figure 4.23 - Magnetization density ((001) projection) induced at 10 K by a field of 4.6 T in the [101] direction of U₃Pt₃In. Contour levels are from -0.01 (dashed) to 0.41 in steps of 0.02 $\mu_B$/Å³. Taken from Ref. 30.](image)

Considering the average (room temperature) interatomic distances for the two U sites (Table 4.1), the hybridization on the U(4f) and U(4g) atoms can be calculated separately in the same way as described in Section 4.1.2. The $p$, $d$, and $f$ hybridizations at the two sites and the total conduction-electron - $f$-electron hybridization are shown in Table 4.8. As can be seen, the
hybridization is smaller for the U(4f) atoms than for the U(4g). Within the Doniach phase diagram \((T_s \text{ versus } V_f)\) presented before, one may conjecture that the hybridization on the 4f sites "pushes" \(\text{U}_2\text{Pt}_2\text{In}\) towards magnetic order in a stronger way than the hybridization at the 4g sites. Therefore, a stronger site susceptibility may be found at the 4f sites.

**Table 4.8:** \(p, d, f\) and total hybridization at the two \(U\) sites in \(\text{U}_2\text{Pt}_2\text{In}\).

<table>
<thead>
<tr>
<th></th>
<th>(V_{1s} \text{ (eV)})</th>
<th>(V_{1s} \text{ (eV)})</th>
<th>(V_{1s} \text{ (eV)})</th>
<th>(V_{1s} \text{ (eV)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(U(4f))</td>
<td>0.136</td>
<td>0.764</td>
<td>0.164</td>
<td>0.793</td>
</tr>
<tr>
<td>(U(4g))</td>
<td>0.144</td>
<td>0.781</td>
<td>0.151</td>
<td>0.825</td>
</tr>
</tbody>
</table>

The ratio of the orbital and spin magnetic moments was also estimated and found to be approximately the same for the two sites. \(|\mu_1/\mu_s| \approx 1.8\). This value corresponds to values frequently found for \(U\) ions in intermetallic compounds [48] and indicates an appreciable quenching of the orbital moment, when compared to the free-ion \(U^{3+}\) and \(U^{4+}\) configurations, due to hybridization processes.

The total moment measured at 10 K in a field of 4.6 T applied along the [101] direction was 0.139(9) \(\mu_B/\text{f.u.}\). This moment is about 24% lower than that found in the magnetization measurements (Section 4.2.1). Although the magnetization was not measured for fields applied along the [110] direction, a value of 0.182 \(\mu_B/\text{f.u.}\) at 4.6 T can be estimated by considering \(M_{[101]} \approx M_c \cos^2 \phi + M_s \sin^2 \phi\), where \(\phi\) is the angle between the [101] and the \(c\) direction. The neutron experiments are only sensitive to the magnetization associated with the localized 5f-states, which is normally larger than that obtained by bulk measurements. The difference is attributed to a negative conduction-electron polarization [49]. Thus, the positive discrepancy in the case of \(\text{U}_2\text{Pt}_2\text{In}\) is unusual and at least two possibilities exist for this additional conduction-electron polarization: it can arise from either the \(\text{Pt} 5d\)-electrons or a fraction of the \(U 5f\)-states that is delocalized [30]. A positive conduction-electron polarization has also been found in the heavy-fermion superconductor \(\text{UPd}_2\text{Al}_3\) [50].

**4.3.2. Single-ion scaling and the two-channel Kondo model**

Irrespective of the microscopic mechanism responsible for the NFL behaviour in \(\text{U}_2\text{Pt}_2\text{In}\), it is of interest to investigate single-ion Kondo scaling of the NFL properties. Within the two-
channel Kondo effect (TCKE - see Section 2.3). The specific heat can be expressed as

\[ c/T = B' - (A'/T) \ln(T/T_K) \]  

[51]. Using the values \( A' = 0.251 \text{R} \) and \( b = 0.41 \) from the TCKE, one obtains \( T_K = 23.2 \text{K} \) and \( B' = 204.3 \text{mJ/mol K}^2 \). This value of \( T_K \) is close to the Kondo temperature \( 16 < T_K < 21 \text{K} \), which can be deduced from the susceptibility data, assuming that the paramagnetic Curie temperature \( \theta \) is 3-4 times larger than \( T_K \) [52]. The value of \( B' \) is however extremely high, since it should account for a temperature independent electronic or crystal-field background in \( c/T \).

This value of \( T_K \) in \( \text{U}_2\text{Pt}_2\text{In} \) is also consistent with the one extracted from thermoelectric-power data taken on a single crystal [53]. In the temperature range 5-150 K, the thermopower is negative with a minimum at \( T_{\text{min}} \approx 25 \text{K} \). Similar minima were reported for several other heavy-fermion compounds exhibiting spin-fluctuation phenomena, with \( T_{\text{min}} \sim T_K \) [54].

With the value of \( T_K \), the coefficient \( a \) of the power law in the resistivity, 

\[ \rho/\rho_0 = 1 + a (T/T_K)^\alpha \]

\( \alpha \) can be calculated: \( \alpha_a = 2.89 \) and \( \alpha_c = 0.71 \) for \( \alpha_a = 1.2 \) and \( \alpha_c = 0.9 \), respectively.

The unusual low-temperature susceptibility data yield further support for NFL behaviour. The theoretical expressions for the magnetic susceptibility of a NFL compound are

\[ \chi = -\ln(T/T_0) \]  

or \( \chi = -1 - bT^\beta \) (\( \beta < 1 \)), depending on the type of system (see Section 2.3). In \( \text{U}_2\text{Pt}_2\text{In} \), \( \chi_a(T) \) is dominated by antiferromagnetic correlations below 10 K, therefore, no low-temperature analysis can be done confidently. However, \( \chi_a(T) \) continues to rise, at least down to 2 K. Analysing \( \chi_a \) \( (T < 10 \text{K}) \) with a term \( \chi_a = 1 - b'(T/T_K)^\gamma \) one finds \( \beta = 0.7 \) and \( b' = 0.25 \), but the limited temperature range where this behaviour occurs does not allow for a reliable estimate of the exponent \( \beta \).

The results of the scaling analysis within single-ion Kondo models are summarized in Table 4.9. The reduced values of the parameters should be considered as rough estimates since the data were not corrected for the phononic contributions. The high value of \( b' \) indicates that the specific heat cannot be fully described by the TCKE expression. Furthermore, single-ion models are normally applied in diluted systems where small amounts of an f-element are used to partially replace a non-magnetic rare earth or actinide element (e.g. systems like \( \text{Y}_1\gamma\text{U}_{1-x}\text{Pd}_3 \) and \( \text{Th}_1\gamma\text{U}_{1-x}\text{Pd}_3\text{Al}_3 \) [51, 55]), while \( \text{U}_2\text{Pt}_2\text{In} \) should be considered as a Kondo-lattice system. A clear indication that the TCKE does not apply to \( \text{U}_2\text{Pt}_2\text{In} \) is that the entropy does not saturate at the value \( \frac{1}{2} \text{Rln2} \) as expected for this model. Nevertheless, the observed scaling of the low temperature properties shows that the Kondo temperature, being a characteristic temperature of
the heavy-fermion character of U$_3$Pt$_2$In, can also be taken as a characteristic temperature of its non-Fermi liquid behaviour.

<table>
<thead>
<tr>
<th>Table 4.9</th>
<th>Parameters from single-ion scaling of some low-temperature properties of U$_3$Pt$_2$In.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha / T = \alpha \left( T / T_K \right) \ln \left( D / T / T_K \right) + B'$</td>
<td>$a$-axis $\alpha = 1.2$ $\alpha = 0.9$</td>
</tr>
<tr>
<td>$\rho = \rho_0 \left[ 1 + \alpha \left( T / T_K \right) \right]$</td>
<td>$\rho_0 = 115 \mu \Omega \cdot \text{cm}$ $\rho_0 = 210 \mu \Omega \cdot \text{cm}$</td>
</tr>
<tr>
<td>$\alpha = 2.89$ $\alpha = 0.71$</td>
<td>$\beta = 0.7$</td>
</tr>
<tr>
<td>$\chi = \chi(T=0) \left[ 1 - B' \left( T / T_K \right) \right]$</td>
<td>$\chi(0) = 14 \times 10^{-3} \text{ m}^3/\text{mol}$</td>
</tr>
<tr>
<td>$p = 0.25$</td>
<td></td>
</tr>
</tbody>
</table>

### 4.3.3. Kondo disorder

An alternative mechanism which can lead to NFL behaviour is the Kondo disorder model [56], where the Kondo effect on each $f$-electron atom sets a different temperature scale, resulting in a broad range of effective Kondo temperatures. One should note that the residual resistivity values of the U$_3$Pt$_2$In single-crystals are large, $\rho_{\text{res}}$ and $\rho_{\text{nc}}$ equal 110 and 200 $\mu \Omega \cdot \text{cm}$ respectively, which indicates that disorder is present in the crystals. The origin of this disorder remains unclear. The single-crystal X-ray and neutron-diffraction structure refinement with final agreement factors of 4.3% and 2.6% respectively, are considered to indicate a high crystalline quality. A small percentage of site inversion (Pt and In inversion) seems also to be excluded by the neutron-diffraction structure refinement. It is also possible that the disorder is somehow related to the polymorphism of U$_3$Pt$_2$In and the presence of two U sites with different magnetic susceptibilities.

Specific-heat measurements performed on a polycrystalline sample in the temperature range 0.3 K < $T$ < 5 K yield the same logarithmic divergency as measured on the single crystals. This shows that the NFL behaviour is found for the USi$_2$-type of structure (polycrystals) as well as for the ZrAl$_2$-type of structure (single crystals). Therefore, the NFL behaviour in U$_3$Pt$_2$In is not related to the presence of two different crystallographic U sites and the difference in U site susceptibility is not a main ingredient in the origin of the NFL behaviour.
On the other hand, it is clear that the \( \rho_0 \) values found do not reflect bare residual resistivities. This may be concluded from the following: i) there is a strong current-orientation dependence of the values of \( \rho_{0,i} \) with \( \rho_{0,i} = 0.56\rho_{0,\alpha} \) at zero field, which cannot simply be attributed to impurity or defect scattering; ii) both \( \rho_{0,i} \) and \( \rho_{0,\alpha} \) vary in field, which indicates that at least part of \( \rho_0 \) is caused by scattering mechanisms other than scattering at crystallographic defects.

### 4.3.4. Magnetic critical point

An appealing scenario for the origin of the non-Fermi liquid behaviour in U\(_2\)Pt\(_2\)In is the proximity to a quantum critical point [57]. This is reflected in the location of U\(_2\)Pt\(_2\)In at the border line between magnetic and non-magnetic compounds in a Demichel-type of diagram for the U\(_2\)T\(_2\)X series (X = In, Sn). Tuning the quantum critical point with an external parameter, e.g. a magnetic field or (chemical) pressure, should elucidate the applicability of this scenario. Magnetoresistance measurements show a tendency towards a \( \rho \sim T^2 \) law as the field strength increases, suggesting that the magnetic field shifts U\(_2\)Pt\(_2\)In away from the quantum critical point towards a Fermi-liquid regime. Specific-heat measurements in field were inconclusive in this respect due to the presence of an important contribution from the In nuclear moments.

The proximity of U\(_2\)Pt\(_2\)In to a quantum critical point is best probed with pressure experiments and chemical substitutions. Usually, compounds located at a magnetic instability are tuned towards the Fermi-liquid regime by applying pressure since a reduction of the interatomic distances results in an increase of the hybridization. On the other hand, chemical substitution of U by a larger non-magnetic element like Th should have the opposite effect. Resistivity measurements under pressure were carried out on U\(_2\)Pt\(_2\)In up to \( p = 1.8 \) GPa and will be presented in Section 6.1, while some preliminary results of studies on Th-doped U\(_2\)Pt\(_2\)In will be presented in Section 6.2.

The absence of static magnetism in U\(_2\)Pt\(_2\)In has been confirmed by detailed muon spin relaxation and rotation (\( \mu \)SR) experiments, which will be presented in Chapter 5. As discussed in Chapter 3, the \( \mu \)SR technique is a very powerful probe as it enables the detection of tiny ordered moments (which might be overlooked by other techniques). The \( \mu \)SR technique may also be used to investigate whether Kondo disorder is the origin of non-Fermi liquid behaviour.
References


