Evolution of Magnetism and its Interplay with Superconductivity in Heavy-Fermion U(Pt,Pd)3

Keizer, R.J.

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Chapter 3

Theory

This theory chapter starts with a short introduction to the properties of heavy fermions and their relation to magnetism and superconductivity. Next we present an introduction to unconventional superconductivity in UPt$_3$. The superconducting state is described within several Ginzburg-Landau models in which the symmetry of the superconducting gap function plays an important role. The remaining part of this chapter deals with the principles of μSR. In μSR experiments the muon depolarisation function reflects the time and spatial distribution of the local magnetic fields. The most important issue is how to interpret the muon depolarisation function.

3.1 Introduction

The term heavy fermion describes a class of intermetallic compounds that have, below a characteristic temperature, $T^*$, an enhanced effective mass, $m^*$, which amounts roughly up to $10^2$-$10^3$ times the free electron mass. Heavy-fermion behaviour is predominantly found in intermetallic compounds that contain the 4f element Ce or Yb or the 5f element U or Np. Heavy-fermion materials are characterised by an anomalously large electronic low-temperature specific heat coefficient, $\gamma$. For ordinary metals the $\gamma$-value is of the order of 1-10 mJ/mol K$^2$, while for a heavy-fermion metal the $\gamma$-value amounts to 100-1200 mJ/mol K$^2$.

Most heavy-fermion systems are close to an antiferromagnetic instability which is attributed to a competition between Kondo and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. The Kondo effect gives rise to a low-temperature screening of the f-moments
by the conduction electrons. In a Kondo lattice system, the \( f \)-moments interact with each other via the conduction electrons. The resulting indirect exchange between the \( f \)-moments is described by the RKKY interaction. The strength of both effects depends on the exchange energy \( J \), between the \( f \)-electrons and the conduction electrons. For a small \( J \) the RKKY interaction dominates, which may result in long-range magnetic order. In UPt\(_3\) antiferromagnetic order is observed with a very small ordered moment of 0.02 \( \mu_B / \text{U-atom} \). However, by replacing 5 at.\% Pt by Pd antiferromagnetic order with a moment of 0.6 \( \mu_B / \text{U-atom} \) can be readily induced. In several other heavy-fermion systems extremely small ordered moments are observed as well (e.g. in URu\(_2\)Si\(_2\), where the ordered moment is 0.03 \( \mu_B / \text{U-atom} \)).

A most interesting observation is that in a number of heavy-fermion compounds (CeCu\(_2\)Si\(_2\), URu\(_2\)Si\(_2\), UPd\(_2\)Al\(_3\), UNi\(_2\)Al\(_3\), UPt\(_3\)) the antiferromagnetic order coexists with superconductivity. According to the standard BCS model strong magnetic interactions suppress superconductivity. The large effective mass leads to Cooper pairs with small spatial extension and therefore to large Coulomb repulsion between the two conduction electrons. This makes electron-phonon coupling as the interaction mechanism unlikely. Therefore it has been suggested that the formation of Cooper pairs is mediated by electron-electron interactions. UPt\(_3\) is the compound for which most evidence is available that unconventional superconductivity is realised.

### 3.2 Unconventional superconductivity

#### 3.2.1 Superconductivity in UPt\(_3\)

In the past decade a host of experiments has demonstrated that the superconducting properties of heavy-fermion UPt\(_3\) deviate drastically from the standard BCS behaviour. In spite of all the research efforts, the key question whether UPt\(_3\) is a genuine unconventional superconductor, i.e. a superconductor that has a superconducting gap function with a lower symmetry than the Fermi surface, is still not settled unambiguously. The experiments conducted to probe the unconventional ground state in UPt\(_3\) can roughly be divided into two categories. To the first category belong experiments that probe the structure of the superconducting gap by measuring the temperature variation of the electronic excitation spectrum. The observed temperature variations in the form of power laws of, for instance, the specific-heat [1], the velocity of sound [2] and the thermal conductivity [3], strongly
suggest the presence of point nodes and/or line nodes in the gap, as predicted for unconventional superconductors. However, the relevant temperature regime $T < T_c (\approx 0.5 \text{ K})$, has not been probed reliably yet, especially because the contribution from impurity scattering, which is not easily quantified, obscures the intrinsic behaviour. The second category of experiments is directed towards exploring the multicomponent phase diagram with three vortex phases in the $B$-$T$ plane [1,4,5]. The phase diagram, obtained by dilatometry [7,8] on a high-quality single-crystalline sample is shown in figure 3.1 for a magnetic field along and perpendicular to the hexagonal axis. All phase lines are of second order, although for the B-C phase line, a weakly first order transition cannot be excluded. Second order phase transitions allow for the study of the phase diagram by means of Ginzburg-Landau (GL) theory. In the past years several GL-models have been worked out in order to understand the observed field and pressure dependence of the three vortex phases [6].

In section 3.2.2 we focus on the pairing state in unconventional superconductors. The gap structure is the topic of section 3.2.3. Important for the understanding of unconventional superconductivity is the symmetry of the order parameter, which is discussed in section 3.2.4. In section 3.2.5 we will review different GL-scenarios, assuming different gap structures.

### 3.2.2 Unconventional pairing

The origin of the pairing potential in a conventional superconductor lies in electron-phonon coupling. An effective attractive interaction of the conduction electrons leads to the formation of Cooper pairs formed by two conduction electrons with opposite spin ($S = 0$). The pairing state of a conventional superconductor is known as s-wave pairing which refers to the absence of an orbital momentum for the Cooper pair ($L = 0$). In analogy to the spectroscopic notation, s-wave, p-wave, and d-wave are used to denote $L = 0, 1, 2$. For electron-phonon coupling, the pairing is standard s-wave, but other pairing mechanisms can favour a different pairing. We will from this point on refer to non s-wave pairing ($L \neq 0$) as unconventional pairing.
A Cooper pair formed by two spin 1/2 quasiparticles has a total spin of either $S=0$ or $S=1$. For $S=0$ the Cooper pair is in a singlet state and the orbital momentum is even ($L=0, 2, \ldots$). For $S=1$ the projection of the spin on the orbital momentum, $L$, labels three different states with $S_z=0, \pm 1$. For the triplet pairing the Cooper pair has an orbital momentum which is odd ($L=1, 3, \ldots$). The wave-functions of unconventionally paired electrons have a larger spatial extension than those of s-wave paired electrons [9], which creates the possibility to overcome the short-range Coulomb repulsion. Because electron-phonon interaction is also short-range, another coupling mechanism likely exists in heavy fermion superconductors. Note that for an unconventional pairing state ($L \neq 0$) the symmetry of the pairing state is lower than the symmetry of the lattice.

Figure 3.1  Superconducting phase diagram of UPt$_3$ for $B \perp c$ and $B || c$, constructed from anomalies detected by thermal expansion and magnetostriction [7,8].
3.2.3 The energy gap

Important for superconductivity is the existence of a gap, $\Delta_k$, in the quasi-particle excitation energy, $E_k$ [10]:

$$E_k = \left( \xi_k^2 + |\Delta_k|^2 \right)^{\frac{1}{2}}$$  \hspace{1cm} (3.1)

Here $\xi_k$ is the single particle energy relative to the Fermi energy, $E_F$. For conventional superconductors the gap is nearly isotropic, although a strong anisotropy of the gap function is allowed as long as the symmetry of the gap function is equal to the symmetry of the lattice. The coherent two particle state is separated from the ground state by $2\Delta$. In an isotropic BCS-superconductor the number of electrons excited over an energy gap is given by [11]:

$$n \approx \exp(-\Delta / k_B T)$$  \hspace{1cm} (3.2)

This manifests itself in an exponential temperature dependence of various physical quantities, such as the specific heat and the nuclear relaxation rate. For unconventional superconductors, the superconducting gap function is strongly anisotropic with possibly nodes in the gap function. The minimum excitation energy is lower in the region of the node and the number of excited particles is determined by the geometry of this region. This will result in a power-law temperature dependence of various physical quantities [12]. For p-wave pairing point-nodes on the Fermi-surface exist, while for d-wave pairing there exists at least one line-node. For both p-wave and d-wave superconductivity, several extra point- or line-nodes can exist. The shape of the gap determines the low-temperature power-law behaviour of the thermodynamic quantities. By investigating the low-temperature power-laws, the existence of point- or line-nodes can be studied. From the shape of the nodes it can be determined whether the form of the pairing is s-wave, p-wave or d-wave. However, small amounts of impurities have a large effect on the low-temperature power laws. Due to impurities a broadening of point- or line-nodes occurs leading to areas of the Fermi-surface that are gapless [13]. These gapless areas have a large influence on the low-temperature power-law behaviour, which complicates the analysis. Until now the different experiments gave no consistency about the gap structure, so that the symmetry representation could not be determined unambiguously.
3.2.4 The symmetry of the order parameter

The symmetry of the order parameter determines the temperature dependence of the thermodynamic quantities. It is therefore important to determine the symmetry of the order parameter. In this section we closely follow a paper of Yip and Garg \[14\] in which the symmetry of the gap function is discussed for several point groups. The symmetry group of interest for UPt$_3$ is the hexagonal group $D_{6h}$. The superconducting gap function immediately below $T_c$ is described by a linear combination of the basis functions, $\psi_i^{\mu}$, of the irreducible representation, $\Gamma^j$, for the symmetry group $D_{6h}$. For singlet pairing the gap function is described by a single even function, $\Delta_0(k)$, while for a triplet superconductor it is described by an odd vectorial function, $d(k) = (d_x, d_y, d_z)$:

$$\Delta_0(k) = \sum_{\mu=1}^{l_j} \eta_\mu \psi_i^{\mu}(k), \text{ even parity,}$$

$$d_n(k) = \sum_{\mu=1}^{l_j} \eta_\mu \psi_i^{\mu}(k,n), \text{ odd parity,}$$

where $\eta_\mu$ are arbitrary complex numbers and $l_j$ is the dimensionality of $\Gamma^j$. In the odd case the basis functions depend on the pseudospin index ($n = x, y, z$) in addition to $k$. The basis functions $\psi_i^{\mu}$ are not unique, but can be written in a more general form. In the most

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>Even parity</th>
<th>$\Gamma$</th>
<th>Odd parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1, $(k_1^2 + k_2^2)$, $k_x^2$, ...</td>
<td>$A_{1u}$</td>
<td>$k_y z$; $(k_x x + k_y y)$; Re $k_z^2 r_z$;</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>Im $k_+^6$</td>
<td>$A_{2u}$</td>
<td>Im: $k_x r_x$; $k_y^2 r_y$; $k_z^6 k_z z$</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$k_z$ Im $k_+^3$</td>
<td>$B_{1u}$</td>
<td>Im: $k_3^3 z$; $k_1^2 k_z r_z$; $k_1^4 k_z r_z$</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$k_z$ Re $k_+^3$</td>
<td>$B_{2u}$</td>
<td>Re: $k_3^3 z$; $k_1^2 k_z r_z$; $k_1^4 k_z r_z$</td>
</tr>
<tr>
<td>$E_{1g}$</td>
<td>(Re, Im): $k_z k_+; k_z k_+^5$</td>
<td>$E_{1u}$</td>
<td>(Re, Im): $k_z z$; $k_x r_x$; $k_y^2 k_z r_z$; $k_z^2 z$; $k_y^2 k_z r_z$; $k_z^6 k_z r_z$</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>(Re, Im): $k_+^2; k_+^4$</td>
<td>$E_{2u}$</td>
<td>(Re, Im): $k_x r_x$; $k_x^2 k_z z$; $k_y^3 r_y$; $k_x^3 r_x$; $k_x^5 r_x$; $k_x^4 k_z z$</td>
</tr>
</tbody>
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*Note that more than one basis function is given for the identity representation.*
general form the basis functions $\psi^\mu_a$ can be written as a linear combination of $N$ independent basis-function multiplets, $\psi^\mu_a\cdot a=1,2,\ldots,N$, where $N=l_j$ and $N=3l_j$ for the pseudospin singlet and triplet cases, respectively.

$$\psi^\mu_a(k) = \sum_{a=1}^{l_j} F^{ja}(k)\psi^{ja}_\mu(k), \quad \text{singlet,}$$

$$\psi^\mu_a(k,n) = \sum_{a=1}^{3l_j} F^{ja}(k)\psi^{ja}_\mu(k,n), \quad \text{triplet,}$$

(3.4)

where the functions $F^{ja}(k)$ are arbitrary but invariant under all operations in the point group. The irreducible basis functions for a superconducting gap with hexagonal symmetry $D_{6h}$ are listed in Table I. For the two-dimensional (2D) representations, $E_{1g}$ and $E_{2g}$, the partners in the multiplet (i.e. functions corresponding to different values of index $\mu$ with the same index $a$) are given by the real and imaginary parts of the complex functions.

In the next sections a number of different Ginzburg-Landau scenarios will be discussed. The most important difference between these models is the symmetry of the order parameter. For a single 2D representation (E-model) the gap function is described by

$$\Delta_E = \eta_x\Gamma_{E,x} + \eta_y\Gamma_{E,y},$$

where $\Gamma_{E,x}$ and $\Gamma_{E,y}$ are the basis functions of the E-representation and $\eta_x$, $\eta_y$ are the complex components of these basis functions forming a vector order parameter $\eta=(\eta_x, \eta_y)$. In the AB-model the total gap is characterised by

$$\Delta_{AB} = \eta_A\Gamma_A + \eta_B\Gamma_B,$$

where $\Gamma_A$ and $\Gamma_B$ are the basis functions for the A- and B-representation and $\eta_A$, $\eta_B$ are the complex components of the two 1D representations.
3.2.5 Ginzburg-Landau theory

3.2.5.1 Introduction

The thermodynamic properties of the superconducting state can be described in terms of the free energy, $F$. Ginzburg and Landau assumed that close to the transition temperature $T_c$, the free energy may be expanded in terms of the order parameter, $|\psi|$. In the absence of magnetic fields and gradients, the free energy can be described by a Taylor expansion in terms of the order parameter:

$$F = a|\psi|^2 + \frac{1}{2} \beta |\psi|^4 + ...$$  \hspace{1cm} (3.5)

Here $\alpha = \alpha_0(T-T_c)$ and $\alpha_0, \beta > 0$ for a stable second order phase transition. The first two terms of the expansion should be sufficient as long as one stays close to the second-order phase transition at $T_c$. In an applied magnetic field the order parameter is no longer uniform, so that the contribution from field gradients should be added to the free energy. The contribution of the gradients can be written as:

$$F_{\text{GRAD}} = \frac{1}{2m^*} \left( -i e^* \nabla + e^* A \right) |\psi|^2$$  \hspace{1cm} (3.6)

Here $A$ is the magnetic vector potential and $m^*$ and $e^*$ are the charge and the mass of the superconducting Cooper pairs, respectively. Several heavy fermion superconductors show an antiferromagnetic transition well above the superconducting transition. In that case the free energy is described in terms of two coupled order parameters: the ordered moment and the superconducting gap. Although the Ginzburg-Landau analysis can be applied more generally, we will focus here on the situation of UPt$_3$.

The superconducting properties of the system strongly depend on the symmetry of the order parameter. The aim of the Ginzburg-Landau analysis is to determine the symmetry of the order parameter. In order to come to a description of unconventional superconductivity in UPt$_3$, several scenarios have been developed on the basis of generalised Ginzburg-Landau (GL) theories of superconductivity, where the free energy is purely derived by symmetry arguments. The most studied scenarios for the UPt$_3$-phase diagram can be divided into three classes. (i) The double transition can occur for a triplet order parameter described by the one-dimensional (1D) representation of the crystal point group symmetry $D_{6h}$ of UPt$_3$, when the spin-orbit coupling interaction is negligible. (ii) The second mechanism for multiple superconducting phases in UPt$_3$ is the presence of a vector order
parameter. The order parameter belongs to a two-dimensional (2D) representation of the $D_{6h}$ group. (iii) It is also possible that there are two nearly degenerate 1D representations of the $D_{6h}$ group. In scenario (i) and (ii) a symmetry breaking field (SBF) is required to lift the degeneracy of the spin or the 2D order parameter, respectively. The most likely candidates for the symmetry breaking field are the weak antiferromagnetic order [15] or the incommensurate structural modulation [16]. The most developed models consider the antiferromagnetic order as the SBF of the superconducting vector order parameter. Evidence for the antiferromagnetic order as a symmetry breaking field is found in the pressure dependence of the ordered moment. Neutron-diffraction measurements under hydrostatic pressure indicate that the ordered moment vanishes at the same critical pressure as the splitting of the superconducting transition, $\Delta T_c = T_c^+ - T_c^-$ [17]. These measurements suggest a direct relation between the splitting of $T_c$ and the ordered moment ($\Delta T_c \propto m^2$). For scenario (iii) there is no need for an additional SBF, but an accidental near-degeneracy of the superconducting gap function is assumed. Within this description there is no intrinsic physical reason for the closeness of the critical temperatures belonging to the different representations. In the next three sections we will present examples for all three scenarios.

### 3.2.5.2 E-model

The low-temperature properties of UPt$_3$ are determined by both the antiferromagnetic and the superconducting order parameters. The total free energy with respect to the normal state consists therefore of three components:

$$F = F_M + F_S + F_{MS} \quad (3.7)$$

Here $F_M$ and $F_S$ describe the antiferromagnetic and the superconducting contributions and $F_{MS}$ is the coupling term of the antiferromagnetic and the superconducting order parameters. The free energy related to the antiferromagnetic order with $T_N = 6$ K can be described by a Ginzburg-Landau expansion of the ordered moment, $m$.

$$F_M = \alpha_M m^2 + \frac{1}{2} \beta_M m^4 \quad (3.8)$$

Below $T_N$ an ordered moment is formed with $m^2 = -\alpha_M/\beta_M$ and $\alpha_M = \alpha_{M_0} (T - T_N)$. This moment saturates at $m_0 = 0.02 \mu_B$/U-atom. The free energy of the superconducting state is expanded in terms of a vector order parameter, $\eta = (\eta_x, \eta_y)$, describing the complex components of a 2-dimensional gap function ($E_{1g}, E_{2g}, E_{1u}, E_{2u}$):
\[ F_S = \alpha_S |\eta|^2 + \frac{1}{2} \beta_1 |\eta|^4 + \frac{1}{2} \beta_2 |\eta|^2 | \tag{3.9} \]

Here \( \alpha_S = \alpha_{S_0} (T - T_c) \) and \( \alpha_{S_0} \), \( \beta_1 \) and \( \beta_2 \) are the Ginzburg-Landau coefficients which are positive. In the system described by eq. 3.9 the components of the superconducting order parameter are degenerate. In order to lift this degeneracy a symmetry breaking field \( (\varepsilon) \) is needed. This symmetry breaking field can be provided by either the antiferromagnetic order or the structural modulation. For the antiferromagnetic order the symmetry breaking field is proportional to the moment squared \( (\varepsilon = \gamma m^2) \). The free energy determined by the coupling between the antiferromagnetic order and superconductivity can be expanded as:

\[ F_{SM} = \gamma |m \cdot \eta|^2 + \alpha_{SM} m^2 |\eta|^2 \tag{3.10} \]

The first term of this expression is responsible for the symmetry breaking. The non-symmetry breaking invariant term \( \alpha_{SM} m^2 |\eta|^2 \) can be absorbed into \( \alpha_S |\eta|^2 \), which just shifts \( T_c \) by \( -\alpha_{SM} m^2 / \alpha_{S_0} \). For this reason one uses in general only the symmetry breaking expression:

\[ F_{SM} = -\gamma m^2 \left( |\eta_x|^2 - |\eta_y|^2 \right) \tag{3.11} \]

In order to minimise the total free energy it has to be rewritten in the components \( |\eta_x|^2 \) and \( |\eta_y|^2 \):

\[ F = F_M + \alpha_S \left( |\eta_x|^2 + |\eta_y|^2 \right) + \frac{1}{2} \beta_S \left( |\eta_x|^4 + |\eta_y|^4 \right) + \beta_1 |\eta_x|^2 |\eta_y|^2 - \gamma m^2 \left( |\eta_x|^4 - |\eta_y|^4 \right) \tag{3.12} \]

Here \( \beta_S = \beta_1 + \beta_2 \) and \( \beta_3 = \beta_1 + \beta_2 \cos(2(\phi_x - \phi_y)) \). By minimising the free energy with respect to \( |\eta_x|, |\eta_y|, m \) and \( \phi_x - \phi_y \) one obtains four coupled equations for the equilibrium state. The magnetic term is assumed to be constant in the superconducting state, because the moment is nearly saturated. The two superconducting phases can be characterised by a normalised order parameter. The stable phases of eq. 3.12 are the \((1, 0)\) phase with only \( |\eta_x| \) different from zero and the \((1, \alpha)\) phase where both amplitudes are nonzero and have a relative phase \( \phi_x - \phi_y = \pi/2 \). A double superconducting transition is found for \( \beta_1, \beta_2, \gamma > 0 \) with the following solutions:

\[ (1, 0) \text{ phase:} \quad T_c^+ = T_c + \frac{\gamma m^2}{\alpha_{S_0}} \tag{3.13} \]

\[ \begin{align*}
|\eta_x|^2 &= \frac{\alpha_{S_0}}{\beta_1 + \beta_2} (T_c^+ - T) \\
|\eta_y|^2 &= 0
\end{align*} \tag{3.14} \]

\( T_c < T < T_c^+ \)
(1,αi) phase:

$$T_c^+ = T_c - \frac{\beta_1 \gamma m^2}{\beta_2 \alpha S_0}$$

$$|\eta_1|^2 = \frac{\alpha S_0}{2\beta_1} \left(T_c^+ - T\right)$$

$$|\eta_2|^2 = \frac{\alpha S_0}{2\beta_1} \left(T_c^- - T\right)$$

where

$$T_c^{\mp} = T_c + \frac{\beta_1 \gamma m^2}{\beta_2 \alpha S_0}$$

The thermodynamical step in the specific heat divided by temperature can be derived from the free energy by $\Delta(c/T) = -\frac{\partial^2 F}{\partial T^2}$ for both transitions. The steps are relative to the normal state, because we considered the free energy with respect to the normal state. The calculated steps are:

$$\Delta_{NA} c(T_c^+) / T_c^+ = \frac{\alpha S_0^2}{\beta_1 + \beta_2}$$

$$\Delta_{NB} c(T_c^-) / T_c^- = \frac{\alpha S_0^2}{\beta_1}$$

Experimentally the ratio $\beta_2/\beta_1$ is determined from the ratio of the relative steps in the specific heat. In UPt$_3$ the ratio $\beta_2/\beta_1$ is close to the weak-coupling estimate of $\beta_2/\beta_1 = 1/2$. In chapter 5 and 6 we will compare the splitting of the superconducting transition predicted by equations 3.13 and 3.15 with the measured splitting, by making use of:

$$\Delta T_c = T_c^+ - T_c^- = \frac{\beta_1 + \beta_2 \gamma m^2}{\beta_2 \alpha S_0}$$

A disadvantage of the Ginzburg-Landau expansion is that it is only valid near the phase transition. This means that the description breaks down when $\Delta T_c$ becomes too large. A limitation of the Ginzburg-Landau expansion up to fourth order is that it does not describe the temperature dependence of $c/T$. The theoretical $c/T$ is constant as function of $T$ with steps at $T_c^+$ and $T_c^-$. In order to account for the temperature dependence of the specific heat as function of temperature, the free energy should be expanded to higher order terms. There are however four independent sixth-order terms, and also $\alpha S_0$ and $\beta_1$ can have higher order temperature corrections. The large amount of parameters which are not accessible to experimental verification make higher order models difficult to interpret.

Model calculations of the specific heat with one extra sixth order term, of the form $\lambda_6(|\eta_1|^2|\eta_2|^2+|\eta_1|^4|\eta_2|^2)$, were performed by Thalmeier [18]. With this extra term nothing changes for the (1,0) phase. However the transition to the (1,αi) phase occurs at a
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Figure 3.2 Left: Temperature dependence of the normalised squared components $|\eta_2|^2$ and $|\eta_0|^2$ of the superconducting order parameter ($\eta_0^2 = \alpha_{s_0} T_c / 2\beta_1$). The values chosen for the model parameters are $\alpha_{s_0} T_c / 2\beta_1 = 0.53$; $\beta_2 / \beta_1 = 0.5$; $\gamma m^2 / \alpha_{s_0} T_c = 0.034$; $\delta / \beta_1 = 1.0$ and $T_c = 0.53$ K.

Right: Specific heat, $(c/T)/(c_0/T_c)$, as a function of temperature calculated for the same model parameters as above ($c_0 = \alpha_{s_0}^2 T_c / \beta_1$). The dashed lines in both pictures represent the solutions without sixth order correction ($\delta = 0$).

reduced $T_c^-$. Below $T_c^-$ the temperature dependence of $|\eta_1|^2$ and $|\eta_0|^2$ are no longer linear. For large $\lambda_\phi$ a third re-entrant superconducting phase transition, $T_{c3}$, occurs. Below $T_{c3}$ the (1,0) phase is found again. This re-entrant phase transition is in the model calculations accompanied by a large peak in the specific heat. Thalmeier suggested that the peak in the specific heat of UPt$_3$ at 18 mK [19] could be explained by a re-entrant superconducting transition. It is however very dangerous to apply this Ginzburg-Landau expansion in such a large temperature range, because the modelled specific heat has not the correct temperature dependence and also entropy conservation is violated in the model. Moreover, specific heat measurements in a magnetic field above the critical field [19] indicate that the anomaly at 18 mK does not have a superconducting origin.

We also performed calculations adding the sixth order term, $\delta |\eta|^6 / 3$, to the free energy. The details of these calculations can be found in Appendix I and the results for some reasonable values of the model parameters are shown in figure 3.2. The linear temperature dependence of $c/T$ observed experimentally in UPt$_3$ can not be reproduced by this model calculation, but the complete set of sixth order corrections may lead to a better description.
So far, we have discussed only the zero field properties. In an applied magnetic field the order parameter is no longer uniform, so that the free energy analysis must include the contributions from gradients of the order parameter. The field term of the free energy, \( F_B \), for a two dimensional order parameter of the hexagonal \( D_{6h} \) group is given by [20]:

\[
F_B = \Phi_0 \left( D_x \eta_x \right)^2 + \frac{\gamma m^2}{\alpha_{s_0}} (1,0) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_1 K_4}} (T_c - T)
\]

\[
K_3 \left( D_x \eta_x D_y^* \eta_y + D_y \eta_x D_x^* \eta_y + \text{c.c.} \right) +
\]

\[
K_4 \left( D_x \eta_x \right)^2 + \frac{\gamma m^2}{\alpha_{s_0}} (0,1) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_2 K_4}} (T_c^* - T)
\]

where \( D_j = \partial_j - iA_j \) with \( A \) the vector potential and the applied magnetic field is normalised by \( \phi_0/2\pi \) (where \( \phi_0 \) is the quantum of flux). The linearised solutions of equation 3.20 are anisotropic and depend strongly on the assumptions made for the order parameter. In the most simple case the ordered moment is assumed to be always perpendicular to a field in the basal plane. The solutions of this model have been worked out by Hess et al. [20], who makes use of a different definition for the coefficients \( K_i \). After transforming the coefficients \( K_i \) to ours, the linearised solutions for the upper critical field for \( B_L \perp c \) are:

\[
B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_1 K_4}} (1,0) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_2 K_4}} (0,1) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_1 K_4}}
\]

\[
T_c^* = T_c - \frac{\gamma m^2}{\alpha_{s_0}}
\]

The (1,0) and the (0,1) phase correspond to the experimental A- and C-phase, respectively. A critical point only exists when \( K_1 > K_2 \). However the model predicts that there is no tetracritical point for \( B \parallel c \):

\[
B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_1 K_4}} (1,0) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_2 K_4}} (0,1) \text{ phase:} \quad B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{s_0}}{\sqrt{K_1 K_4}}
\]

This is not in agreement with the experimental observation that the tetracritical point exists for all field directions. Although the phenomenological GL theories are formally the same for any of the 2D representations, the predictions can depend on the symmetry of the Fermi surface and the Cooper pair basis functions. The \( K_3 \)-term of equation 3.20 prevents a
crossing of the two $B_{c2}(T)$ curves for $B \parallel c$. Sauls [21] and Yin and Maki [22] suggest an
order parameter for which the mixing-term, $K_3$, vanishes. Sauls chooses an odd parity $E_{2u}$
order parameter with the spin projection along the c-axis ($d(k) = d_{z2}$) for which $K_1 = K_3 = 0$
if one assumes cylindrical symmetry. Yin and Maki consider an $E_{2g}$ order parameter which
is a d-wave axial state, so that $K_3$ vanishes. Both representations can describe the
superconducting phase diagram with a tetracritical point for all directions.

3.2.5.3 AB-model

The AB-model is in several aspects very similar to the E-model. In the E-model the
components of a 2D order parameter couple to each other, while in the AB-model the
coupling of two nearly degenerate 1D order parameters is assumed. The free energy in this
case is given by [23]:

$$F_S = \alpha_A |\eta_A|^2 + \alpha_B |\eta_B|^2 + \frac{1}{2} \beta_A |\eta_A|^4 + \frac{1}{2} \beta_B |\eta_B|^4 +$$

$$\beta_1 |\eta_A \eta_B|^2 + \frac{1}{2} \beta_2 \left[ (\eta_A^* \eta_B)^2 + (\eta_A \eta_B^*)^2 \right]$$

(3.23)

Here $\alpha_{A,B} = \alpha_{S_0} (T - T_{A,B})$ where $T_A$ and $T_B$ are the transition temperatures ($T_A > T_B$) for
the 1D order parameters $\eta_A$ and $\eta_B$. The first four terms of the free energy are the
conventional terms for both order parameters, where $\beta_A$, $\beta_B > 0$. The terms with $\beta_1$ and $\beta_2$
are responsible for the coupling between the order parameters. Also here the model can be
described by a vector $\eta = (\eta_A, \eta_B)$ with complex components. It is even possible to
transform the free energy of the AB-model into the free energy of the 2D-model. The
parameter range for a double superconducting transition is $\beta_2 > 0$, $\beta_{A,B} > \beta_1 - \beta_2 = \beta$.
and $\phi_A - \phi_B = \pi/2$. For this parameter range the minimum of the free energy has the following
stable solutions:

(1,0) phase: $T_c^+ = T_A$

$$|\eta_A|^2 = \frac{\alpha_{S_0}}{\beta_A} (T_A - T)$$

$$|\eta_B|^2 = 0$$

$$T_c^- < T < T_c^+$$ (3.25)
\[ T_c = \frac{\beta_B T_B - \beta_A T_A}{\beta_B - \beta_A} \]  

(3.26)

\[ |\eta_A|^2 = \alpha_S \left( T_A^* - T \right) \frac{\beta_B - \beta_A \beta_B - \beta^2}{\beta_A^2} \]

\[ |\eta_B|^2 = \alpha_S \left( T_B^* - T \right) \frac{\beta_B - \beta_A \beta_B - \beta^2}{\beta_B^2} \]

\[ T < T_c^- \]

(3.27)

where

\[ T_A^* = \frac{\beta_B T_A - \beta_A T_B}{\beta_B - \beta_A} \]

(3.28)

The step in the specific heat divided by temperature can be derived from the free energy by

\[ \Delta c/T = -\frac{\partial^2 F}{\partial T^2} \]

for both transitions. The steps are relative to the normal state, because we considered the free energy with respect to the normal state. The calculated steps are:

\[ \Delta_{NA} c(T_c^+)/T_c^+ = \frac{\alpha^2_{S_0}}{\beta_A} \]

\[ \Delta_{NB} c(T_c^-)/T_c^- = \frac{\beta_A + \beta_B - 2\beta^2}{\beta_A \beta_B - \beta^2} \]

(3.29)

In an applied magnetic field the order parameter is no longer uniform, so that the free energy analysis must include the contributions from gradients of the order parameter. The field term of the free energy, \( F_B \), for two coupled 1D order parameter of the hexagonal \( D_{6h} \) group is given by:

\[ F_B = K_A |D_1 \eta_A|^2 + K_B |D_1 \eta_B|^2 + K_A' |D_2 \eta_A|^2 + K_B' |D_2 \eta_B|^2 + B^2 / 8\pi \]

(3.30)

where \( D_j = \partial_j - iA_j \) with \( A \) the vector potential and the applied magnetic field is normalised by \( \phi_0/2\pi \) (where \( \phi_0 \) is the quantum of flux). The difference between the E-model and the AB-model is that there is not a mixing term in the AB-model like the \( K_3 \)-term for the E-model shown in equation 3.20. The AB-model is therefore invariant under field rotation in the basal plane. All kinds of order parameters are allowed, the parity of the order parameter is not important. It is even possible to have two order parameters of opposite parity. However it is assumed that one of the order parameters belongs to the A representation and the other to the B representation. When both order parameters belong to the A-representation or both belong to the B-representation additional gradient terms should be added. Additional mixing terms can avoid crossing of the phase lines like in the 2D-model. One then has to apply the same arguments as for the 2D-model in order to let the mixing terms vanish. The linearised solutions of the upper critical field for the AB-model for \( B \perp c \) is given by:
Chapter 3

(1,0) phase: \[ B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{S_{A}}(T_{A} - T)}{\sqrt{K_{A}K_{A}^{\prime}}} \]

(0,1) phase: \[ B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{S_{B}}(T_{B} - T)}{\sqrt{K_{B}K_{B}^{\prime}}} \]  \hspace{1cm} (3.31)

The (1,0) and the (0,1) phase correspond to the experimental A- and C-phase, respectively. A critical point can only exist when \( K_{A}K_{A}^{\prime} > K_{B}K_{B}^{\prime} \). The upper critical field for \( B \parallel c \) is given by:

(1,0) phase: \[ B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{S_{A}}(T_{A} - T)}{K_{A}} \]

(0,1) phase: \[ B_{c2} = \frac{\Phi_0}{2\pi} \frac{\alpha_{S_{B}}(T_{B} - T)}{K_{B}} \]  \hspace{1cm} (3.32)

The phase diagram for the AB-model is qualitatively the same as for the 2D-models of Sauls [21] and Yin and Maki [22]. The only distinct difference between the two models can be found in the pressure dependence of the phase diagram. The \( p-T \) phase diagram of the AB model has the same topology as the \( B-T \) phase diagram. The \( p-T \) phase diagram has a tetracritical point where the superconducting A, B and C-phase meet with the normal state. In the E-model however there is a bicritical point where the B and C-phase meet with the normal phase. In order to understand this difference one has to keep in mind that in the 2D-model a symmetry breaking field is needed. The degeneracy between the components is restored at a critical pressure, because the SBF is suppressed. In the AB-model both order parameters are suppressed under pressure, but with different rates. This means that below the critical pressure \( T_{A} > T_{B} \) while above the critical pressure \( T_{B} > T_{A} \). This leads to a crossing of the order parameters, while in the 2D-model they merge. A direct consequence for the \( B-T \) phase diagram above the critical pressure is that in the 2D-model the B and C-phase always meet at a bicritical point, while in the AB-model the C-phase is the most stable phase at high pressures. Sound velocity experiments [24] which indicate the presence of a tetracritical point support the AB-model. A tetracritical point is also inferred from the Ehrenfest relation by van Dijk et al. [25]. However, specific heat experiments by Sieck [26] seem to indicate the absence of a tetracritical point.

Besides the E-model discussed in the previous section and the AB-model discussed in this section, there are several variations of these models. For example (i) the AE-model, which has a mixed 1D and 2D representation [27,28], (ii) the super conducting glass state [27], which is a model based on the \( E_{1g} \) representation with the order parameter oriented randomly in the basal plane. (iii) In the next section we will discuss the 1D representation.
model proposed by Machida and Ohmi. In this model the spin degeneracy is lifted by a symmetry breaking field.

### 3.2.5.4 1D-rep with odd parity

Recently, much attention has been focused on the Ginzburg-Landau models that employ the triplet pairing state as advocated by Machida [29], because detailed NMR experiments reported by Tou et al. [30, 31] present strong indications for a triplet pairing state. As symmetry class for the pairing functions the 1D-representation of the $D_{6h}$ group with odd parity are considered. When spin-orbit coupling is absent, this representation is described by a three-component order parameter $\eta = (\eta_x, \eta_y, \eta_z)$ whose components label the spins of the Cooper pairs. In the first models of Machida and Ozaki [29,32] an ordered moment, $m = (m, 0, 0)$ that lies in the basal plane, pointing along the hexagonal $x$-axis, was assumed to act as symmetry breaking field. In their most recent models [33,34] Machida and Ohmi assume antiferromagnetic fluctuations characterised by a triple-$q$ vector with $q_1 = (1/2, 0, 0)$ and its equivalent positions $q_2$ and $q_3$. The three fluctuation modes give rise to an extra term to the free energy:

$$F_{SM} = -\sum_{i=1}^{3} \varepsilon_i |q_i \cdot \eta|^2$$

with $\varepsilon_i > 0$. $\varepsilon_i$ is proportional to the amplitude of the antiferromagnetic fluctuations, $m_i^2$, which is the magnetic intensity measured in the elastic neutron scattering experiment. The equivalency of the three modes is broken by the incommensurate structural modulation observed by transmission electron microscopy [16], such that for instance, $\varepsilon_1 > \varepsilon_2 = \varepsilon_3$. The phenomenological GL free energy of the superconducting state in this model is then given by [34]:

$$F_S = \alpha_S |\eta|^2 + \frac{1}{2} \beta_1 |\eta|^4 + \frac{1}{2} \beta_2 |\eta|^2 - \varepsilon |x \cdot \eta|^2 - \lambda |z \cdot \eta|^2$$

Here $\alpha_S = \alpha_S - (T - T_c)$ and $\varepsilon = \varepsilon_1 - \varepsilon_2 > 0$ and $q_1 \parallel x$. The last term, $\lambda |z \cdot \eta|^2$, which is somewhat ad hoc, expresses a weak anisotropy of the order parameter in spin space. This term reflects the fact that the Knight shift changes below $T_c$ for $B = 0.2$ T parallel to the $c$-axis [31]. The free energy can be written as:

$$F_S = \sum_{j=x,y,z} \alpha_s (T - T_c^j) |\eta_j|^2 + \frac{1}{2} \beta_1 |\eta|^4 + \frac{1}{2} \beta_2 |\eta|^2$$
with $T_c^x = T_c + \varepsilon / \alpha_{S_0} > T_c^x = T_c + \lambda / \alpha_{S_0} > T_c^y$ for $\varepsilon > \lambda > 0$. Below $T_c^+ = T_c^x$ the A-phase is characterised by $\eta_x \neq 0$ and $\eta_y, \eta_z = 0$. The second transition from the A-phase to the B-phase is characterised by $\eta_x = 0$ and $\eta_y, \eta_z = 0$, with a phase difference between $\eta_x$ and $\eta_z$ of $\pi/2$. It can be proven that the third transition at $T = T_c^y$ is never realised in zero field. Minimising the free energy leads to the following solutions:

(1,0,0) phase: $T_c^+ = T_c^x$

$$|\eta_x|^2 = \frac{\alpha_{S_0}}{\beta_1 + \beta_2} (T_c^+ - T)$$

$$|\eta_y|^2 = 0; \quad |\eta_z|^2 = 0$$

$T_c^- < T < T_c^+$ (3.36)

(1,0,\alpha i) phase: $T_c^- = \frac{\beta_2 T_c^x - \beta_1 T_c^y}{2\beta_2}$

$$|\eta_x|^2 = \frac{\alpha_{S_0}}{2\beta_1} (T_c^- - T)$$

$$|\eta_y|^2 = 0; \quad |\eta_z|^2 = \frac{\alpha_{S_0}}{2\beta_1} (T_c^- - T)$$

$T < T_c^-$ (3.37)

where $T_c^{+*} = \frac{\beta_2 T_c^x + \beta_1 T_c^y}{2\beta_2}$ (3.38)

The thermodynamical step in the specific heat divided by temperature can be derived from the free energy by $\Delta(c/\gamma) = -\partial^2 F / \partial T^2$ for both transitions. The expressions for the specific heat steps are exactly the same as for the E-model (see equation 3.18).

The calculations so far are valid in zero field only. In an applied magnetic field the order parameter is no longer uniform, so that the free energy analysis must include the contributions from gradients of the order parameter. The field term of the free energy, $F_B$, for a one dimensional representation with odd parity is given by [29,34]:

$$F_B = \sum_{\nu=x,y,z} K_1^y \left( |D_\nu \eta_\nu|^2 + |D_\nu \eta_\nu|^2 \right) + K_2^z |D_\nu \eta_\nu|^2 + \frac{1}{2} \Delta \chi_p |\mathbf{B} \cdot \eta|^2$$

(3.39)

where $D_\nu = \partial_\nu - i A_\nu$ with $A$ the vector potential, $1/2 \Delta \chi_p$ is the difference of the susceptibilities in the normal and superconducting state and the applied magnetic field is normalised by $\phi_0 / 2\pi$ (where $\phi_0$ is the quantum of flux). The odd parity state is characterised by a non-vanishing spin susceptibility, which leads to $B^2$ terms which are quadratic in $\eta$. In contrast to the 2D representation model there is no mixing of the three components $\eta_\nu$ in the 1D representation, so that the tetracritical point is not washed out. There are two kinds
of gradient terms ($K_1^\gamma$ and $K_2^\gamma$). Because of the antiferromagnetic symmetry breaking these terms differ according to:

\[
K_1^K = K_1 - \zeta_1 m^2, \quad K_2^K = K_2 - \zeta_2 m^2, \\
K_1^\gamma = K_1 + \zeta_1 m^2, \quad K_2^\gamma = K_2 + \zeta_2 m^2, \\
K_1^z = K_1^+ + m, \quad K_2^z = K_2^+ - m,
\]

(3.40)

The linearised solutions for the upper critical field are [34]:

**B\perp z**

\[
B_{c2}^x = \frac{\phi_0 \alpha s (T_{c2}^x (B_{c2}^x) - T)}{2\pi \sqrt{K_1^K K_2^K}} \\
B_{c2}^y = \frac{\phi_0 \alpha s (T_{c2}^y (B_{c2}^y) - T)}{2\pi \sqrt{K_1^\gamma K_2^\gamma}} \\
B_{c2}^z = \frac{\phi_0 \alpha s (T_{c2}^z (B_{c2}^z) - T)}{2\pi \sqrt{K_1^z K_2^z}}
\]

(3.41)

**B\parallel z**

\[
B_{c2}^x = \frac{\phi_0 \alpha s (T_{c2}^x (B_{c2}^x) - T)}{2\pi K_1^K} \\
B_{c2}^y = \frac{\phi_0 \alpha s (T_{c2}^y (B_{c2}^y) - T)}{2\pi K_1^\gamma} \\
B_{c2}^z = \frac{\phi_0 \alpha s (T_{c2}^z (B_{c2}^z) - T)}{2\pi K_1^z}
\]

(3.42)

where $T_{c2}^j (B) = T_{c2}^j - \frac{1}{2} \chi_p B^2$. Thus under the condition $K_1^K K_2^K > K_1^\gamma K_2^\gamma$ the phase lines for $B\perp z$ meet in a tetracritical point, while under the condition $K_1^K > K_1^\gamma > K_1^z$ the phase lines for $B\parallel z$ meet in a tetracritical point. The phase diagram is schematically plotted in figure 3.3. For the superconducting A-phase only $\eta_x$ is non-zero. For the B- and C-phase the order parameter depends on the field orientation. For $B\perp x$ the C-phase is characterised by $\eta_x$ and the B-phase is characterised by $\eta_x + i \eta_y$. The phase transition from $\eta_x + i \eta_y$ to $\eta_x + i \eta_z$ is never realised. For $B\parallel z$ the C-phase is characterised by $\eta_y$ and in the B-phase a rotation of the $d$-vector occurs in low fields from $\eta_x + i \eta_z$ to $\eta_x + i \eta_y$ at $\frac{1}{2} \Delta \chi_p B_{c2}^2 = \lambda$.

Under pressure the antiferromagnetic fluctuations disappear above a critical pressure $p_c$. The topology of the superconducting phase diagram above $p_c$ is important for the verification of this model. In the E-model there is a bicritical point where the B and C-phase meet with the normal phase. The $p-T$ phase diagram of Machida and Ohmi's
model has the same topology as for the AB model. Which means that the $p-T$ phase
diagram has a tetracritical point where the superconducting A, B and C-phase meet with
the normal state. Sound velocity [24] and dilatation [25] experiments indicate the presence
of a tetracritical point, but specific heat experiments by Sieck [26] seem in favour of a
bicritical point.

In spite of all experimental and theoretical effort since 1984, when superconductivity
in UPt$_3$ was discovered [35], the nature of the unconventional superconducting state is not
completely understood. Knigavoko and Rosenstein [36] proposed recently the existence of
magnetic skyrmions in UPt$_3$. There exists a class of solutions in Machida and Ohmi's
model where the vortices carry two units of magnetic flux: the magnetic skyrmion. The
main issue in almost all old and new Ginzburg-Landau models stays the same: the
symmetry of the superconducting order parameter.
3.3 The principles of μSR

In section 2.3 we presented the experimental aspects of the μSR technique is presented. From the intensity versus time histogram one can reconstruct the time dependence of the μ+ depolarisation function, $G(t)$, which reflects the spatial and temporal distribution of the magnetic fields at the muon site. An important issue is how to interpret the depolarisation function. In the following sections the muon depolarisation function is examined for the most important cases. In section 3.3.1 we will discuss the depolarisation functions for Zero field μSR, in section 3.3.2 for Longitudinal field μSR and in section 3.3.3 for Transverse field μSR. For a more extensive theoretical description we refer to the book of A. Schenck [37]. For a review of magnetic materials studied by μSR see refs. 38 and 39. An overview of heavy fermion materials studied by μSR can be found in refs. 39 and 40.

3.3.1 Zero field μSR

In a zero field (ZF) μSR experiment one measures the time dependence of the polarisation of the muons in a sample under the action of internal magnetic fields. These local fields are either of electronic origin or caused by the nuclear magnetic moments of the atoms. Nuclear dipole fields are usually static in the time window of μSR (fluctuation time $\tau \geq 10^{-4}$s), while electronic fields may be of static or dynamic nature. If all the muon spins precess in the same static magnetic field, oriented at an angle $\theta$ from the initial muon spin direction, $S_{\mu}$, the Larmor equation is:

$$G(t) = \cos^2 \theta + \sin^2 \theta \cos(\omega_\mu t)$$

(3.43)

with $\omega_\mu = 2\pi \gamma_\mu B_\mu$, where $\gamma_\mu$ is the gyromagnetic ratio of the muon and $B_\mu$ is the magnetic field at the muon site. Equation 3.43 is one of the basic equations of the μSR technique. For a polycrystalline magnet the spatial average of equation 3.43 has to be calculated. If the spatial distribution is isotropic (no texture) the result is:

$$G(t) = \frac{1}{3} + \frac{2}{3} \cos(\omega_\mu t)$$

(3.44)

The oscillating component reflects the magnetic order in the sample. We suppose here that there is only one type of muon localisation site and that for all these sites $B_\mu$ is the same. If there is disorder, i.e., if there is a distribution of the local fields, then the oscillation can be strongly damped and even disappear.
Figure 3.4 The fluctuating-rate dependence of the dynamical Kubo-Toyabe function. The numbers indicate the fluctuating rate in units of $\Delta$. The static Kubo-Toyabe function corresponds to the curve labelled with 0.

Another common case is that of an isotropic Gaussian distribution of internal fields with an average zero field given by:

$$f(B_i) = \frac{1}{\sqrt{2\pi}} \frac{\gamma_i}{\Delta} \exp\left(-\frac{\gamma_i^2 B_i^2}{2\Delta^2}\right), \quad (i = x, y, z) \quad (3.45)$$

where $\Delta^2/\gamma_i^2 = \langle B^2 \rangle$ represents the second moment of the field distribution along one Cartesian axis (the second moment of the three dimensional field distribution is $M_2 = 2\Delta^2/\gamma_i^2$). This kind of distribution is, for example, found for static nuclear magnetic moments or in a dense spin glass system. In this case an analytical formula has been derived for $G(t)$, the so called Kubo-Toyabe function, $G_{KT}(t)$.

$$G(t) = G_{KT}(t) = \frac{1}{3} + \frac{2}{3} \left(1 - \frac{\Delta_{KT}^2 t^2}{2}\right) \exp\left(-\frac{\Delta_{KT}^2 t^2}{2}\right) \quad (3.46)$$

$G_{KT}(t)$ has a minimum for $t = \sqrt{3}/\Delta$ and saturates if $t\Delta$ is large enough to a value of 1/3. The initial time dependence is well approximated by the parabolic form, $G_{KT}(t) \approx 1 - \Delta_{KT}^2 t^2$, or a Gaussian form, $G_{KT}(t) \approx \exp(-\Delta_{KT}^2 t^2)$. 
In fluctuating fields, the Kubo-Toyabe function is modified to the so-called dynamical Kubo-Toyabe function $G_{\text{KT}}^{\text{dyn}}(t, v)$, which, with the exception of some limiting cases, cannot be calculated analytically, see figure 3.4. These fluctuations are characterised by a fluctuation rate $v$. The dynamics is calculated using the strong collision model, which means that every fluctuation destroys completely the correlation between the field distribution before and after the event. The form of $G_{\text{KT}}^{\text{dyn}}(t, v)$ depends strongly on $v$. For slow fluctuations ($v/\Delta \ll 1$), only the $1/3$ term of equation 3.46 will be modified to $1/3\exp(-2/3vt)$. If $v/\Delta$ is sufficiently large the depolarisation function is given by:

$$G(t) = \exp(-2\Delta^2 t / v) = \exp(-\lambda t)$$

(3.47)

This is the motional narrowing limit. If the motion is fast enough, the $\mu^+$ will experience the average field leading to a field distribution which is narrower than the real field distribution.

**Figure 3.5** The magnetic field dependence of the longitudinal depolarisation function derived for a static isotropic Gaussian field distribution. The numbers indicate the magnetic field in units of $\Delta \gamma_\mu$. The Kubo-Toyabe function corresponds to the curve labelled with 0.
3.3.2 Longitudinal field $\mu$SR

In zero field studies it is not always possible to distinguish between static or fluctuating fields. However, by measurements in a longitudinal field (LF) configuration it is in most cases possible to identify whether the field is fluctuating or static. By applying $B_{\text{ext}}$ parallel to $S_\mu=(0,0,S_z)$ and choosing $B_{\text{ext}}$ much bigger than the internal fields, any static distribution of internal fields will not influence the time evolution of the muon polarisation. This is called the decoupling of the muon spin from static internal fields. For internal fields that are Gaussian distributed, $f(B_z)$ in equation 3.45 will be replaced by:

$$f(B_z) = \frac{1}{\sqrt{2\pi}} \frac{\gamma_\mu}{\Delta} \exp\left(-\frac{\gamma_\mu^2 (B_z - B_{\text{ext}})^2}{2\Delta^2}\right)$$

(3.48)

Hayano et al. [41] have derived the depolarisation function $G_{\text{KT}}(t,B_{\text{ext}})$ as a function of applied field, which has the form:

$$G_{\text{KT}}(t,B_{\text{ext}}) = 1 - \frac{2\Delta^2}{\gamma_\mu^2 B_{\text{ext}}^2} \left[ 1 - e^{-\frac{1}{2}\Delta^2 \gamma_\mu^2 B_{\text{ext}}^2 t} \cos(\gamma_\mu B_{\text{ext}} t) \right]$$

$$+ \frac{2\Delta^2}{\gamma_\mu^3 B_{\text{ext}}^3} \int_0^\Delta e^{-\frac{1}{2}\Delta^2 \gamma_\mu^2 B_{\text{ext}}^2 y} \cos\left(\frac{\gamma_\mu B_{\text{ext}}}{\Delta} y\right) dy$$

(3.49)

Figure 3.5 demonstrates that $G_{\text{KT}}(t,B_{\text{ext}})$ for the static case is strongly field dependent and gradually removes the time dependence of the polarisation. On the other hand fast fluctuations of the internal fields will lead to a depolarisation even in a large longitudinal field. For a fast dynamical process the relaxation of the muon spin leads to an exponential depolarisation characterised by equation 3.47 with a slightly reduced value for $\Delta$.

3.3.3 Transverse field $\mu$SR

In the transverse field (TF) configuration the external magnetic field $B_{\text{ext}}$ is applied perpendicular to the initial muon polarisation $S_\mu$. The arrangement of the set-up is described in chapter 2.2. The local magnetic field at the interstitial sites of the implanted muon can be determined from the Larmor precession frequency. One expresses the measured frequency or frequencies in the form of a Knight shift:

$$K = \frac{|B_\mu - B_{\text{ext}}|}{|B_{\text{ext}}|} = \frac{\langle \omega \rangle}{\omega_0} - 1$$

(3.50)
where \( \alpha_0 = \gamma_\mu B_{\text{ext}} \). Here, we consider only metals in the paramagnetic state that are exposed to a magnetic field. The local magnetic field, \( B_\mu \), at the interstitial site where the muon comes to rest can in general be written as follows:

\[
B_\mu = B_{\text{ext}} + B_{\text{dip}} + B_{\text{con}} + A_{\text{con}} \vec{x} B_{\text{ext}} + B_{\text{dia}} \quad (3.51)
\]

\( B_{\text{dip}} \) represents the dipolar fields of the localised lattice spins. The third and the fourth term are called the direct and the indirect hyperfine contact field, respectively, and are connected with the presence of the muon itself. The direct hyperfine contact field \( (B_{\text{con}}) \) results from the spin density at the muon site which is induced by the polarisation of the conduction electrons. In the paramagnetic state this polarisation is induced by an external field. \( B_{\text{con}} \) is proportional to the Pauli susceptibility \( \chi_{\text{Pauli}} \) of the conduction electrons and is usually assumed to be temperature independent and isotropic in contrast to the other contributions. The indirect contact field is due to the RKKY interaction between localised moment and the muon. The effective contact coupling constant \( A_{\text{con}} \) is temperature independent, so that the indirect contact field is proportional to the susceptibility tensor, \( \vec{\chi} \), and the applied magnetic field. The last contribution of equation 3.51 is due to the diamagnetic response of the electron cloud screening the muon charge. The diamagnetic screening produces only a very small contribution, \( B_{\text{dia}} \), to the local magnetic field. For materials with enhanced effective electron masses, \( m_{\text{eff}} \), the small diamagnetic contribution is reduced by a factor \( m_{\text{eff}}/m_{\text{e}} \). For heavy-electron compounds the diamagnetic contributions are therefore negligible.

In order to separate the different contributions to the local magnet field the experimental Knight shift is usually compared to the calculated one. If the principal axes of the crystal structure are chosen as a co-ordinate frame, the dipolar field contribution can be written as:

\[
B_{\text{dip}} = \tilde{A}_{\text{dip}} \vec{x} B_{\text{ext}} \quad (3.52)
\]

where the dipolar tensor \( \tilde{A}_{\text{dip}} \) is given by:

\[
\tilde{A}_{\text{dip}}(i, j) = \sum \frac{1}{r_f} \left( \frac{3x_i x_j}{r_f^2} - \delta_{ij} \right) \quad (3.53)
\]

The dipolar field at site \( r_\mu \) is determined from the sum over all \( \ell \) moments at positions \( r_\ell \), \( \vec{r}_{\ell} \vec{r}_\mu = (x_1, x_2, x_3) = (x, y, z) \), \( r = |\vec{r}| \) and \( \delta_{ij} \) is Kronecker's symbol. In order to calculate this finite sum, the following trick has to be used: define a so called Lorentz sphere with radius \( r_L \), and separate the sum into a part inside the sphere and a part outside the sphere. If one chooses the radius large enough, the summation over the outer region can be approximated.
with an integral. The magnetic field resulting from this integral yields the Lorentz field \( B_L = \frac{1}{3} \mu_0 M \) and the demagnetisation field \( B_{\text{dem}} = -\bar{N} M \). Where \( M \) is the magnetisation and \( \bar{N} \) is the demagnetisation tensor related to the shape of the sample. Note that for a sphere \( N = 1/3 \), so that \( B_L + B_{\text{dem}} = 0 \).

The issue is now to decompose the different Knight shift contributions in order to compare experimental data with calculations. Experimental Knight shift results can be easily corrected for demagnetisation and Lorentz fields. Therefore we omit these terms in the following discussion. The Knight shift is related to the susceptibility tensor (which is diagonal) according to:

\[
K_\mu = K_{\text{con}} + b \cdot (\bar{A}_{\text{tot}} \bar{\chi} b) \tag{3.54}
\]

where \( b = B_{\text{ext}} / |B_{\text{ext}}| \) is the unit vector parallel to the applied magnetic field, \( K_{\text{con}} \) is the Knight shift due to the direct contact field and \( \bar{A}_{\text{tot}} = \bar{A}_{\text{dip}} + \bar{A}_{\text{con}} \) is the total hyperfine coupling tensor. In contrast to \( K_{\text{con}} \) and \( \chi_{\text{pauli}} \), the contribution from the localised \( f \)-electronic moments will exhibit a strong temperature dependence. \( K_{\text{con}} \) can therefore be determined from the experimental data \( K_\mu (\chi) \) by extrapolating to \( \chi \rightarrow 0 \). The elements of \( \bar{A}_{\text{tot}} \bar{\chi} b \) can be determined experimentally from the Knight shift anisotropy for the principle axes. The Knight shift is simply given by

\[
K_i = A^i_{\text{tot}} \chi_i \tag{3.55}
\]

With the knowledge of \( \chi_i \) the tensor elements \( A^i_{\text{tot}} \) can be determined from the observed Knight shift \( K_i \). Because \( \bar{A}_{\text{tot}} \) is the sum of a traceless dipolar tensor and a scalar contact part, \( \bar{A}_{\text{tot}} \) can be decomposed using \( A_{\text{con}} = 1/3 \text{ Tr}(\bar{A}_{\text{tot}}) \). By comparison of the experimentally determined \( \bar{A}_{\text{dip}} \) with the theoretical values calculated with the use of equation 3.53 it is often possible to determine the actual muon stopping site. If a sample orders magnetically below the ordering temperature and the muon stopping site is known, then it is easy to calculate from the local field in the ordered state, measured by zero field \( \mu\text{SR} \), the size of the ordered moment.
References

[40] A. Amato, Rev. Mod. Phys. 69, 1119 (1997).