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MAGNETIC PHASE DIAGRAM IN SOME KONDO-LATTICE COMPOUNDS: MICROSCOPIC AND MACROSCOPIC STUDIES

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presented by
Daniel-Aurelian Andreica
Lic. Phys. “Babeș-Bolyai” University, Cluj-Napoca, ROMANIA
born 11.12.1964
citizen of ROMANIA

accepted on the recommendation of

PD Dr. A. Schenck, examiner
Prof. Dr. H. R. Ott, co-examiner
Prof. Dr. J. Sierro, co-examiner

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Abstract

The aim of this work was to investigate the effects of the chemical substitution and external pressure on the physical properties of some Yb and Ce Kondo lattice systems. The effect of the chemical substitution on the physical properties of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and YbCu$_{5-x}$Al$_x$ has been studied, primarily using macroscopic techniques (transport and magnetic measurements) and µSR. In parallel, a pressure cell suitable for µSR experiments was developed.

The effects of the chemical substitution and of the external pressure on the physical properties of a Kondo lattice system could be compared for the nonmagnetic YbCu$_2$Si$_2$ sample by substituting Cu by Ni (Ni/Cu in the following). While by using external pressure magnetic ordering is induced at a critical pressure $p_c$, the magnetic order driven by the chemical substitution develops in an unusual way, i.e., in a fraction of the sample that depends on the Ni concentration ($x$ in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$). The fraction of the sample that orders magnetically at low temperatures scales with the probability, for a Yb ion, to have at least two Ni ions as nearest neighbors. This result points to the effect of disorder, induced by the chemical substitution, on the ground state properties of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The transition temperature, $T_m$, of the magnetic fraction of the sample increases with the increase of the Ni concentration $x$.

The temperature dependence of the electrical resistivity and thermoelectric power ($S$) of the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples could be explained using models that take into account the combined effect of the crystal electric field, magnetic correlations and the Kondo effect. While the disorder induced by the chemical substitution has a drastic effect on the residual resistivity of the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples, it has none on the temperature dependence of the thermoelectric power. This fact was evidenced by comparing the $S(x,T)$ dependencies for the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples with the $S(p,T)$ dependencies for CeCu$_2$Si$_2$.

For nonmagnetic Yb Kondo lattices, the Doniach phase diagram predicts a reduction of the Kondo temperature $T_K$, and an increase of the magnetic correlations between the 4f-moments with the increase of the applied pressure. Both effects were observed in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The increase of the magnetic correlation between the Yb magnetic moments with the increase of the Ni concentration $x$ in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ is evidenced by the increase of the magnetic transition temperature upon the Ni/Cu substitution. A model, taking into account correlated and uncorrelated fluctuations of the Yb moments was proposed to explain the muon spin relaxation rates measured in zero field and longitudinal field configurations. A scaling law for the temperature dependence of the fluctuation rate of the 4f moments allowed the estimation of the Kondo temperature, which decreases with the increase of the Ni concentration supporting the previous results.

The Al/Cu substitution in YbCu$_{5-x}$Al$_x$ drives the system from a nonmagnetic ground state, in YbCu$_4$Al, to a magnetic ground state in YbCu$_3$Al$_2$. The YbCu$_{3.5}$Al$_{1.5}$ sample is close to a quantum critical point, as evidenced by macroscopic measurements. Our µSR measurements confirmed the magnetic transition temperature of YbCu$_3$Al$_2$. The slowing of the fluctuations of the Yb magnetic moments in this compound was observed via the increase of the muon
spin relaxation rate with the decrease of the temperature close to the magnetic transition. Above 2 K, the temperature dependence of the muon relaxation rate is similar for all investigated compounds. However, it increases continuously with the decrease of the temperature, for YbCu$_{3.5}$Al$_{1.5}$, while it tends to saturate, in YbCu$_4$Al. We suggest that in YbCu$_{3.5}$Al$_{1.5}$ the zero field muon spin relaxation rate originates from a spin-glass like distribution of slow fluctuating Yb magnetic moments (or small ferromagnetic quasistatic Yb clusters).

We have developed a pressure cell, with a particular design, suited for μSR experiments. The μSR spectra at different temperatures, of all materials used in its fabrication, were recorded and analyzed. With the last design, the pressure cell supported 17 kbar at room temperature (10 kbar at low T). Some tests are underway aiming to reduce this difference. The particular design of the pressure cell is due, in part, to the discovery of an oscillating signal in teflon (C$_2$F$_4$), arising from the muons stopping between two fluorine atoms.

Using CeRh$_2$Si$_2$, we performed tests of the pressure cell, up to 7 kbar. CeRh$_2$Si$_2$ has two magnetic transition temperatures, $T_{N1}$ and $T_{N2}$. We found the suppression, by the applied pressure, of the magnetic transition temperatures, in agreement with results obtained in macroscopic measurements. However, the magnetic structure proposed from neutron scattering under pressure measurements, cannot explain our μSR results. Moreover, according to the neutron scattering results the ordered moment decreases with increasing pressure, while the μSR results reveal a pressure independent ordered moment, at least up to 5 kbar. This result indicates a well localized 4f moment for the Ce ions, in agreement with the large magnetic transition temperature of CeRh$_2$Si$_2$, $T_{N1} = 36$ K.
Kurzfassung

Das Ziel dieser Arbeit war es den Einfluss von chemischer Substitution und äusseren Druck auf die physikalischen Eigenschaften von einigen Yb- und Ce- Kondogittern zu bestimmen.

Die Wirkung der chemischen Substitution auf die physikalischen Eigenschaften von Yb(Cu_{1-x}Ni_x)Si_2 und YbCu_5$_x$Al$_{1-x}$ wurde dabei primär mit makroskopischen Techniken (Transport- und magnetischen Messungen) und mit µSR-Spektroskopie untersucht. Parallel dazu wurde eine für µSR-Experimente geeignete Druckzelle entwickelt.

Die Effekte der chemischen Substitution (Ni/Cu) und des äusseren Druckes auf die physikalische Eigenschaften eines Kondogittersystems konnten mit Hilfe der nichtmagnetischen Probe YbCu2Si2 verglichen werden. Während durch äusseren Druck die magnetische Ordnung bei einem kritischen Druck $p_c$ induziert wird, entwickelt sich diese Ordnung durch Anwendung von chemischer Substitution in einer unüblichen Art, d.h. nur in einem Teil der Probe, dessen Grösse von der Ni-Konzentration (x in Yb(Cu_{1-x}Ni_x)Si_2) bestimmt wird. Der Bruchteil der Probe, der bei tiefen Temperaturen magnetische Ordnung aufweist, skaliert mit der Wahrscheinlichkeit, dass ein Yb-Ion wenigstens zwei Ni-Ionen als nächste Nachbarn besitzt. Dieses Ergebnis weist auf die Wirkung von der durch chemische Substitution induzierte Unordnung auf die Grundzustandseigenschaften von Yb(Cu_{1-x}Ni_x)Si_2 hin. Die Übergangstemperatur $T_m$ des magnetischen Probenbruchteils erhöht sich mit der Ni-Konzentration x. Wir können behaupten, dass die Ni/Cu-Substitution eine Abnahme der magnetischen Übergangstemperatur $T_m$ zur Folge hat.

Die Temperaturabhängigkeit der elektrischen Leitfähigkeit und der thermoelektrischen Kraft $S$ der Yb(Cu_{1-x}Ni_x)Si_2-Probe konnte anhand eines Modells, das die kombinierten Wirkungen des elektrischen Kristallfeldes, der magnetischen Korrelationen und des Kondoeffektes berücksichtigt, erklärt werden. Während die durch chemische Substitution induzierte Unordnung eine drastische Wirkung auf den Restwiderstand der Yb(Cu_{1-x}Ni_x)Si_2-Probe hat, ist keine solche Wirkung auf die Temperaturabhängigkeit der thermoelektrischen Kraft zu beobachten. Diese Tatsache ergab sich durch den Vergleich der $S(x,T)$-Abhängigkeiten für Yb(Cu_{1-x}Ni_x)Si_2-Proben mit den $S(p,T)$-Abhängigkeiten für CeCu_2Si_2.

Für nichtmagnetische Yb-Kondogitter sagt das Phasendiagramm von Doniach eine Abnahme der Kondotemperatur $T_K$ sowie eine Erhöhung der magnetischen Korrelationen mit dem Steigen des äusseren Drucks voraus. Beide Effekte wurden in Yb(Cu_{1-x}Ni_x)Si_2 beobachtet. Die Zunahme der magnetischen Korrelationen zwischen den Yb magnetischen Momenten mit der Zunahme der Ni-Konzentration x in Yb(Cu_{1-x}Ni_x)Si_2 macht sich in einer Zunahme der magnetischen Übergangstemperatur durch Ni/Cu Substitution bemerkbar. Ein Model, welches korrierte und unkorrierte Fluktuationen der magnetischen Momente der Yb Atome berücksichtigt, wurde vorgeschlagen, um die im Nullfeld und Longitudinalfeld gemessenen Myonrelaxationsraten zu erklären. Ein Skaliergesetz für die Temperaturabhängigkeit der Fluktutationsrate der 4f Momente erlaubte es die Kondotemperatur abzuschätzen.
welche mit Zunahme der Ni-Konzentration abnimmt. Das Resultat bestätigt das vorherige Ergebnis.

Die Al/Cu Substitution in YbCu_{5.4}Al treibt das System von einem nichtmagnetischen Grundzustand in YbCu_{4}Al in einen magnetischen Grundzustand in YbCu_{3}Al_{2}. Die YbCu_{3.5}Al_{1.5}-Probe befindet sich in der Nähe eines quantenkritischen Punktes, wie aus makroskopischen Messungen hervorgeht. Die μSR-Messungen bestätigen die magnetische Übergangstemperatur von YbCu_{3}Al_{2}. Die Verlangsamung der Fluktuationen der 4f-Momente wurde über die Zunahme der Myonspinrelaxationsrate mit abnehmender Temperatur in der Nähe des magnetischen Übergangs beobachtet. Oberhalb von 2 K ist die Temperaturabhängigkeit der Myonrelaxationsrate ähnlich für alle untersuchten Verbindungen. Sie steigt jedoch mit fallender Temperatur kontinuierlich in YbCu_{3.5}Al_{1.5} an, während sie gegen einen Sättigungswert in YbCu_{4}Al läuft. Wir schlagen vor, dass die Nullfeld Myonspinrelaxationsraten von einer spinglasähnlichen Verteilung von langsam fluktuirenden Yb-magnetischen Momenten (oder kleinen ferromagnetischen Yb-clustern) stammt.

Wir haben eine speziell für μSR-Experimente geeignete Druckzelle entwickelt. Die μSR-Spektren von allen in der Konstruktion verwendeten Materialien wurden bei verschiedenen Temperaturen gemessen und analysiert. In ihrer endgültigen Form kann die Zelle 17 kbar bei Zimmertemperatur und 10 kbar bei tiefer Temperatur aushalten. Versuche sind noch im Gang, um diese Differenz zu reduzieren. Die spezielle Konstruktion der Zelle ist zum Teil eine Folge der Entdeckung eines osziallerierendes μSR-Signals in Teflon (C_{2}F_{4}).

Mit CeRh_{2}Si_{2}-Proben wurde die Zelle bis zu 7 kbar getestet. CeRh_{2}Si_{2} besitzt zwei magnetische Übergangstemperaturen, T_{N1} und T_{N2}. Wir haben durch Anwendung von äusserem Druck die Unterdrückung der magnetischen Übergangstemperaturen nachgewiesen, im Einklang mit den Ergebnissen aus makroskopischen Messungen. Jedoch kann die auf Neutronenstreumessungen unter Druck basierende magnetische Struktur unsere μSR-Ergebnisse nicht erklären. Nach den Neutronenstreuergebnissen nimmt das geordnete Moment mit zunehmendem Druck ab, während die μSR-Messungen, wenigstens bis 5 kbar, druckunabhängige geordnete Momente zeigen. Dieses Resultat deutet auf gut lokalisierte 4f-Momente hin, im Einklang mit der relativ hohen magnetischen Übergangstemperatur von CeRh_{2}Si_{2}, T_{N1} = 36 K.
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1 Introduction

The present work deals with some of the physical properties of Yb and Ce based Kondo lattice systems. The still puzzling physical properties of these compounds have triggered a large amount of various experiments in recent years. What is the problem? Ce and Yb occupy special places in the lanthanide series of the periodic table. Ce has one 4f electron in the magnetic Ce$^{3+}$ state and none in the Ce$^{4+}$ nonmagnetic state. For ytterbium the situation is similar if one speaks in terms of holes: it has one 4f hole when it is in the magnetic Yb$^{3+}$(4f$^{13}$) state and none in the nonmagnetic Yb$^{2+}$(4f$^{14}$) state. By applying pressure on these compounds, electrons are transferred from the localized 4f levels into the conduction band leading to the stabilization of the 4f$^{13}$ magnetic Yb$^{3+}$ state and of the 4f$^{14}$ nonmagnetic Ce$^{4+}$ state respectively. It is therefore expected that the magnetic interaction between the 4f magnetic moments increases for Yb compounds while it decreases for Ce compounds, with the increase of the applied pressure.

The low temperature physical properties of these compounds are determined by the degree of hybridization between the 4f states and the conduction-band states via two competing interactions:

- the Kondo interaction, leading to a dynamic screening of the localized magnetic moments, i.e., a nonmagnetic ground state.
- the indirect interaction between the localized moments, the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mediated by the conduction electrons, which leads to a magnetic ground state.

An issue of present interest is the behavior of the ground state of Ce and Yb compounds close to the borderline between the magnetic, RKKY-interaction dominated regime, and the pure Kondo region. The hybridization between the 4f states and the conduction electron states, i.e. the competing RKKY and Kondo interactions, was often tuned either by applying pressure or by changing the volume of the unit cell by alloying. While for normal metals or heavy fermion systems the low temperature physical properties are well described within the Fermi-liquid (FL) theory, this is not the case for several doped or pressurized Ce and Yb systems. For them, deviations from the FL picture, i.e. non-Fermi-liquid (NFL) behavior, are noticed in the temperature dependency of several macroscopic physical properties, at low temperatures. The NFL behavior was observed at values of the applied pressure close to the critical value for a magnetic transition at $T = 0$ K, the so called quantum critical point (QCP). Since most published results concerning a QCP in Kondo-lattice systems were obtained with disordered systems, the NFL behavior was often related to pressure-induced disorder until recently when NFL behavior in stoichiometric compounds at zero applied pressure was found, rising again the question about the origin of the NFL properties.

Most of the experiments presented in the literature are concerned with Ce-based Kondo lattice systems while the Yb compounds were less studied, due probably to sample-preparation problems. To fill the gap of information about Yb Kondo lattices, we concentrated our at-
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tention on two of them: Yb(Cu<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>Si<sub>2</sub> and YbCu<sub>5-x</sub>Al<sub>x</sub>. The transition between the non-magnetic ground state of YbCu<sub>2</sub>Si<sub>2</sub> (YbCu<sub>x</sub>Al) and the magnetic ground state of YbNi<sub>2</sub>Si<sub>2</sub> (YbCu<sub>5</sub>Al<sub>2</sub>) was studied as a function of the chemical substitution provided by the Ni/Cu (Al/Cu) replacement. Information about the physical properties of these compounds was obtained from macroscopic (transport and magnetic) and microscopic (µSR) measurements. Through its characteristics, the µSR technique is a useful tool for understanding the physical properties of Kondo lattice systems. Moreover, its sensitivity to phase separation allows one to study the evolution of a certain property in part of the sample’s volume.

The presentation of the work extends over 5 Chapters. A brief introduction into the problem is the subject of Chapter 2. We describe the main interactions present in the system and their competitions for the ground state. The Doniach phase diagram is discussed, pointing to the mirror-like symmetry of the pressure dependence of the magnetic properties of Ce and Yb compounds. This behavior is related to the electron-hole symmetry of their 4f shell. In Chapter 3, the µSR method is presented. After a short introduction, the µSR technique is described together with different measurement setups. For each case, we discuss the information that can be obtained from the µSR spectra for the relevant cases presented in this thesis. The first part of Chapter 4 contains the experimental results for Yb(Cu<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>Si<sub>2</sub>. The dependence of the parameters that describe the macroscopic physical properties of Yb(Cu<sub>1-x</sub>Ni<sub>x</sub>)<sub>2</sub>Si<sub>2</sub> on the Ni concentration x is presented. µSR results obtained in different field configurations follow and they are compared to those obtained using macroscopic methods. The µSR results concerning the YbCu<sub>5-x</sub>Al<sub>x</sub> samples are shown in the second part of Chapter 4. Chapter 5 contains the description of the pressure cell and the puzzling results obtained from our tests on CeRh<sub>2</sub>Si<sub>2</sub>. The design, materials and the parameters of the pressure cell are presented in connection to its specific use. Concluding remarks are presented at the end of Chapter 4 and 5. At the end of the thesis, the Annexes - describing in more detail some calculations - can be found.
2 The problem

In several Ce, Yb and U compounds, generally named Kondo lattices or concentrated Kondo systems (see page 6 for a definition), competing interactions depending on the same parameters lead to different magnetic ground states. In this chapter, a brief presentation of these interactions will be given together with a description of the models that have marked the evolution of the field. The effect of pressure (chemical or external) on the magnetic properties of the Ce and Yb compounds is discussed and the relation between the Doniach phase diagram [DO77] and the physical properties of these compounds is emphasized.

Theoretical background

In the field of strongly interacting electron systems, different classes of compounds are at the focus of present interest. Among them, the intermetallic compounds known as heavy-fermion compounds have been studied most thoroughly. For this class of systems, based on some rare-earth or actinide elements, the attribute “heavy” is connected to the observation of a characteristic energy much smaller than in ordinary metals, which reflects an effective mass \(m^*\) of the conduction electrons orders of magnitude larger than the bare electron mass.

Among the rare-earth compounds, Ce and Yb systems show heavy-fermion behavior with a variety of physical properties and ground states: screening of the rare-earth (RE) magnetic moment via the Kondo effect, magnetic ordering, low-moment magnetism, heavy-fermion superconductivity, Fermi or non-Fermi liquid behavior at low temperatures, valence fluctuations, etc. (see, for example, [GR91]). In addition, the sensitivity of the different properties to the change of some parameters like pressure or chemical composition allows one to study the competition between the different ground states.

It is the proximity of Ce to a fully empty and of Yb to a fully occupied 4f shell what makes the Ce and Yb so sensitive to the applied pressure i.e. owing to this proximity, their electronic configuration may become unstable. In some compounds Ce and Yb are trivalent (Ce\(^{3+}\), Yb\(^{3+}\)) and magnetic with 1 and 13 electrons respectively in the 4f shell. Due to the small spatial extension of the 4f shell, the magnetic properties of these compounds can be described by localized moment models. For example, a Curie-Weiss behavior of the temperature dependence of the magnetic susceptibility is usually found at high temperatures, with an effective magnetic moment close to that of the free ion (for Ce\(^{3+}\), \(\mu_{\text{eff}} = 2.54\ \mu_B\); for Yb\(^{3+}\), \(\mu_{\text{eff}} = 4.54\ \mu_B\)). In other compounds Ce and Yb can loose their 4f electron or respectively fill their 4f shell, changing into the nonmagnetic Ce\(^{4+}\) or Yb\(^{2+}\). Alternatively, they may remain in an intermediate valence (IV) state, between 3 and 4 in the case of Ce and 2 and 3 in the case of Yb. This IV state can be viewed as the dynamic exchange of an electron between the 4f shell and the conduction band and occurs when one of the valence electrons is only loosely coupled to the 4f shell. Relative weak lattice or electronic forces may temporarily squeeze this local electron out of its deeply lying 4f shell, turning it into an itinerant d
electron. This process was found to happen about $10^{13}$ times per second [LA81]. One speaks of inter-configuration fluctuations i.e. fluctuations between the two possible valence states of each ion. These fluctuations are usually related to the strength of the hybridization ($V_{k,f}$) between the localized 4f and the conduction electron wave functions.

There are two mechanisms particularly influenced by the hybridization between the localized 4f and the conduction electron wave functions; they are also the most important interactions in the system:

1. The screening of the local moment via the Kondo interaction of the conduction electrons with the 4f local magnetic moments, i.e. the Kondo effect.
2. The indirect magnetic interaction between the 4f-ions, the RKKY interaction, mediated by the conduction electrons.

If the roles of the crystalline field, lattice disorder, etc. are added we have the ingredients needed to describe the physical properties and the ground state of these compounds.

The **Kondo effect** was first observed for 3d magnetic impurities dissolved in a sea of conduction electrons (see [KO64] and references therein). If the magnetic coupling between the impurities is negligible, strong many-body effects can cause such an impurity to appear as non-magnetic because of the formation of a singlet ground state with the surrounding conduction electrons. The energy gain due to the singlet formation is $k_B T_K$:

$$k_B T_K \approx \frac{1}{N(E_F) \exp \left[ \frac{-1}{J \cdot N(E_F)} \right]}$$

where $N(E_F)$ is the density of states at the Fermi level and $T_K$ the so called Kondo temperature. $T_K$ can vary from a few millikelvin to several hundred Kelvin. In Kondo lattices the formation of the nonmagnetic singlet leads to an anomaly in the density of states $N(E)$ near the Fermi level $E_F$, a sharp peak of width $k_B T_K$, the so called Kondo or Abrikosov-Suhl resonance. In the above formula $J$ ($J_{k,f}$ in the following) is the exchange coupling constant between the localized electrons and the conduction electrons.

The classical signature of the Kondo effect is a minimum in the temperature dependence of the electrical resistivity followed by a logarithmic increase with decreasing temperature. Kondo [KO64] has shown that this effect is the result of conduction-electron (s) spin-flip scattering by the localized magnetic moments (S). Using the exchange Hamiltonian:

$$\mathcal{H} = - J S \mathbf{s}, \text{ with } J < 0,$$

(2-1)

Kondo calculated the scattering probability of the conduction electrons by the magnetic impurity. In a third-order perturbation calculation of the transition probability, he derived a $\ln(T/T_K)$ behavior of the "magnetic resistivity" above a characteristic temperature $T_K$.

The observed minimum in the $\rho(T)$ dependence derives from the interplay between the monotonically decreasing phonon resistivity and the logarithmically increasing spin-dependent contribution. The coupling constant $J$ ($J_{k,f}$ in the following) depends on the hy-
bridization matrix between the localized and conduction electron states and on the position of the $f$ level $E_f$ with respect to the Fermi level $E_F$ [SC66]:

$$J_{kf} \equiv \frac{V_{kf}^2}{E_F - E_f}.$$  \hspace{1cm} (2-2)

At $T << T_K$ a Kondo system can be described by the Fermi liquid model [NO74].

The most frequently adopted theoretical model to describe the magnetic impurities in a host lattice is the **Anderson impurity model** [AN61], for a magnetic impurity having one 4$f$ electron or hole:

$$H = \sum_{k,M} \epsilon_k n_{kM} + \sum_M E_0 n_M + \frac{U}{2} \sum_{M,M'} n_M n_{M'} + \sum_{k,M} \left( V_{kf} a_{kM}^+ c_M + V_{kf}^* c_M^+ a_{kM} \right).$$  \hspace{1cm} (2-3)

The importance of this model resides in that it furnished a basis for the description of both the Kondo effect [K064] and the intermediate valence (IV) phenomena [LA81]. In Eq. 2-3 the indexes $k$ and $M$ distinguish between operators referring to the conduction electrons and the localized electrons respectively. $a$, $c$ are creation/annihilation operators and $n$ the corresponding number operators. $\epsilon_k$ is the conduction electron energy and $E_0$ is the energy of the 4$f$ states, both defined with respect to the Fermi energy.

The impurity model (a lattice model would envision a periodic array of such impurities) describes a $N_f$-fold degenerate local $f$-orbital with binding energy $E_M$ and $f-f$ Coulomb repulsion $U$, hybridized via a matrix element $V_{ kf}$ to conduction band electrons. $U$ is the energy needed to add a second 4$f$-electron to the localized 4$f^{1}$ state. It acts to separate energetically the valence states $f^n$ while $V_{ kf}$ enables valence fluctuations through electron transfer to the conduction band. Depending on the strength of $V_{ kf}$, the 4$f^n$ and 4$f^{n+1}$ levels have a nonzero occupation probability resulting in intermediate $f$-level occupation (i.e. intermediate valence) for large hybridization strengths. This implies both charge and spin fluctuations at the 4$f$-ion site. If $V_{ kf}$ is small enough the two ionic configurations are energetically well separated, a situation that corresponds to the so called nearly integer-valence limit or Kondo regime. The 4$f$ and the conduction electrons can still exchange their spin components but no charge transfer is allowed. In this case the mixed $f$/conduction electron ground state is a singlet and, as temperature $T$ decreases, the magnetic susceptibility $\chi(T)$ changes from Curie like to Pauli like below the Kondo temperature $T_K$.

To explain the magnetic and transport properties of some Ce alloys Comut and Coqblin [CO72] and Bhattacharjee and Coqblin [BH76a] have discussed the Kondo effect in the presence of the crystalline field. They used a modified Anderson Hamiltonian (in the limit of large $U$) that describes the resonant-scattering character of the cerium impurities, taking into account combined spin and orbit exchange scattering:

$$H = \sum_{k,M} \epsilon_k n_{kM} + \sum_M E_M n_M - \sum_{k, k', M, M'} J_{MM'} c_{kM}^+ c_{k'M} c_{k'M}^+ c_{kM} + \sum_{k, k', M} V_{MM'} c_{kM}^+ c_{k'M} c_{k'M}^+ c_{kM}.$$  \hspace{1cm}

Here the index $M$ denotes the quantum number characterizing an eigenstate of energy $E_M$ in the presence of the crystal field. $V_{MM'}$ represent the pure direct scattering and $J_{MM'}$ are the exchange coupling parameters.
Chapter 2  The problem

\[ J_{MM'} = \frac{V_{ff}}{2} \left( \frac{1}{E_M} + \frac{1}{E_{M'}} \right). \]

They reduce to (Eq. 2-2) for large \( M-M' \) splitting \( (E_M >> E_{M'}) \), since the energies \( E_M \) are defined with respect to the Fermi energy. Details about the relation of these models with the experiment are given in Chapter 4.1, where our measurements of the temperature dependence of the electrical resistivity and the thermoelectric power of Yb(Cu_{1-x}Ni_x)_{2}Si_2 are discussed.

The Kondo effect was also observed in more concentrated 4f or 5f systems. Because of the small extension of the 4f(5f) wave function, the concentration of the 4f(5f) magnetic ions in a nonmagnetic host can be surprisingly high without preventing the Kondo effect to appear. These alloys are called \textit{concentrated Kondo systems} and, when the magnetic ions build up a regular lattice, \textit{Kondo lattices}.

In Kondo lattices, at temperatures well below \( T_K \), a narrow resonance in the density of states near the Fermi level is formed due to the strong coupling between the conduction electrons and the localized \( f \) electrons. The \textit{Fermi liquid theory} [NO74] is useful to describe the physical properties at these temperatures, i.e. below a characteristic temperature \( T_{coh} \), but above any magnetic or superconducting transition. \( T_{coh} \) denotes the temperature at which coherence effects arise in the Kondo-lattice system leading to the formation of a band of heavy quasiparticles with a width of order \( k_B T_{coh} \). In the Fermi liquid theory, a one-to-one mapping of the non-interacting electron states to interacting electron states is assumed close to the Fermi energy. The states are described in terms of quasiparticles that have enhanced effective mass (\textit{heavy fermions}) due to the interactions with the other particles. The heavy mass of the quasiparticles is reflected (for \( T \to 0 \)) in the large values of the electronic coefficient \( \gamma \) of the specific heat \( (C/T = \gamma = \text{const.}) \), an enhanced Pauli susceptibility \( (\chi = \text{const.}) \), a huge \( T^2 \) term in the electrical resistivity \( (\rho = \rho_0 + A T^2) \), etc.\(^1\).

Due to the high localization of the 4f moments, antiferromagnetic intersite interactions between the 4f magnetic moments can occur if mediated by the conduction electrons. This is the so-called indirect \textit{RKKY interaction} ([KI87] and references therein) that tends to establish a magnetic ground state. Roughly, the mechanism of the RKKY interaction can be described as follows:

- Near a rare-earth ion \( S_1 \), the spins of the conduction-electron spins are polarized due to an \( s-f \) interaction identical with that described by Eq. 2-1. The obtained conduction electron spin polarization \( P_1(r) \) is extends over a long range and alternates in sign [YO-57].
- A second ion \( S_2 \), situated at a distance \( R \), senses the conduction electron polarization. The resultant indirect interaction between \( S_1 \) and \( S_2 \) is the RKKY interaction.

\(^1\) For some reviews on heavy fermion systems - experiment and theories - consult [GR91], and references therein.
The spatial dependency of the RKKY interaction is given by a term $F(2k_F R)$ where $F(x) = (x \cos x - \sin x)/x^4$ and $k_F$ is the Fermi vector. It explains the existence of modulated magnetic structures [GE-62]. The strength of the RKKY interaction is characterized by an energy $k_B T_{RKKY}$ which can be expressed as

$$k_B T_{RKKY} \propto J_{sf}^2 N(E_F),$$

where $N(E_F)$ denotes the density of states at the Fermi level and $J_{sf}$ the exchange coupling parameter.

Note that the energy scales of both the Kondo and the RKKY interactions depend on $J_{sf}$, the exchange-coupling constant between the conduction electrons and the 4f localized electrons. Considering the scales defined by $T_K$ and $T_{RKKY}$, Doniach [DO77] was the first to propose that the low temperature ground state of such a system is a consequence of the competition between the demagnetizing on-site Kondo scattering and the intersite RKKY interaction. The model can be pictured in a "Doniach phase diagram" like that presented in the Figure 2-1. The heavy-fermion regime is located close to the magnetic instability region ($J_c$) where the Kondo and the RKKY interaction have similar strengths.

Within this simple model the compounds with stable $f$ moments (i.e. small hybridization, small $J_{sf}$), characterized by $T_{RKKY} > T_K$, are magnetic at low temperatures. On the other hand if the hybridization between the $f$ states and the conduction electron states is large ($T_K > T_{RKKY}$, large $J_{sf}$), a paramagnetic ground state is expected at low temperatures.

Since $J_{sf}$ is sensitive to changes of such parameters as pressure or chemical composition, and therefore can be changed experimentally, a transition from a magnetic state (usually antiferromagnetic, AFM) to a spin...
liquid state (or inverse) can be induced. The latter may show the properties of a Landau Fermi liquid with strongly renormalized particles (heavy fermions). Since short-range, short lived (quantum) AFM fluctuations, indicating the interactions between quasiparticles, are constituents of the coherent FL phase, these fluctuations should grow in space and time when approaching the AFM phase transition. The solid line in Figure 2-1 represents the ordering temperature of the AFM phase. One can observe that, in the “magnetic region”, the ordering temperature $T_M$ immediately below $J_c$ is lower than $T_{RKKY}$. One explanation is that the magnetic moment of the 4f shell is reduced due to the screening effect of the conduction electrons (magnetic ordering with reduced magnetic moments).

**Ce vs. Yb compounds:** one important consequence of applying pressure is that electrons can be squeezed out from the 4f levels. From a magnetic point of view, as one can see in Figure 2-2, the result is opposite for Ce and Yb compounds. In the Yb compounds, the applied pressure should stabilize the magnetic ground state while in the Ce compounds the applied pressure drives the system towards a nonmagnetic ground state. This mirror behavior of Ce and Yb compounds reflects the electron-hole symmetry of the electronic configuration of the Ce and Yb ions.

The effects on the magnetic states of these types of compounds are quite different when chemical (or external) pressure is applied, especially in the region close to $J_c$, the magnetic instability region. Often, the Fermi liquid picture breaks down (non-Fermi liquid behavior) at low temperatures as evidenced in thermal or transport properties measurements [PI96]. Models based on

- multi-channel Kondo effect [CO96],
- distribution of Kondo temperatures [MI96],
- proximity to a quantum critical point (QCP) [MI93],
- Griffiths phase [CA98] i.e. magnetic clustering, due to disorder, in the paramagnetic phase close to the QCP, etc.,

successfully explained particular measurements, but up to date the non-Fermi liquid behavior is not fully understood. Details about the NFL behavior and the different models dealing with it will be presented in Chapter 4, when the experimental results are discussed.

Since almost all previous μSR investigations were performed on Ce samples (due perhaps to the difficulty in preparing Yb samples), we have started a systematic study of the microscopic properties of Yb compounds. Our results are discussed in correlation with experimental results in similar Ce compounds, when available, and with experimental results obtained using macroscopic techniques. The effect of the chemical substitution on the magnetism of the Yb ions was investigated in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and YbCu$_{5-x}$Al$_x$ (see Chapter 4). CeRh$_2$Si$_2$ was used as a test material for the μSR investigations under external pressure (using a homemade Cu-Be pressure cell) because of the fast decrease of its antiferromagnetic transition temperature with the applied pressure (see Chapter 5).
3. The μSR method

In this chapter the μSR technique and method are described. The data analysis for particular cases relevant to the present study is also presented.

3.1 Introduction

Known as μSR, the muon spin rotation (relaxation, resonance) technique is increasingly employed for the microscopic investigation of magnetic properties of condensed matter. The key words that would describe the μSR method are:

- Polarized muons are implanted into a sample.
- The spin of the muon precesses around a local magnetic field.
- The muon decays ($\tau_\mu = 2.2 \mu$sec) by emitting a positron preferentially along the muon spin.
- The positrons are detected and the events registered in histograms, the μSR spectra.

μSR belongs to the family of NMR (Nuclear Magnetic Resonance), PAC2, EPR (Electronic Paramagnetic Resonance), Neutron scattering and Mössbauer experimental methods. It is complementary to them by the time widow that can be accessed in a typical experiment, see Figure 3-1.

Applied to solid state physics, the μSR method is a very useful tool for the investigation of hyperfine fields, of the static and dynamic behavior of the nuclear and electronic magnetic moments, of critical phenomena etc. It is also sensitive to phase separation and therefore it is often used to distinguish between the competition and coexistence of different (magnetic) ground states. Very small magnetic moments (down to $10^{-3} \mu_B$) or short range ordering phenomena, not accessible by other methods, can also be detected in μSR experiments.

One should keep in mind that the muon (as γ PAC) maps the field's magnitude.

---

2 Perturbed Angular Correlation, see for example [KA95a]

---

Figure 3-1: The time window of a μSR experiment compared with other methods (from [KA00]). $1/\tau_c$ is the fluctuation rate of the field sensed by the nuclear probes or the rate of spin fluctuations.
distribution, or dynamic behavior at an interstitial site (EPR, NMR or Mössbauer techniques probe the field at the nucleus of an atom at a regular lattice site) and is strongly sensitive to the spatial arrangement of the surrounding magnetic moments. Therefore, although the μSR technique cannot be used to determine magnetic structures it is sometimes a good test for them. A big advantage of the μSR technique, compared to NMR, is that one can measure in true zero field, at all temperatures and in all types of samples. Since the muon is a spin 1/2 particle no quadrupolar effects have to be taken into account. Nevertheless, there are some limitations:

- muon diffusion at high temperatures can mask the intrinsic magnetic behavior by mimicking spin fluctuations (see Chapter 3.3.2),
- the limits of the μSR time window, related with the time resolution of the detectors and the finite lifetime of the muon,
- The muon is not an innocent probe i.e. it introduces local lattice distortions at the place where it comes at rest. It can also modify the crystalline electric field (CEF) levels, (see for example [FE95], [TA97] and [PI99]) of its surrounding ions,
- the muon site(s) cannot always be determined, thus limiting the interpretation of measurements.

### 3.2 The technique

For μSR experiments the muons (μ⁺, μ⁻) are obtained from the pion (π⁺, π⁻) decay. The pions are obtained by colliding an accelerated proton (p) beam (≈ 600 MeV) with a target (Carbon target at PSI). In the following, when not specified, only positive muons will be considered (μ⁻ are less utilized in the investigation of the solid state since they might be captured by the atoms). The relevant nuclear reactions are:

\[ p + p \rightarrow p + n + \pi^+ \]  
\[ p + n \rightarrow n + n + \pi^+ \]

for the pion production, and

\[ \pi^+ \rightarrow \mu^+ + \nu_\mu \quad (\tau_\pi = 26 \text{ ns}) \]

for the muon production.

Due to parity violation in the weak interaction, the muons obtained from the pion decay are 100% spin polarized, i.e. their spin is oriented oppositely to their momentum in the pion rest frame (Figure 3-2).

![Figure 3-2: Spin and momentum of decay products of the pion seen in the pion rest frame.](image)
3.2 The technique

According to their selection conditions one distinguishes two types of muon beams:

1. **Surface muons**, obtained from the pions decaying at rest near the surface of the production target. The surface beam is 100% polarized (see Figure 3-2) and ideally monochromatic, with a $\mu^+$ momentum of 29.8 MeV/c, which corresponds to a kinetic energy of 4.1 MeV. Due to its small energy, this type of beam can be stopped in thin samples, usually of around 160-200 mg/cm$^2$. As an illustration see Figure 3-3 [AM98]; a series of samples Al/SiO$_2$ samples with different Al thickness were used. Since the $\mu$SR signal of Al and SiO$_2$ are very different, their contribution to the global signal can be determined easily. For Al, a penetration depth of around 0.6 mm is obtained.

A muon beam of lower energy (ultra slow muons) can be obtained by further reducing the energy of the incoming muons to the eV-keV range. The energy (and therefore the penetration depth) of this type of beam is tunable. Therefore, the study of the magnetic properties that depend on the distance from the surface of the sample is possible. Even though this technique has been developed only very recently, several successful experiments have been performed: study of surfaces and multilayers, measurement of the field penetration depths in superconductors, etc.. For more details and examples, see [MO99].

2. A **high-energy beam** is obtained from pions that leave the target at high energies. They are collected over a certain solid angle by quadrupole magnets and directed on to an 8 m decay section consisting of a long superconducting solenoid with a field of 5 T. If the pion momentum is not too high, a large fraction of the pions will have decayed before they reach the end of the solenoid. The exit of the solenoid may be viewed as a diffuse source of muons. Usually only the decay muon occurring along (forward muons) or opposite to (backward muons) the direction of the pion momentum are selected, to keep a large degree of (backward or forward) polarization. However, the polarization of a high-energy muon beam, in the laboratory frame, is limited to around 80%. The range of this type of beam in matter is larger than that of the surface beam, therefore it can be used to study massive samples or samples inside of recipients, e.g. samples inside pressure cells.
A study of the penetration depth and signal amplitudes when using a pressure cell will be presented in Chapter 5. In Figure 3-4 a typical high energy muon beam line is presented. Different magnets are used to transport the muon beam to the sample. All are tunable, so both the momentum and the beam spread can be controlled precisely. The magnets are either quadrupole (Q) magnets as beam collimators, or bending (A) magnets (for momentum selection). Slits (F) are used to limit the lateral beam extension and its intensity. The long superconducting solenoid, the so-called $\mu$-channel, is typical only for the high-energy muon beams. Instead of the $\mu$-channel, for a surface beam one finds the separator, a device that combines electric and magnetic fields to clean the beam from impurities (especially positrons and protons). At higher electric and magnetic fields, it can be used to rotate the muon spin - see Chapter 3.5. For high-energy muon beams, a spin rotator is not effective because of the high momentum of the particles.

Some of the physical properties of the muon are summarized in Table 3-1:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass ($m_\mu$)</td>
<td>$206.76835(11) \ m_e = 0.1126096 \ m_p = 105.6595 \ MeV/c^2$</td>
</tr>
<tr>
<td>charge</td>
<td>$+e$</td>
</tr>
<tr>
<td>spin ($\hbar/2$)</td>
<td></td>
</tr>
<tr>
<td>magnetic moment $\mu_\mu$</td>
<td>$3.1833455(5) \ \mu_p$</td>
</tr>
<tr>
<td>gyromagnetic ratio $\gamma$</td>
<td>$2\cdot\pi \cdot 13.553879 (\pm 0.2 \ ppm) \ kHz/G$</td>
</tr>
<tr>
<td>g factor</td>
<td>$2.002331848(17)$</td>
</tr>
<tr>
<td>lifetime ($\tau_\mu$)</td>
<td>$2.19703(4) \ \mu s$</td>
</tr>
</tbody>
</table>

**Table 3-1: Physical properties of the muon [SC85]**. With $m_e$, $m_p$ we have denoted the electron and respectively the proton mass. The magnetic moment of the muon is given in units of the proton magnetic moment.

The muon can be considered as a light proton, with a quite large gyromagnetic ratio. Implanted in a sample its spin will sense the magnetic field at the site where it comes to rest and will precess around it with a frequency $\omega = \gamma B$. 

**Figure 3-4:** Typical high-energy muon beam (here, the $\mu E_1$ beam line at PSI). The different components are described in the text. For the $\mu$SR experiment environment, see below.
3.2 The technique

The muon has a lifetime $\tau_\mu$. It decays in a positron and two neutrini,

$$\mu^+ \rightarrow e^+ + e^- + \nu_e + \bar{\nu}_\mu.$$ 

The parity-conservation is also violated in the muon decay, therefore the muon decay has an anisotropic spatial distribution, i.e. the positrons are preferentially emitted along the spin direction. The probability $dP(\theta,E,t)$ of finding a positron with energy between $E$ and $E + \Delta E$ at a time between $t$ and $t + \Delta t$ in the solid angle $d\Omega$ located at the angle $\theta$ with respect to the muon spin at the moment of the decay is given by

$$\frac{dP}{d\Omega dE dt} = C(E) e^{-t/\tau_\mu} W(E,\theta),$$

where $C(E)$ is the energy distribution function and $W(E,\theta)$ is the angular distribution of the decay positrons. The latter can be expressed as

$$W(E,\theta) = 1 + A(E) \cos \theta.$$ 

$A$ is called the initial asymmetry and is strongly dependent on the positron energy (for more details see [SC85]).

In Figure 3-5 the polar diagram of the angular distribution of positrons from the muon decay is shown; dashed line: the angular distribution of the decay pions with maximum energy; full line: integrated over all positron energies with $C(E)$ as the weight function. The big arrow indicates the actual direction of the muon spin at the moment of the decay.

The high polarization of the muon beam and the asymmetric decay of the muon are the basic features on which the $\mu$SR technique rests.

By recording the emitted positrons in different detectors (forward (F), backward (B), ... ) placed around the sample, the time evolution of the muon polarization, i.e. the $\mu$SR spectra, is obtained. In Figure 3-6 a typical experimental arrangement is shown. Each incoming muon gives a start-clock signal and each emitted positron a stop-clock signal. The event is stored in a histogram, containing the raw $\mu$SR spectrum.

The time evolution of the muon polarization $P(t)$ can be deduced from the time dependence of the asymmetric decay-positron distribution. In the so-called time differential $\mu$SR technique many (millions) of muon decays are recorded one by one in different directions.
The obtained raw μSR spectra can be fitted with the following formula:

\[ N_{e^+}(t) = B + \frac{N_0}{\tau_\mu} \exp\left(-t / \tau_\mu\right) \left[ 1 + A P_r(t) \right] \]

where \( B \) is a time independent background, \( N_0 \) is a normalization constant and the exponential accounts for the \( \mu^+ \) decay. \( A \) is the asymmetry and \( P_r(t) \) reflects the time dependence of the \( \mu^+ \) polarization (\( r \) indicates the direction of observation):

\[ P_r(t) = \hat{n} \cdot P(t)/P(0) \]

where \( P(t) \) is the time dependence of the \( \mu^+ \) polarization vector and \( \hat{n} \) is an unit vector in the direction of observation.

\( A = 1/3 \) when all positron energies are sampled with equal probability (see above). In practice, values of \( A \) of 0.25 are found (due to the possible reduction of polarization of the muon beam, geometry of the positron counters, non-uniform energy sensitivity of the detectors, ...). For \( P(0) = \pm \hat{n} \), \( P_r(t) \) is the normalized muon spin autocorrelation function:

\[ P_r(t) = \pm G(t) \quad \text{with} \quad G(t) = \frac{\langle S(t)S(0) \rangle}{\langle S(0)^2 \rangle}, \]

which depends on the average value, distribution and time evolution of the internal fields i.e. contains the physics of the magnetic interactions of the \( \mu^+ \) inside the sample.

If the sample exhibits phase separation (e.g. domains with different ground states) or if the muons stop in magnetically inequivalent sites in the same magnetic domain, \( P_r(t) \) is simply the sum of the different contributions: \( A \sum_i P_{r_i} \). If the muons are uniformly implanted into the sample, the relative amplitudes \( A_i \) of the different components are a direct measure of the associated volume fractions.
As it was already specified different informations as local field magnitude and/or distribution, spin dynamics, etc., can be obtained from a μSR experiment. Three ways to access these informations are commonly used: the zero field, longitudinal field and transverse field techniques. In the following, they will be briefly presented together with relevant examples.

3.3 Zero field (ZF) μSR

In the zero-field (ZF) configuration the muon is only subject to the internal magnetic fields at the place where it comes to rest, the muon site. By muon site, we denote all crystallographically equivalent sites in the unit cell. They might become magnetically inequivalent at temperatures below a magnetic transition temperature or in transverse field (TF) experiments. In zero-field experiments the local fields are due either to nuclear magnetic moments (often static in the time window of the μSR experiment) or to electronic moments. In the following we assume that the initial $\mu^+$ polarization and the direction of observation are the same, $\mathbf{P}(0) || z$ (for a more general case see Appendix A).

In the absence of an externally applied field the main contributions to the magnetic fields at the muon site arise from the hyperfine dipolar and contact fields of the surrounding magnetic moments:

$$ B_\mu = B_{\text{dip}} + B_c, $$

with

$$ B_{\text{dip}} = \sum_i \frac{1}{r_i^3} \left( \frac{3(m_i \cdot r_i) r_i}{r_i^2} - m_i \right). \tag{3-1} $$

where $r_i$ is a vector from the muon to the $i^{th}$ magnetic moment $m_i$, and the summation runs over all magnetic moments. The contact field contribution will be described in more detail in Chapter 3.5.

3.3.1 Static magnetic fields

The Gaussian/Lorentzian field distributions generated by nuclear or electronic magnetic moments and the field distribution created by an incommensurate magnetic structure are presented on the following sub-sections.

3.3.1.1 Magnetic fields of nuclear origin

Since the nuclear magnetic moments are randomly oriented, their dipolar contribution to the local field can be described in terms of a field distribution which, in cubic systems, is

\[ B = 2m/r^3 \] for $m = 1 \mu_B$ and $r = 1 \text{Å}. \]

---

3. For an estimate, the magnetic field $B$ created by a magnetic moment $m$ at distance $r$ along the orientation of the moment is $B = 2m/r^3$ and equals about 2 T for $m = 1 \mu_B$ and $r = 1 \text{Å}$. 

15
isotropic ($\Delta_x = \Delta_y = \Delta_z = \Delta$ in the equation below) and Gaussian (dense system of arbitrary oriented magnetic moments):

$$f(B) = \left(\frac{\gamma_u}{\sqrt{2\pi} \Delta}\right)^3 \exp\left(-\frac{\gamma_u^2 B_x^2}{2\Delta_x^2}\right) \exp\left(-\frac{\gamma_u^2 B_y^2}{2\Delta_y^2}\right) \exp\left(-\frac{\gamma_u^2 B_z^2}{2\Delta_z^2}\right).$$  \hspace{1cm} (3-2)

i.e a product of Gaussian field distributions along the three coordinate axis. $\Delta/\gamma_u$ is the width of the field distribution (the half width at max $/\sqrt{e}$). It can be calculated from the second moment of the Gaussian field distribution $\Delta^2 = \frac{1}{2} M_{2F}^2$ [SC85]. For a polycrystalline sample in the absence of quadrupole effects$^4$, one has

$$M_{2F,\text{poly}} = \frac{4}{3} \gamma_u^2 \sum_{i=1}^{N} \left(\frac{m_i}{r_i^3}\right)^2.$$ \hspace{1cm} (3-3)

The magnetic moment was denoted by $\mathbf{m}$, $m^2 = I(I+1)\gamma^2 \hbar^2$, where $I$ is the nuclear spin and $\gamma$ is the gyromagnetic ratio of the nucleus. For more detailed calculations, see [SC85].

### 3.3.1.2 Magnetic fields of electronic origin

Static fields or static field distributions of electronic origin are usually observed below a magnetic transition temperature. Several situations can be found:

- For typical ferromagnetic or antiferromagnetic ordering, a well-defined magnetic field at the muon site should be observed (in the case of an ideal sample, the field at all muon sites should be a $\delta$-function).

- In most of the samples, small displacements of the ions from their ideal positions, vacancies or other defects create a field distribution (often of Gaussian shape) that can be very large if the ordered moments are of the order of 1 $\mu_B$.

- Particular cases are the dilute spin glasses. In dilute spin glasses the field distribution is created by rare but large magnetic moments and can be described by a Lorentzian function:

$$f(B_j) = \frac{1}{\pi^2} \left( \frac{a}{a^2 + B_j^2} \right),$$ \hspace{1cm} (3-4)

Figure 3-7: Source of field distribution (Lorentzian) in almost perfect samples (see Chapter 5.2).

---

$^4$ The contribution from a single ion is $M_2 = 4m^2 \gamma_u^2 / (3r^6) = B^2 \gamma_u^2 / 3$, where $B$ is calculated in footnote 1. The contribution at $r = 1$ Å from a ion having $m = 1$ $\mu_B$ is $M_2 = 8 \cdot 10^5$ MHz$^2$.
where \( a \) is the half width at the half maximum (HWHM) of the field distribution. A similar \( f(B) \) is to be expected also in samples with typical ferromagnetic or antiferromagnetic ordering if the defects are rare, i.e. for almost-perfect samples, see Figure 3-7.

If several magnetically inequivalent muon sites are involved, the muons will sense different field distributions. In most of the cases, the different contributions can be distinguished in the analysis of the \( \mu SR \) spectra.

### 3.3.1.3 Incommensurate magnetic structures

If the magnetic ordering is incommensurate with respect to the crystal lattice the field distribution becomes more complicated. The case of a single-\( k \) incommensurate sine-modulated structure will be considered here. The multiple-\( k \) structure and the helical structure are described in Appendix B and Appendix C, respectively.

The magnetic structure of a compound can be generally described using

\[
m_i = M \cos(2\pi k r_i + \phi),
\]

where \( M \) is the magnetic moment that is modulated, \( r_i \) is the coordinate of the magnetic moment, \( \phi \) is a phase factor and \( k \) is a vector in the reciprocal space that describes the magnetic modulation. If the components of \( k \) are rational numbers (with respect to the lattice parameters), the magnetic structure is commensurate with the crystallographic unit cell. If at least one of the components of \( k \) is an irrational number, the magnetic and the crystallographic unit cell are incommensurate in that direction of the direct space.

Different from the commensurate magnetic structures, where a \( \delta \)-function field distribution at the muon site is expected for ideal samples, incommensurate magnetic structures will lead to intrinsic field distributions. The field distribution in the case of incommensurate (sinusoidal) magnetic structures is usually approximated with a sinusoidal spatial distribution of fields:

\[
B_\mu = B_{\text{max}} \cdot \sin \theta,
\]

**Figure 3-9: Notations used for the calculation of \( B_{\text{dp}} \)**
leading to:

\[
\frac{f(B)}{B} = \frac{2}{\pi \sqrt{B_{\text{max}}^2 - B^2}} \quad (3-6)
\]

for \(0 \leq B_{\mu} \leq B_{\text{max}}\) (Figure 3-8). As it will be shown below this is only a special case of a more general field distribution.

Assuming a magnetic structure described by Eq. 3-5 with the notations used in Figure 3-9,

\[
m_i = M \cos(2\pi k \cdot R_i + \varphi),
\]

the dipolar field at the muon site can be calculated using Eq. 3-1:

\[
B_{\text{dip}} = \sum_i \frac{1}{r_i^3} \left[ \frac{3(m_i \cdot r_i) r_i}{r_i^2} - m_i \right],
\]

\[
B_{\text{dip}} = \sum_i M \cdot \cos(2\pi k \cdot R_i + \varphi) \left[ \frac{3(I_M \cdot r_i) r_i}{r_i^5} - \frac{I_M}{r_i^3} \right],
\]

where \(I_M\) is a unit vector in the direction of the magnetic moment \(M\):

\[
M = M \cdot I_M.
\]

By making the substitution \(R_i = r_i + r_{\mu}\) [PI98] (Figure 3-9) and using trigonometric relations we get:

\[
B_{\text{dip}} = \cos 2\pi (k \cdot r_{\mu}) \sum_i M \cdot \cos(2\pi k \cdot r_i + \varphi) \left[ \frac{3(I_M \cdot r_i) r_i}{r_i^5} - \frac{I_M}{r_i^3} \right] - \sin 2\pi (k \cdot r_{\mu}) \sum_i M \cdot \sin(2\pi k \cdot r_i + \varphi) \left[ \frac{3(I_M \cdot r_i) r_i}{r_i^5} - \frac{I_M}{r_i^3} \right].
\]

\[
(3-7)
\]

The magnetic fields at the muon site, generated with Eq. 3-7, lie in a plane and define an ellipse (see Figure 3-10). The corresponding field distribution \(f(B)\) is presented in Figure 3-11 (in this particular case it’s a field distribution calculated for one of the 2-2 (96g in Wickoff notation) muon sites in CeAl₂, see Appendix B).

Notice that:

- Eq. 3-7 is valid independently of the type of magnetic structure considered (commensurate or incommensurate)
- the two lattice sums on the right hand side of the equation can be calculated separately. We will denote them \(S_{\text{cos}}\) and \(S_{\text{sin}}\):

\[
B_{\text{dip}} = S_{\text{cos}} \cdot \cos(2\pi k \cdot r_{\mu}) - S_{\text{sin}} \cdot \sin(2\pi k \cdot r_{\mu})
\]

\[
(3-8)
\]
• Eq. 3-8 expresses that the end points of $B$ describe an ellipse. In the case of an incommensurate structure, all the points on the ellipse are generated and each of them only once i.e. $kr_{ni} \neq k(r_{ni} + R_n)$ for all direct lattice vectors $R_n = n_1a + n_2b + n_3c$ where $n_1, n_2$ and $n_3$ are integers.

The fields at the muon sites can be generated by

$$B_{\text{dip}} = S_{\cos} \cdot \cos \alpha - S_{\sin} \cdot \sin \alpha,$$

which describes all the points of an ellipse.

![Figure 3-10: Dipolar fields at the muon site for an incommensurate magnetic structure.](image)

![Figure 3-11: Field distribution for an incommensurate magnetic structure.](image)

The field distribution at the muon site can be easily computed if $S_{\cos}$ and $S_{\sin}$ are perpendicular to each other (we denote them $B_{\text{min}}$ and $B_{\text{max}}$: $B_{\text{min}} < B < B_{\text{max}}$). In that case:

$$f(B) = \frac{2}{\pi} \frac{B}{\left( B^2 - B_{\text{min}}^2 \right)^{3/2} \left( B_{\text{max}}^2 - B^2 \right)^{1/2}}.$$  (3-9)

$f(B)$ is presented in Figure 3-11. Therefore:

• In the general case, the field distribution for an incommensurate magnetic structure is given by Eq. 3-9.
• In order to have a field distribution like that presented in Figure 3-8, one of the lattice sums ($S_{\cos}$ or $S_{\sin}$) that appear in Eq. 3-8 should be zero.
• The field distribution originating from an incommensurate magnetic structure can be similar to that created by a commensurate magnetic structure if $S_{\cos}$ and $S_{\sin}$ have values close to each other, i.e. the two peaks at $B_{\text{min}}$ and $B_{\text{max}}$ are superposed (unresolved).
3.3.1.4 ZF μSR spectra

In this section, μSR spectra typical for the above mentioned static field distributions are described, together with the suitable functions used to fit the observed $P(t)$ dependencies.

3.3.1.4.1 One field at the muon site (δ-function field distribution centered at $B$)

In this simple case, all the muons sense the same magnetic field $B$, see Figure 3-12. This situation might occur in ideal single-domain single-crystals with one (magnetically equivalent) muon site. The time dependence of the $\mu^+$ polarization as seen in the backward detector is

$$P_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\omega t), \quad (3-10)$$

where $\theta$ is the angle between the magnetic field and $P(0)$ (defines the $z$ axis). $\omega = \gamma_B \mu_B$ is the Larmor precession frequency of the muon spin around the local magnetic field. A simulated μSR spectrum ($B = 50$ G, $\theta = 30^\circ$) is presented in Figure 3-13. Fitting the μSR spectrum to the above equation, information about the orientation of the local field in the laboratory coordinates (see Appendix 1 for a discussion) can be obtained. In the case of a polycrystalline sample the average over all $\theta$ angles yields (the rule is sometimes valid also for multidomain single crystals)

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \cos(\omega t) \quad (3-11)$$

for the $z$ direction, and constant $P_x$ and $P_y$. The one-third term in the above equation can be easily understood by considering that since the magnetic fields can have all the orientations, on the average one third of the muons will see fields parallel to their initial polarization and will not precess while two thirds of them will see fields perpendicular to their initial polarization and will precess around them with $\omega = \gamma_B B$.

---

**Figure 3-12:** The components of the μSR signal in the case of a δ-function field distribution centered at $B$.

**Figure 3-13:** μSR spectra simulated for the situation presented in Figure 3-12.
3.3.1.4.2 Isotropic Gaussian magnetic field distribution with zero average

In this case muons located at different sites see different fields. This leads to a loss of the polarization of the muon ensemble. The time dependence of the polarization can be computed by integrating Eq. 3-10 over the field distribution:

\[ P_\perp(t) = \int f(B_\mu) [\cos^2 \theta + \sin^2 \theta \cos \omega t] \, d^3 B_\mu \]

For an isotropic Gaussian field distribution, Eq. 3-2, the integration leads [KU67]:

\[ P_\perp(t) = \frac{1}{3} + \frac{2}{3} \left( 1 - \Delta^2 t^2 \right) \exp \left( -\frac{\Delta^2 t^2}{2} \right) \]

see Figure 3-14, where the 1/3 term has the same meaning as above and \( \Delta/\gamma_\mu \) is the width of the field distribution written in general as:

\[ \Delta^2 / \gamma_\mu^2 = \left\langle B_x^2 \right\rangle = \left\langle B_y^2 \right\rangle. \]

\( P_\perp(T) \) is called Kubo-Toyabe (or Gaussian Kubo-Toyabe) depolarization function. Other features of \( P_\perp(t) \) are:

- It has a minimum at \( t_{\text{min}} = \sqrt{3} / \Delta \).
- The minimum value, \( P_\perp(t_{\text{min}}) = 0.036 \), is independent of \( \Delta \).
- The shape of \( P_\perp(t) \) is Gaussian at early times (dotted line in Figure 3-14) and it can be approximated by

\[ P_\perp(t) = \exp(-t^2 \Delta_G^2 / 2) \]  \hspace{1cm} (3-12)

with \( \Delta_G = \sqrt{2} \Delta \).

- Knowing \( \Delta \) (via the second moment of the field distribution) the time \( t_{\text{min}} \) corresponding to the \( P_\perp(t) \) minimum, i.e. the maximum depolarization, can be estimated. The recovery of the 1/3 term appears above around \( 2t_{\text{min}} \).

If the field distribution along different axes is not the same (for example if the muon site environment is anisotropic, i.e., anisotropy of the second moment of the field distribution) \( \Delta_x, \Delta_y \) and \( \Delta_z \) in Eq. 3-2 are not equal and a modified Kubo-Toyabe depolarization function will describe the \( \mu \)SR data. It can be shown that as a function of the anisotropy of the second moment, both the position of the minimum and the recovery at high times are affected (for details see [SZ87], [DA90], [SO95]).
For an isotropic Lorentzian field distribution (See Eq. 3-4), $P_z(t)$ takes the following form:

$$P_z(t) = \frac{1}{3} + \frac{2}{3} (1 - \frac{\Delta}{t}) \exp(-\frac{\Delta}{t}),$$

see Figure 3-15, where $\Delta$ is proportional to the half width at half maximum of the Lorentzian field distribution. $P_z(T)$ is the, so-called, Kubo-Lorentz depolarization function. It has a minimum at $t_{\text{min}} = \frac{2}{\Delta}$ with $P_z(t_{\text{min}}) = 0.24$, independent of $\Delta$.

### 3.3.1.4.3 Gaussian field distribution around a nonzero magnetic field

This case is a generalization of the ideal $\delta$-field case presented at the beginning of this chapter. If the sample is not perfect or the alignment of the magnetic moments is not perfect, a field distribution (e.g. Gaussian or Lorentzian) might smear out the magnetic field at the muon site:

$$B_\mu = B_0 + B_1,$$

where $B_0$ is the local field and $B_1$ is given by an isotropic field distribution around a zero mean value. $P_z(t)$ for a polycrystal (or a multi-domain single crystal) was calculated by Kornilov and Pomjakushin [KO91] (see also [LA00]):

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \exp\left(-\frac{1}{2} \Delta^2 t^2\right) \left[ \cos(\omega t) - \frac{\Delta^2 t^2}{\omega t} \sin \omega t \right],$$  \hspace{1cm} (3-13)

where $\omega = \gamma_B B_0$. If $B_0 = 0$ ($\omega = 0$) Eq. 3-13 reduces to the Kubo-Toyabe function. When the field width $\gamma_B \Delta$ is small compared to the average field $B_0$ at the muon site, the term $\Delta^2 t^2/\omega t$ can be neglected and

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \exp\left(-\frac{1}{2} \Delta^2 t^2\right) \cos(\omega t),$$

![Figure 3-15: Kubo-Lorentz depolarization function, for $\Delta = 0.13$ MHz, solid line. The vertical lines indicate the time windows at PSI and ISIS.](image)

![Figure 3-16: Gaussian depolarization function for a field distribution around a nonzero mean value (see text).](image)
which represents a Gaussian depolarization function (Figure 3-16) with the same origin for
the 1/3 term as in Eq. 3-11. For the case of a Lorentzian field distribution around a mean
value $B_0$ the results are similar [PI00].

3.3.1.4.4 Incommensurate magnetic structures

The depolarization $P(t)$ of the muons in a polycrystalline sample where the field distribution
is given by Eq. 3-6,

$$f(B) = \frac{2}{\pi} \frac{1}{B_{\text{max}}^2 - B^2},$$

has the form

$$P(t) = \frac{1}{3} + \frac{2}{3} J_0(\gamma \mu B_{\text{max}} t), \quad (3-14)$$

see also Figure 3-17, where $J_0(x)$ is the zero order Bessel function. This function is charac-
terized by a strongly damped (intrinsic damping, even in ideal samples) oscillation and a
phase shift compared to a cosine function with the same argument.

There is no analytical $\mu$SR fit-function available for a spectrum generated by the general
field distribution arising from an incommensurate magnetic structure (Eq. 3-9),

$$f(B) = \frac{2}{\pi B_{\text{max}}^2} \frac{B}{(B^2 - B_{\text{min}}^2)^{1/2}} \left(\frac{B_{\text{max}}^2 - B^2}{B_{\text{max}}^2 - B_{\text{min}}^2}\right)^{1/2}.$$
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However, from the simulated μSR spectra, Figure 3-18 (for the field distribution presented in Figure 3-11), some observations can be formulated:

- A fit of the μSR spectra (Figure 3-18) using Eq. 3-14 gives $B_{\text{max,fit}} = B_{\text{max}}$, but says nothing about $B_{\text{min}}$. Moreover, it may lead to a misinterpretation of the data if the difference is ascribed to another contribution or to postulate a second (effectively non-existing) site, since the Fourier transform of the μSR spectra - the field distribution - has two peaks.
- The simulated μSR spectra presented in Figure 3-18 could be fitted with a phenomenological function like

$$P(t) = A_1 J_0(y_\mu B_1 t) + A_2 \cos(y_\mu B_2 t + \phi) \exp(-\lambda t) + A_3,$$

(3-15)

with $A_1 = 6A_2$, $B_1 = B_{\text{max}}$, $B_2 = B_{\text{min}}$, $\phi = -105$ deg, $\lambda = 1.256$ MHz and $A_3 = A_1/2$. A fit using Eq. 3-15 provides the same value for $B_{\text{max}}$ as the fit with a Bessel function alone and also offers information about $B_{\text{min}}$. Knowing $B_{\text{max}}$ and $B_{\text{min}}$, the field distribution can be computed using Eq. 3-9.

3.3.2 Time-dependent fields

In general, the field at the muon site is not static. Field fluctuations are due either to fluctuating magnetic moments or to muon diffusion. Since in both cases the effects on the muon depolarization are the same if described by a Markovian process (see below), in the following only the case of static field distribution and a jumping muon will be discussed.

Consider a static field distribution described by $\Delta$, which is identified by a $P^0_z(t)$ depolarization function in the μSR spectra if the muons do not diffuse. Further, the muons are allowed to jump from one site to another (the jumps are considered instantaneous events). $\tau_0$ is the mean time spent by the muon in each site ($1/\tau_0 = \nu$, the jump (fluctuation) rate). At each site the muon sees the local field (from the static field distribution), i.e. the equilibrium is attained at each transition (strong collision model, [KE78]). The time evolution of the muon depolarization between two jumps is given by the static $P^0_z(t)$ depolarization function. It is also considered that the field at the muon site at a moment $t$ has a value that is totally uncorrelated with that at the previous moment $t - \Delta t$ (Markovian process). The relaxation function $P^\nu_z(t)$ consists of contributions from muons that did not jump, performed 1 jump, ..., $n$ jumps, ... up to the time $t$:

$$P^\nu_z(t) = \sum_{0}^{\infty} P^n_z(t)$$

with

$$P^0_z(t) = P^0_z(t) \exp(-\nu t),$$

24
where a Poisson distribution of the jumping probabilities was considered i.e. \( \exp(-vt) \) is the probability that the muon did not hop until time \( t \). The next term is obtained in the same manner,

\[
P_1(t) = \frac{v}{0} \int \exp[-v(t-t_1)] P_0^0(t-t_1) \exp(-v t_1) P_0^0(t_1) \, dt_1,
\]

considering that the muon experienced a jump at time \( t_1 \) (\( 0 < t_1 < t \)). Higher order \( P_n(t) \) terms can be determined in the same way ([HA79], [DA92]). Finally, an integral form for \( P_\alpha(t) \) that can be used for numerical simulations is obtained:

\[
P_\alpha(t) = P_0^0(t) \exp(-v t) + \int_0^t P_\alpha(t-t') P_0^0(t') \exp(-v t') \, dt'.
\]

For example, for

\[
P_\alpha^0(t) = \frac{1}{3} + \frac{2}{3} \left( 1 - \Delta^2 t^2 \right) \exp\left( -\frac{\Delta^2 t^2}{2} \right),
\]

i.e. a Kubo-Toyabe static depolarization function, \( P_\alpha(t) \) calculated for different values of the \( \Delta/v \) ratio are presented in Figure 3-19. The resulting \( P_\alpha(t) \) depolarization function is called Dynamical Kubo-Toyabe (DKT).

![Figure 3-19: Dynamical Kubo-Toyabe depolarization function (see text) for different values of the \( \Delta/v \) ratio. The time is given in units of \( \Delta \).](image-url)
Note that:

- the effect of the fluctuating fields is to flatten the $P_z(t)$ dependence, i.e. to reduce the $\mu^+$ depolarization. This effect is similar to the motional narrowing effect in NMR.
- for small values of $v/\Delta$ the DKT function is Gaussian at early times and only the $1/3$ term is affected by the fluctuations.
- DKT becomes exponential at high $v/\Delta$ values.

A different approach to obtain the DKT function using the Laplace transformation technique is given in [HA79] and [SC85]. However, no simple analytical form exists for the DKT function. In some limiting cases the following equations can be used:

- for slow fluctuation rates, $v/\Delta \ll 1$:
  \[ P_z(t) = \frac{1}{3} \exp\left(-\frac{2}{3} v t\right) + \frac{2}{3} \left(1-\Delta^2 t^2\right) \exp\left(-\Delta^2 t^2/2\right), \]
  i.e. only the $1/3$ term is affected by the fluctuations for quasi-static field distributions.

- in the case of fast fluctuation rates, $v/\Delta \gg 1$:
  \[ P_z(t) = \exp(-\lambda t), \quad \text{with} \quad \lambda = 2\Delta^2/v, \]
  \[ (3-16) \]
  i.e. an exponential $\mu^+$ depolarization function. It involves spin-flip transitions induced by the fluctuating magnetic fields with components perpendicular to $P(0)$. The term $2\Delta^2$ is the second moment of the static field distribution described at the beginning of this chapter.

### 3.4 Longitudinal field (LF) $\mu$SR

The hallmark of fast fluctuating fields is an exponential $\mu^+$ depolarization function. Since particular static field distributions may also lead to an exponential-like $\mu^+$ depolarization, the ZF experiments alone do not allow the separation of the static and the dynamic contributions in the $\mu$SR spectra. By applying a strong magnetic field ($B > 10B_{\text{int}}$) along the initial muon polarization, $P(0)$, the static field distribution, $B_{\text{int}}$, will no more affect the time evolution of the $\mu^+$ polarization (decoupling of the $\mu^+$-spin from the static internal fields). However, fluctuations of the local fields perpendicular to $P(0)$ can induce $\mu^+$ spin-flip transitions leading to a depolarization similar to that observed in zero field:

\[ P_z(t) = \exp(-\lambda t), \]

with a slightly smaller relaxation rate given by [AB61],

26
\[
\lambda = \gamma_p \left( \langle B_z^2 \rangle + \langle B_y^2 \rangle \right) \frac{\tau_0}{1 + \omega^2 \tau_0^2},
\]
or
\[
\lambda = \frac{M_{2,F}^2 \tau_0}{1 + \omega^2 \tau_0^2},
\]
where, for a polycrystalline sample, \( M_{2,F} \) is \( M_{2,\text{poly}} \), given by Eq. 3-3. If \( \omega^2 \tau^2 \ll 1 \), i.e. in the fast fluctuation regime, then \( \lambda = 2 \Delta^2 / \nu \), identical with Eq. 3-16. For more details on the field fluctuations and their effect on the \( \mu^+ \) relaxation rate the reader can consult [SC85], [DA92], [DA96].

### 3.5 Transverse field (TF) \( \mu \text{SR} \)

In a transverse field \( \mu \text{SR} \) experiment, an external field is applied perpendicular (transverse) to the muon polarization, causing the muon spins to precess around the field. With the so-called "surface" muons, for which the muon spin and the muon momentum are antiparallel, an applied field perpendicular to the muon momentum would bend the muon beam. Therefore the muon spin is rotated using a spin rotator (see Page 12) before entering the sample space and the field is applied parallel to the muon momentum, i.e. perpendicular to the muon spin, see Figure 3-20. The \( \mu \text{SR} \) signal is recorded in the "Up" (U), Down (D) and Right (R, not shown) detectors.

![Figure 3-20: Spin rotation for a TF \( \mu \text{SR} \) experiment. The muon beam does not bend because the magnetic field is applied parallel to the muon momentum \( p \). The spin is rotated by a combination of electric and magnetic fields. In the sample, the spin precesses in the vertical plane. The \( \mu \text{SR} \) signal is measured in the Up (U), Down (D) and Right (R, not shown) detectors.](image)

Therefore (as shown in Figure 3-20), the muon spin is not rotated by 90° relative to the muon momentum but by an angle of approx. 50°. This does not affect the results of the following discussion, only the value of the initial polarization along the observation direction is reduced.
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The muon spin precesses around the local field \( B_\mu \) at the site where the muon comes at rest. The local magnetic field \( B_\mu \) can be determined from the (average) Larmor precession frequency \( \langle \omega \rangle = \gamma_\mu B_\mu \). The relative field (or frequency) shift contains information about the microscopic magnetic hyperfine fields induced by the external field \( B \) in the investigated compound. The TF technique is mostly used to investigate the compounds in their paramagnetic phase and possibly, to determine the muon stopping site.

\[
K = \frac{|B_\mu| - |B|}{|B|} = \frac{|B_\mu|}{|B|} - 1 = \frac{\langle \omega \rangle}{\omega_0} - 1,
\]

where \( \omega_0 = \gamma_\mu B \) and

\[
B_\mu = B + B_{hf} + (B_{dem} + B_L).
\]

The last two terms are the demagnetization and Lorentz fields, which can be calculated from the bulk magnetization and demagnetization tensor (see, for example [SC85]).

\( B_{hf} \) are the internal fields induced by the external field \( B \). The frequency shift, corrected for the contribution of \( B_{dem} + B_L \) furnishes the \( \mu^+ \) Knight shift \( K_\mu \).

For the rare-earth and actinide compounds (i.e. systems with local magnetic moments), the \( \mu^+ \) Knight shift can be written as

\[
K_\mu = K_0 + K_f,
\]

where \( K_0 \) and \( K_f \) correspond, respectively, to the contributions to \( B_{hf} \) arising from the polarization of conduction electrons and localized \( f \) moments induced by \( B \).

As in \( s \)- or \( p \)-electron metals, \( K_0 \) is a result of the Pauli paramagnetism of the conduction electrons and their Fermi contact interaction with the \( \mu^+ \):

\[
K_0 = \frac{8\pi}{3} \rho S(r_\mu) \chi_{\text{Pauli}},
\]

where \( \rho S(r_\mu) \) is the spin density enhancement factor at the \( \mu^+ \) site, averaged over the electrons at the Fermi surface. The Pauli susceptibility \( \chi_{\text{Pauli}} \) is usually temperature independent and isotropic.

\( K_f \) at low temperature is usually much larger than \( K_0 \) and contains two contributions of the localized \( f \) moments:

- The dipole-dipole interaction between the field \( B \) induced \( f \) moments and the \( \mu^+ \)
- An indirect RKKY interaction between the induced \( f \) moments, producing an additional spin polarization of the conduction electrons at the \( \mu^+ \) site, which results in an increased hyperfine contact field.
Since both contributions are proportional to the susceptibility component due to the \( f \) moments \( (\vec{\chi}_f) \), \( K_f \) is given by

\[
K_f = \frac{1}{B^2} \left( \vec{B} \cdot \vec{A}_f \cdot \vec{\chi}_f \cdot \vec{B} \right)
\]

\[
= \frac{1}{B^2} \left( \vec{B} \cdot \vec{A}_{\text{dip}} \cdot \vec{\chi}_f \cdot \vec{B} \right) + \frac{1}{B^2} \left( \vec{B} \cdot \vec{A}_c \cdot \vec{\chi}_f \cdot \vec{B} \right).
\]

where \( \vec{\chi}_f \cdot \vec{B} \) is the localized moment induced by the external field, \( \vec{A}_{\text{dip}} \) is the dipolar coupling tensor, and \( \vec{A}_c \) is the hyperfine contact coupling tensor. \( \vec{A}_{\text{dip}} \) is traceless, symmetric, and depends on the given crystallographic structure and the assumed \( \mu^+ \) site:

\[
A_{\text{dip}}^{ij} = \sum_f \frac{1}{r^3} \left( \frac{3 \vec{r}_f r_j r_i}{r^2} - \delta_{ij} \right),
\]

where the sum runs over the localized \( f \) moments inside the Lorentz sphere and \( \vec{r} = (r_1, r_2, r_3) \) is the vector connecting the \( \mu^+ \) site and the considered \( f \) moment.

Since the hyperfine contact coupling is normally independent of the direction of \( \vec{B} \), one can write \( \vec{A}_c = A_c \vec{E} \) where \( \vec{E} = (E^y, E^z) = (\delta^y, \delta^z) \) is the unit tensor. \( A_c \) contains information about the effective exchange interaction \( J_{kf} \) between the \( f \)-moment and the conduction electrons:

\[
A_c \propto J_{kf} N(E_F) \sum_f \frac{2k_F r \cos(2k_F r) - \sin(2k_F r)}{(2k_F r)^2},
\]

which, as it was shown in Chapter 2, is a key parameter for the Kondo and the RKKY interactions.

For polycrystalline sample of a compound with axial symmetry

\[
K_{\text{iso}} = \frac{1}{3} A_c \left( \chi_\parallel + 2 \chi_\perp \right) + \frac{1}{3} A_{\text{dip}} \left( \chi_\parallel - \chi_\perp \right)
\]

and in the case of a strong anisotropy of the magnetic susceptibility

\[
K_{\text{iso}} \equiv \left( A_c - \frac{A_{\text{dip}}}{2} \right) \chi_{\text{poly}} \quad \text{for} \quad \chi_\perp \gg \chi_\parallel,
\]

or

\[
K_{\text{iso}} \equiv \left( A_c + A_{\text{dip}} \right) \chi_{\text{poly}} \quad \text{for} \quad \chi_\perp \ll \chi_\parallel.
\]
where by $\chi_{\text{poly}}$ one denotes the magnetic susceptibility of the polycrystalline sample:

$$\chi_{\text{poly}} = \frac{\chi_\parallel + 2\chi_\perp}{3}.$$ 

From the $K_{\text{iso}}(\chi_{\text{poly}})$ dependence the value of the coupling constant $A_c$ can be determined, provided that the muon site is known.
4 Experimental results:  
chemical substitution

We have investigated the effect of the chemical substitution, Ni/Cu in YbCu$_2$Si$_2$ and Al/Cu in YbCu$_4$Al, on the physical properties of these compounds. We will point out the effect of the chemical substitution: chemical pressure, chemical disorder and electron doping, on the ground state properties of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and YbCu$_{5-x}$Al$_x$.

YbCu$_2$Si$_2$ is a compound of particular interest, after the discovery of its pressure-induced magnetism [AL96]. The interest in the other investigated compound, YbCu$_{5-x}$Al$_x$ (see Chapter 4.2), resides in the proximity of this compound to a quantum critical point (QCP) at $T \to 0$, for $x = 1.5$ [BA99]. In YbCu$_{3.5}$Al$_{1.5}$, a NFL behavior was observed in transport and thermodynamic measurements at low temperatures.

The term chemical pressure, used above, denotes the lattice pressure obtained via an adequate chemical substitution. In a simple picture one can increase the lattice pressure at the A site in an AB compound by substituting the B ion by a smaller one, C. It is assumed that the structure type does not change upon the substitution and that the unit cell volume of AC is smaller than that of AB. Roughly speaking, by preparing the AB$_{1-x}$C$_x$ series, an entire range of chemical pressures can be continuously generated. This method for generating pressure is widely adopted to investigate the phase diagram of heavy-fermion systems. The pressure obtained by chemical substitution is, however, considered “impure” compared to the external hydrostatic pressure (which has a pure volume effect). The main reasons are that:

- Chemical substitution introduces disorder - which finally proved out to be the main ingredient for many of the NFL theories$^5$ (more details are given below).
- It produces electron doping if the original and substituting atoms are not from the same group of the periodic table of elements. The substitution might also affect the density of states at the Fermi level, $N(E_F)$, another important parameter for describing the ground state of such a system.

As it will be shown in this chapter, the ground state of the investigated Yb series is determined rather by the two “side” effects presented above, of the chemical substitution, than by its volume effect.

Chemical substitution can also be used when the maximum available pressure (e.g. from a Cu-Be clamped cell) is below the required pressure needed to investigate the system, for example to drive the system through a magnetic phase transition. In that case, chemical substitution can be employed to get close to the magnetic transition and then the external pressure is adjusted to drive the system through the transition. This offers also a way to compare external pressure and chemical substitution effects.

$^5$ However, the disorder is not the only ingredient of the NFL behavior as proven by the discovery of the stoichiometric NFL compounds ([ST00] and references therein).
4.1 Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$

In the literature, YbCu$_2$Si$_2$ is known as an intermediate (IV) valence compound with a non-magnetic ground state and an enhanced specific heat coefficient. The Sommerfeld coefficient of the specific heat is $\gamma = 135$ mJ/molK$^2$ [SA76] and the valence of the Yb ion is close to 2.8 at 4 K [NE85]. YbNi$_2$Si$_2$, on the other side of the series, is an antiferromagnet below $T_N = 2.1$ K [BO91] with a helical magnetic structure [AN95]. Substituting Cu by Ni, the unit-cell volume decreases. In terms of chemical pressure one therefore expects that the pressure on the Yb ions is higher in YbNi$_2$Si$_2$ (magnetic) than in YbCu$_2$Si$_2$ (nonmagnetic), in agreement with the Doniach phase diagram (Figure 2-2, Chapter 2).

With Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ we have investigated the chemical substitution-induced nonmagnetic-magnetic transition in a Kondo lattice system. One of the goals was to search for the critical concentration $x_c$ at which the system is at the edge between magnetic and non-magnetic ground states ($x_c$ is the equivalent of $J_c$ in the Doniach phase diagram (Chapter 2) or $p_c$, the critical pressure at which YbCu$_2$Si$_2$ becomes magnetic [AL97]). For this purpose, nine compounds with $x = 0, 0.125, ..., 1$ were prepared. Their physical properties were explored using transport, thermodynamic and $\mu$SR measurements. As shown below, we have found that the occurrence of the magnetism in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ is related rather to the number of Ni nearest neighbors of an Yb ion than to a critical concentration $x_c$ [AN00], see Chapter 4.1.5.2. This result evidences the role of the disorder induced by the chemical substitution on the physical properties of the ground state of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.

External pressure was applied on compounds of selected concentrations but the maximum available pressure of 7-8 kbar was not high enough to change the ground state of the system. This result is in agreement with the electrical resistivity measurements [AL97] and the Mössbauer experiments [WI99], where a magnetic transition in YbCu$_2$Si$_2$ was observed only after applying around 80 kbar, a pressure too high to be obtained (up to now) in a clamped pressure cell.

4.1.1 Sample preparation

The Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples were prepared and analyzed by X-ray and transport measurements in collaboration with Dr. K. Alami-Yadri from Université de Genève. The elemental metals used to prepare the samples were Yb 4N from Ames Laboratories, USA, Cu 6N, Ni 6N and Si 6N from Fluka, Switzerland.

The high vapor pressure of Yb makes the preparation of the Yb alloys rather difficult. To overcome the possible loss of Yb by evaporation during the sample preparation we have chosen a sealed container method ([JA81], see Figure 4-1) using tantalum tubes of 10 mm diameter and 0.5 mm wall thickness as containers. Resistance heating (pure Joule heating) provided the heat needed for the melting of the sample. To avoid a tantalum contamination of the sample (Ni reacts readily with Ta), a special method was employed to prepare the samples prior to fusion:
4.1 \( Yb(Cu_{1-x}Ni_x)_{2}Si_2 \)

a) Ni being very reactive and having a high melting point, the (Cu-Ni-Si) part of the sample was first melted together (CuNiSi in the following) in an arc furnace. The melting point of the mixture is lower than that of Ni.

b) The CuNiSi sample was broken into pieces and mixed with pieces of Yb.

c) Around 1% excess of Yb compared to the exact stoichiometry was used each time to compensate for the losses due to Yb evaporation. When the mixture is heated, the excess Yb provides a thin protective film on the inner side of the Ta tube diminishing the probability of a reaction of the (still) unreacted Ni from CuNiSi with tantalum.

d) The Ta tube was evacuated, sealed in an Argon atmosphere and mounted inside the furnace. The furnace itself was then evacuated (the furnace is inside a glass bell, see Figure 4-1) and then the tube was heated several times.

**Figure 4-1:** On the left picture a schematic view of the resistance furnace is presented. The drawing at right depicts the method used for the sample preparation.

The heating time and current depend on the Ni concentration in the sample, the length of the tube and the length of the sealed part. A current of around 500 A for 4 minutes was utilized for \( YbCu_2Si_2 \), and 600 A for 3 minutes for \( YbNi_2Si_2 \). During heating, the tube turns to a light red color. From the “color temperature”, the melting temperature was estimated to about 1200-1300 °C using a pyrometer. It was possible to shake and turn the sample during heating. These last procedures were not applied for Ni containing samples due to the high chemical reactivity of Ni (or NiCuSi with a higher Ni concentration) with Ta, which leads to the perforation of the Ta tube.

It is easy to determine whether the sample had or had not reacted chemically with the Ta tube. If it did, a white point shows up during heating, where the reaction starts, and develops very fast through the walls of the Ta tube. There is nothing to prevent it, but to decrease the current, search for the cleaning tools and prepare another sample. A thin Yb film, producing sparkles when removed, covers everything inside the glass bell.
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After melting and cooling down the sample, the tube was removed and cut into 1-3 mm thick disks using a diamond saw. Each disk was then analyzed by X-ray diffraction and optical microscopy to check for the homogeneity of the sample inside the tube and for microcracks and holes. Several samples suitable for transport properties measurements were then cut from the selected disks.

YbCu$_2$Si$_2$ and YbNi$_2$Si$_2$ crystallize in the tetragonal ThCr$_2$Si$_2$-type structure, ([BO66], [RI69] see Figure 4-2), space group I4/mmm. The structure can be described as a sequence of planes of the same atoms R-X-T-X-R-X-T-X-R (where, in our case, R = rare earth (Yb), T = transition metal (Cu or Ni) and X = Si) perpendicular to the c-axis. The interatomic distances between rare earth atoms in the planes are about 4 Å whereas between planes the distance is near 5 Å. The atomic positions in the unit cell are:

- R in 2(a): (0, 0, 0), (1/2, 1/2, 1/2),
- T in 4(d): (0, 1/2, 1/4), (1/2, 0, 1/4), (1/2, 0, 3/4), (0, 1/2, 3/4),
- X in 4(e): (1/2, 1/2, z), (1/2, 1/2, -z), (0, 0, 1/2 + z), (0, 0, 1/2 - z).

Figure 4-2: Lattice structure of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The position of the R, T and X atoms (see text) in the tetragonal unit cell are shown.

![Figure 4-2: Lattice structure of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.](image)

Figure 4-3: The Ni concentration (x) dependence of the lattice parameters and the unit cell volume of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The lines are guides to the eye.

![Figure 4-3: The Ni concentration (x) dependence of the lattice parameters and the unit cell volume of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.](image)
The results of the X-ray analysis for the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples are presented in Figure 4-3. They indicate a decrease of the unit cell volume with increasing Ni concentration $x$ (most affected is the $c$ parameter). The coordinate $z$ (not shown here), which is half of the Si-Si dumbbell distance, is almost $x$ independent and has a value around 0.125. The tetragonal ThCr$_2$Si$_2$ structure (Figure 4-2) is preserved over the entire range of Ni concentrations.

In Figure 4-4 the evolution of the X-ray peaks is displayed for different Ni concentrations $x$. Note that the lines corresponding to the $(hk0)$ reflections are almost not displaced while the $(hkl\neq 0)$ lines move to higher values of the diffraction angle $\theta$ with increasing Ni concentration, i.e. indicating smaller inter-planar distances $d$ ($d = 1/\sin \theta$, $\theta < \pi/2$). Small extra reflections in the X-ray diffraction patterns indicate that a small percentage of foreign phases (Yb$_2$O$_3$ and Yb$_2$Cu$_4$Si$_4$) was also formed. Yb$_2$Cu$_4$Si$_4$, behaves like a normal metal (it was synthesized and studied separately) with no magnetic transition down to 1 K. Yb$_2$O$_3$ orders magnetically below 2.1 K and might be responsible for the upturn observed in the temperature dependence of the magnetic susceptibility at low temperatures (see below).

A possibility to calibrate the chemical pressure in terms of external pressure is given by the measurements of the pressure dependence (up to 220 kbar) of the lattice parameters of YbCu$_2$Si$_2$ [W199]. In Figure 4-5 the results of Winkelmann et al. are presented in the pressure range where the change in volume due to the external pressure ($p_{\text{ext}}$) is comparable to the one achieved by chemical pressure ($p_x$). The corresponding chemical pressures are marked with arrows.

The $p_x(p_{\text{ext}})$ correspondence is presented in Figure 4-6. Note the slope change in the $p_x(p_{\text{ext}})$ dependence around 80 kbar. In the high-pressure measurements of the temperature dependence of the electrical resistivity [W199], a pressure-induced magnetic ordering was observed for pressures above 80 kbar, see Figure 4-7. The ordering temperature $T_m$ increases abruptly with the increase of the pressure above $p_c = 80$ kbar and already at about 100 kbar a transition temperature of approx. 4 K was reported.
The unit cell volume of YbNi$_2$Si$_2$ ($x = 1$) corresponds to that of YbCu$_2$Si$_2$ under a pressure of 135 kbar ($T_m = 5$ K). On the other hand, its transition temperature ($T_m = 2.1$ K) corresponds to a pressure of around 95 kbar. The smaller transition temperature of YbNi$_2$Si$_2$ compared to that of the pressed YbCu$_2$Si$_2$ at the same volume might be related to the Ni/Cu substitution (see below). The fact that the pressure at which the slope change in the $p_x(p_{ext})$ dependence is almost identical to the critical pressure $p_c$ ($p_c = 80$ kbar) might suggest a criti-

Figure 4-5: Pressure variation of the unit cell volume of YbCu$_2$Si$_2$ (black points, data taken from [W199]). The correspondence between the external pressure $p_{ext}$ and the chemical pressure $p_x$ (Ni concentration $x$) that produces the same volume change is marked with arrows.

Figure 4-6: The correspondence between the chemical pressure $p_x$ (Ni concentration $x$) and the external pressure $p_{ext}$ that produces the same volume effect.

Figure 4-7: Pressure dependence of the pressure-induced magnetic ordering temperature $T_m$ in YbCu$_2$Si$_2$. Data and curve from [W199].
4.1 Yb(Cu_{1-x}Ni_x)_{2}Si_2

cal concentration x_c \equiv 0.5 for Yb(Cu_{1-x}Ni_x)_{2}Si_2. As it will be shown in Chapter 4.1.5.2 a critical concentration cannot be extracted for Yb(Cu_{1-x}Ni_x)_{2}Si_2. However, the Ni concentration x = 0.5 corresponds to the case where almost 100% of the sample has a magnetic ground state (Figure 4-51, Chapter 4.1.5.1.c).

In Figure 4-8 the pressure dependence of the lattice parameters of YbCu_{2}Si_2 (data from [WI99]) is displayed. With the black squares on the left (a) and the right (c) vertical axis the corresponding lattice parameters of YbNi_{2}Si_2 are reported. The dotted line indicates the critical pressure p_c (see above) and the dashed line the pressure at which the transition temperature of the pressurized YbCu_{2}Si_2 is 2 K (T_m in YbNi_{2}Si_2). In Yb(Cu_{1-x}Ni_x)_{2}Si_2 the lattice parameter a is almost independent of x, while c strongly decreases when x increases (chemical pressure, Figure 4-3). It would be tempting to argue that the occurrence of magnetism upon the Ni/Cu substitution is related to the decrease of c. However, in the “pressed”

![Figure 4-8](image)

**Figure 4-8**: The pressure dependence of the lattice parameters of YbCu_{2}Si_2 (data from [WI99]). Black squares on the left (a) and right (c) vertical axes denote the corresponding lattice parameters of YbNi_{2}Si_2. The dotted line indicates the critical pressure p_c in YbCu_{2}Si_2 and the dashed line the pressure at which the transition temperature of the “pressed” YbCu_{2}Si_2 is 2 K (T_m in YbNi_{2}Si_2).

YbCu_{2}Si_2 the magnetism is observed at larger volumes (see the discussion above) and at much higher values of c that in YbNi_{2}Si_2.

As seen above, the Ni/Cu substitution (Ni has fewer valence electrons than Cu) shifts the onset of magnetic correlations between the Yb ions to lower temperatures compared to the pressed YbCu_{2}Si_2. In YbCu_{5-x}Al_x (Al has more electrons than Cu) the situation is opposite i.e. the unit cell volume increases upon the Al/Cu substitution and the magnetic correlations between the Yb^{3+} ions increase too. When external pressure is applied on YbCu_{5-x}Al_x the unit cell volume is reduced but the magnetic correlations between the Yb^{3+} ions increase further [BA99]. Therefore it appears that also for the Al/Cu substitution in YbCu_{5-x}Al_x the
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electron doping competes with the volume effects for establishing the ground state of the system.

4.1.2 Electrical resistivity

The temperature dependence of the electrical resistivity was measured between 1.2 K and 300 K using a semi-automatic six-sample measurement setup developed at the Université de Genève (Figure 4-9). The classical four-point method was employed. The samples for electrical resistivity $\rho(T)$ and thermoelectric power $S(T)$ measurements were cut/polished into a bar shape using a diamond saw. The dimensions of the samples ($l \cdot w \cdot h$) were about $4 \times 0.6 \times 0.4$ mm. A Keithley 224 programmable current source supplied the current for resistivity measurements and the heating current for the thermoelectric power measurements. A HP 34401A multimeter was used to read the signals from analog nanovoltmeters (Keithley 224) and to communicate with a

![Figure 4-9: Experimental setup used for the $S(T)$ and the $\rho(T)$ measurements.](image)

![Figure 4-10: Electrical resistivity $\rho(x,T)/\rho(x,300)$ of the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples.](image)
Germanium and platinum temperature sensors were used up to 50 K and between 50 K and 300 K, respectively. The temperature was controlled with a Lake-Shore DRC-91C temperature controller (more details about the six-sample measurement setup can be found in [FL88] and [BA88]).

The temperature dependence of the $\rho(x, T) / \rho(x, 300 \text{ K})$ is displayed in Figure 4-10 (errors in the sample form factor determination cancel out in this representation). In Figure 4-11 the concentration dependence of $\rho(x, 1.2 \text{ K}) / \rho(x, 300 \text{ K})$ is presented. The dotted curve is the scaled $x(1-x)$ dependence expected from the Nordheim relation:

$$\rho(0) = \rho_0 x(1-x).$$

As shown in the Figure 4-10 and Figure 4-11, a large contribution to the temperature dependence of the electrical resistivity arises from the disorder-related effects. The peak in the residual resistivity is displaced to slightly lower $x$ values than expected from the Nordheim relation for the lattice disorder. Interestingly, a peak followed by saturation was also observed in the pressure dependence of $\rho_0$ in YbCu$_2$Si$_2$, YbSi, YbInAu$_2$ and YbCuAl [AL97]. Since in that case the effect of the lattice disorder on the residual resistivity $\rho_0$ should not change with the applied pressure, the pressure dependence of $\rho_0$ might have also another origin and was associated [AL97] to the Kondo hole effect [LA85]. A Kondo hole is formed by a missing ion, a dislocation, etc., in a Kondo lattice. At temperatures below the coherence temperature, $T_{coh}$, the heavy quasiparticles would be scattered by the Kondo hole in an analogous way as for the classic Kondo scattering of the conduction electrons on the 4f localized moments. Unfortunately, no theoretical work challenged this hypothesis up to now (to my knowledge). One can speculate that since the Kondo hole residual resistivity depends only on the type of the missing ion [LA85], a nonmagnetic-magnetic transition induced by pressure in a Kondo lattice system (i.e. the missing ion “becomes magnetic”) would also be reflected in the pressure dependence of the Kondo hole residual resistivity (a Doniach phase diagram mapped in the $\rho_0(XH)(p)$ plane). It might be reflected also in the concentration dependence of the residual resistivity (when chemical pressure is applied) but masked by the Nordheim term. In Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ it is, however, difficult to separate the different contributions in the $\rho_0(x)$ dependence.

The temperature dependence of the electrical resistivity, $\Delta \rho$, is presented in Figure 4-12 in a semi-logarithmic plot. To evidence the details of the magnetic resistivity curve, a concentration ($x$) dependent phonon term $\rho_{ph} = a(x)T$ with $a(x) = 0.067 + 0.126x \mu\Omega \text{ cm/K}$ ([AN99], [CA81], [AL97]) was subtracted from the raw resistivity data. The $a(0)T$ term corresponds to the electrical resistivity of LuCu$_2$Si$_2$ [CA81]. Because the temperature dependence of the electrical resistivity for LuNi$_2$Si$_2$ is not known, $a(x)$ for $x = 1$ was obtained by adjusting the resistivity of YbNi$_2$Si$_2$ in such a way that $\rho(x = 1, T) - \rho_{ph}(x = 1, T)$ coincides, at high tem-
temperatures, with \( \rho(p = 90 \text{ kbar}, T) - \rho_{\text{YbCu}_2\text{Si}_2} \) for \( \text{YbCu}_2\text{Si}_2 \) under pressure. A linear relation was then considered for the \( x \)-dependence of the coefficient \( a \). In the following, the result of the subtraction will be called \( \Delta \rho \). Below 300 K a \(-\ln(T)\) slope in the \( \Delta \rho(T) \) dependence is observed for all compounds. For the \( x \geq 0.375 \) compounds, a second slope is clearly visible at lower temperatures.

![Graph](image)

**Figure 4-12**: Plot of \( \Delta \rho(T) = \rho(T) - a(x)T \) for \( \text{Yb(Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2 \).

In Kondo lattice systems, multiple peaks and \(-\ln T\) dependencies in the \( \rho_{\text{mag}}(T) \) dependence are the signature of the presence of crystal electric field (CEF) splitting of the Hund’s rule multiplet. Cornut and Coqblin [CO72] have calculated the resistivity for the general case of \( N \) levels \( E_i \) split by the CEF. They found that if \( \Delta_{n+1,i} > > k_B T > > \Delta_{n,i} \) (\( \Delta_{ij} = E_i - E_j \), i.e. \( T \) is between two well separated CEF levels, the resistivity behaves as \(-\ln T\) with a slope \( c \) proportional to \( (\lambda_n^2 - 1) \):

\[
c \propto N(E_F) J_{Kf}^3 (\lambda_n^2 - 1), \tag{4-1}
\]

where \( \lambda_n \) is the total degeneracy of the \( n \) occupied levels, \( N(E_F) \) is the density of states at the Fermi level and \( J_{Kf} \) is the exchange coupling between the localized and the conduction electrons (note the \( J_{Kf}^3 \) dependence). If the levels are not well separated one can not distinguishing the intermediate steps in the \( \rho_{\text{mag}}(T) \) dependence but rather broad peaks around the neighboring \( \Delta_{i,j} \) values can be observed.

We ascribe the two broad maximums observed in the \( \Delta \rho(T) \) dependence for different Ni concentrations \( x \) to the scattering of the conduction electrons on the CEF ground state (the maximum at low \( T \)) and on the excited CEF levels (the maximum at high \( T \)). The decrease of the of the position of the high \( T \) maximum with the increase of the Ni concentration fol-
allows the decrease of the CEF splitting with the increase of the Ni content in Yb(Cu1-xNi_x)2Si2, in qualitative agreement with inelastic neutron scattering experiments. In tetragonal symmetry the $J = 7/2$ Hund rule multiplet of the Yb$^{3+}$ ion splits into four doublets with a level sequence of about 0 K - 208 K - 266 K - 359 K [WA92] for YbCu2Si2 and 0 K - 87 K - 87 K - 156 K for YbNi2Si2 [GO00].

The signature of the magnetic ordering in the $\rho(T, x)$-data, see Figure 4-10, is observed only for $x = 1$ (at $T_N \sim 2.1$ K), probably due to the large contribution of the disorder effects to the electrical resistivity of the other samples.

### 4.1.3 Thermoelectric power

The temperature dependence of the thermoelectric power, $S(T)$, for the Yb(Cu1-xNi_x)2Si2 alloys was measured in parallel with the $\rho(T)$ measurements on the very same samples. The results, for different Ni concentrations $x$, are displayed in Figure 4-13 ([AN99], [AL99]). The details of the $S(T)$ dependence in the low-temperature region are shown in Figure 4-14.

At high temperatures a broad minimum ($S_{\text{min}}$) is observed in the $S(T)$ dependence of Yb(Cu1-xNi_x)2Si2 for all Ni concentrations $x$. The position of the minimum, at $\sim 100$ K for $x = 0$, shifts down to $\sim 60$ K for $x = 0.625$ and then is rather $x$ independent. The structure of $S(T)$ becomes complicated at low temperatures for the $x > 0$ compounds. The structure of $S(T)$ (note that for independent electrons a linear $S(T)$ dependence is predicted [BH76] for $T \to 0$) and the high values of the thermopower minimum $S_{\text{min}}$ are due to the combined effect of Kondo scattering, crystalline electric field splitting and spin-spin interaction ([PE70], [BH76a], [FI89]), see below.

The sign of the high temperature thermopower (negative) for Yb compounds is opposite to that of Ce compounds, for which the Kondo effect yields positive $S(T)$ at high $T$ (see for example [JA82]). The opposite sign of the $S(T)$ for the Ce and Yb compounds reflects the electron-hole symmetry of the electronic structure of Ce ($4f^1$) and Yb ($4f^13$). The Ce-Yb mirror behavior is best evidenced when comparing the temperature dependence (at different external applied pressures) of the thermoelectric power of CeCu2Si2 with the temperature dependence (at different concentrations $x$) of the thermoelectric power of Yb(Cu1-xNi_x)2Si2, both displayed in Figure 4-15. In the following discussion $x = 0$ (1) indicates a nonmagnetic (magnetic) ground state for Yb(Cu1-xNi_x)2Si2, while $p$ is the external applied pressure on CeCu2Si2 ($p = 0$ for a magnetic ground state, in CeCu2Si2). Some observations can be formulated:

- On the magnetic side, $x = 1$ ($p = 0$), a maximum (minimum) at low temperatures is observed (region II) which is related to the increase of the spin-spin interactions in the system [FI89]. The weight of this contribution diminishes when the systems are driven away from the magnetic side. This contribution is observed even in the $x = 0.125$ compound and increases with the increase of the Ni concentration $x$, saturating for $x \to 1$. It suggests that magnetic correlations between the Yb ions occur in Yb(Cu1-xNi_x)2Si2 for $x > 0$ and that the critical concentration $x_c$ (i.e. the Ni concentration at which
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Figure 4-13: Temperature dependence of the thermoelectric power $S(T)$ of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. Note the broad negative peak at high temperature and the subsequent maximum and minimum at low temperatures (see also Figure 4-14).

Figure 4-14: Low temperature part of the $S(T)$ dependence in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. 
Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ has a magnetic transition temperature at $T = 0$ might be around $x = 0.125$.

- On the nonmagnetic side, $x = 0$ ($p = 60$ kbar), a broad minimum (maximum) is observed in the $S(T)$ dependence at high temperatures (region I). The position of the minimum (maximum) shifts to lower temperatures and its intensity decreases when the magnetic side ($x = 1$, $p = 0$) is approached. This behavior can be related either to the reduction of the Kondo temperature [FI89] or to the reduction of the CEF splitting [BH76].

For YbCu$_2$Si$_2$ the temperature dependence of the thermopower is well described by a two-band model [GO85]. In a two-band model for transition metals ($d$-band narrower than the $s$-band), assuming a Lorentzian form for the density of states with a maximum at $E_0$ and a width $W$, Gottwick et al. [GO85] calculated the temperature dependence of the thermopower:

$$S(T) = \frac{AT}{B^2 + T^2}, \quad (4-2)$$

with

$$A = \frac{2(E_0 - E_F)}{|e|}, \quad B^2 = 3\frac{(E_0 - E_F)^2 + W^2}{\pi^2 k_B^2}.$$

$E_F$ is the Fermi energy. This model was successfully applied in the case of rare-earth intermediate-valence (IV) compounds ([JA82], [PJ94]). For the IV compounds, the $f$-band plays the role of the $d$-band. Eq. 4-2 predicts a single peak in the $S(T)$ dependence for Yb compounds at $T = B$ and a linear behavior at low $T$, $S(T \to 0) = AT$, but cannot explain the low $T$ structure of the $S(T)$ dependence found in many Yb and Ce compounds. A fit of Eq. 4-2 to the YbCu$_2$Si$_2$ data is displayed in Figure 4-16. The parameters used for the fit, $A = 11376 \mu\text{eV}$
and $B = 104$ K, allow the calculation of $(E_0 - E_r) = 5.7$ meV and $W = 27.6$ meV, confirming the results obtained by Jaccard and Sierro [JA82] for the same compound.

- A second minimum (maximum) can also be noticed at low temperatures (region III, see also Figure 4-14). In both cases it appears close to the nonmagnetic side and vanishes when the magnetic side, $x \to 1$ ($p \to 0$), is approached. The origin of this contribution is not yet fully understood.

The theories describing the temperature dependence of the thermoelectric power developed from single impurity models to more elaborate schemes that take spin interactions and CEF effects into account. However, none of these models could explain the low-$T$ structure of the $S(T)$ dependence for Ni concentrations $x > 0$ in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.

### 4.1.4 Magnetic susceptibility

The temperature dependence of the DC magnetic susceptibility, $\chi(T)$, was measured at PSI using a MPM device from Oxford Instruments in the temperature range of 4 K to 300 K. The $(1/\chi)(T)$ dependence for different Ni concentrations is presented in Figure 4-17 (for a better display, the data for different concentrations were shifted vertically - see the legend). The magnetic susceptibility increases ($1/\chi$ decreases) with the increase of the Ni concentration $x$ (see also Figure 4-18). The increase is fast for low values of $x$ and almost zero for $x > 0.625$. At high temperatures $\chi(T)$ was fitted to a Curie-Weiss law: $\chi(T) = \chi_0 + C/(T - \theta_b)$, with $\chi_0$ a temperature independent contribution, $C$ the Curie constant and $\theta_b$ the paramagnetic Curie temperature (no $\chi_0(x)$ dependence was observed, in the limit of the experimental errors). A fit of this equation to the $\chi(T)$ data for YbCu$_2$Si$_2$ is presented in Figure 4-20. The deviations from the C-W law below 100 K for $x > 0$ and below 200 K for $x = 0$ are probably due to CEF effects. Some magnetic impurities (Yb$_2$O$_3$) might affect the low-$T$ magnetic susceptibility in this series.

In Figure 4-18 the $\theta_p(x)$ dependence of the paramagnetic Curie temperature is plotted. In Kondo lattice systems, $\theta_p$ is often related with the Kondo temperature $T_K$ ($T_K \propto |\theta_p|$, [HE93]). The concentration dependence of $\theta_p$ may be therefore understood as a decrease of the Kondo temperature $T_K$ with the increase of the chemical substitution ($x$). One should, however, keep in mind that $\theta_p$ is also influenced by the CEF splitting and that in this type of compounds the CEF and Kondo energy scales are comparable. Since the maximum in the $\rho(T)$ dependence and the minimum in the $S(T)$ dependence are also related with $T_K$ and/or the CEF splitting, we checked for a linear relation between $\theta_p$, $T_{\text{min},S}$ and $T_{\text{max},\rho}$, by plotting

![Figure 4-16: Fit of the $S(T)$ data of YbCu$_2$Si$_2$ to Eq. 4-2.](image-url)
Figure 4-17: Temperature dependence of the reciprocal molar magnetic susceptibility for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The data corresponding to different Ni concentrations $x$ are translated vertically with $t$: 10 mole/emu where $t = 0$ for $x = 1$ and 9 for $x = 0$.

Figure 4-18: The chemical pressure dependence of the paramagnetic Curie temperature. The inset displays the chemical pressure dependence of the effective Yb$^{3+}$ magnetic moment. The lines are guides to the eye.
$T_{\text{min,S}}$ and $T_{\text{max,\rho}}$ as functions of $\theta_p$, Figure 4-19. Both $T_{\text{min,S}}$ and $T_{\text{max,\rho}}$ are linear in $|\theta_p|$. The scattering of the $T_{\text{max,\rho}}$ data at low $|\theta_p|$ might be due either to the difficulty to determine the maximum for some Ni concentrations or to the rise of $T_{\text{max,\rho}}$ at high Ni concentration. In the second case $T_{\text{max,\rho}}$ is no longer linked to $T_K$ but probably to scattering with populated excited crystal field states. Moreover, it is difficult to distinguish between $T_K$ and CEF energy scales for small $x$. A similar study using external pressure would be more enlightening since in that case the disorder effects are less important while the study of samples with low Ni concentration would fill the data gap in Figure 4-19.

The effective magnetic moment of the Yb ions (see the insert in Figure 4-18) calculated from the Curie constant, increases slightly with the Ni concentration $x$ from a value of 4.25 $\mu_B$ for the IV compound YbCu$_2$Si$_2$ ($x = 0$) to a value close to 4.54 $\mu_B$, the magnetic moment of the Yb$^{3+}$ ion, for YbNi$_2$Si$_2$ ($x = 1$).

Shimizu [SH87] has measured the anisotropy of the YbCu$_2$Si$_2$ magnetic susceptibility on a single crystalline sample. The temperature dependencies of $\chi_\parallel$ and $\chi_\perp$ are displayed in Figure 4-20 together with our results obtained on a polycrystalline sample and a C-W fit of our data. We have represented by open circles the values $\chi_{\text{poly}}$ calculated from $\chi_\parallel$ and $\chi_\perp$ using

$$\chi_{\text{poly}} = (2\chi_\perp + \chi_\parallel)/3. \quad (4-3)$$

The anisotropy of $\chi(T)$ increases with decreasing the temperature.

The magnetic structure of YbNi$_2$Si$_2$ was investigated by Mössbauer and neutron diffraction techniques [AN95]. Peaks of magnetic origin were identified in the neutron diffraction spectra at 1.43 K and were indexed with the wavevector $k = (0, 0, 0.8025)$. The magnetic structure is helical with a Yb magnetic moment of 1.47$\mu_B$ lying in the a-b crystallographic plane. The analysis of the a/c ratios for a number of RT$_2$X$_2$ compounds ([AN95] and references therein) indicated that for
4.1 Yb(Cu$_{1.x}$Ni$_{1.2}$Si$_2$)

a/c > 0.408 an oscillatory magnetic structure develops in the crystal. In the Yb(Cu$_{1.x}$Ni$_{1.2}$Si$_2$) series this condition is fulfilled only for $x \geq 0.875$.

The particular location of the rare earth atoms in the crystal structure of ThCr$_2$Si$_2$ type is responsible for the anisotropic character of the magnetic interaction between the magnetic moments of the rare earth atoms that can be observed in the low temperature magnetic properties of several RT$_2$X$_2$ compounds. RNi$_2$Ge$_2$ (R = Dy, Ho, and Er) have a sine-modulated structure and YbNi$_2$Si$_2$ has a helical order [AN95]. The determined magnetic structures (see below) indicate that exchange interactions within the (001) plane are strongly ferromagnetic whereas the couplings between planes are weaker and can be antiferromagnetic.

4.1.5 $\mu$SR measurements

$\mu$SR measurements in zero field (ZF) and longitudinal field (LF) configurations were performed on the Yb(Cu$_{1.x}$Ni$_{1.2}$Si$_2$) samples. Except for some ZF-LF measurements at ISIS (UK) for the $x = 0$ and $x = 0.125$ samples all the other measurements were performed at PSI, using the GPS (General Purpose Spectrometer), LTF (Low Temperature Facility), DOLLY (the clone of GPS) and GPD (General Purpose Decay-Channel Instrument) instruments.

The dynamics of the Yb$^{3+}$ moments in the paramagnetic regime was investigated by measurements in ZF and LF configurations. Low temperature ZF measurements were performed to investigate the physical properties of Yb(Cu$_{1.x}$Ni$_{1.2}$Si$_2$) below the temperature of the magnetic transition and the evolution of the magnetic phase with the Ni concentration $x$.

4.1.5.1. ZF and LF $\mu$SR measurements in the paramagnetic regime

a) YbCu$_2$Si$_2$

For YbCu$_2$Si$_2$ (the $x = 0$ nonmagnetic sample) a Kubo Toyabe depolarization function

$$P(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta t^2) e^{-\frac{\Delta t^2}{2}}$$

(4.4)

fits the ZF $\mu$SR spectra up to around 160 K. In Eq. 4.4, $\Delta$ is the dephasing rate (for details see Chapter 3) due to the field distribution created by the nuclear moments of Yb, Cu and Si (see Table 4.1). $\Delta$ is related to the second moment of the field distribution at the muon site [SC85] which, in the quadrupole limit and for a Gaussian field distribution has the following form (for the case of a half-integer nuclear spin):

$$M_{ZF, Q, I=odd}^{2, poly} = \frac{1}{3} I(I+1)(h \gamma_{\mu} \gamma_N) \frac{8}{3} \left[ 1 + \frac{3}{8} \frac{I+1/2}{I(I+1)} \sum_{j=1}^{N} \frac{1}{r_j^6} \right],$$

(4.5)

$$\Delta^{Q, I=odd}_{ZF} = \sqrt{\frac{1}{2} M_{ZF, Q, I=odd}^{2, poly}}.$$
with $M_2$ the second moment of the field distribution, $I$ the nuclear spin and $r_j$ the distance between the muon and the $j$'th nuclear spin (for the integer-spin case, consult [SC85]). A pure Kubo-Toyabe shape of the $\mu^+$ depolarization function is characteristic for a random field distribution at the muon site. In $\text{Yb(Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$ this field distribution is generated by static and randomly oriented nuclear magnetic moments, Table 4-1.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>natural abundance (%)</th>
<th>spin</th>
<th>gyromagnetic ratio</th>
<th>Electric quadrupole Moment (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$^{171}$</td>
<td>14.4</td>
<td>1/2</td>
<td>0.988</td>
<td>...</td>
</tr>
<tr>
<td>Yb$^{175}$</td>
<td>16.2</td>
<td>5/2</td>
<td>-0.2719</td>
<td>2.8</td>
</tr>
<tr>
<td>Cu$^{63}$</td>
<td>69.2</td>
<td>3/2</td>
<td>1.484</td>
<td>-0.222</td>
</tr>
<tr>
<td>Cu$^{65}$</td>
<td>30.8</td>
<td>3/2</td>
<td>1.588</td>
<td>-0.195</td>
</tr>
<tr>
<td>Ni$^{57}$</td>
<td>1.13</td>
<td>3/2</td>
<td>0.50</td>
<td>0.162</td>
</tr>
<tr>
<td>Si$^{29}$</td>
<td>4.67</td>
<td>1/2</td>
<td>-1.1106</td>
<td>...</td>
</tr>
</tbody>
</table>

Table 4-1: Nuclear abundance, spin, gyromagnetic ratio and electric quadrupole moment for the nuclei of $\text{Yb(Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$

The nuclear magnetic moments were considered static, which is a good approximation in view of the time window of a $\mu$SR experiment (see Figure 3-1). In $\text{YbCu}_2\text{Si}_2$ the Yb$^{3+}$ electronic moments might oscillate too fast (THz) to affect the muon polarization, i.e. the effect of the field distribution arising from these fast fluctuating electronic moments is, due to motional narrowing effects, not accessible in the $\mu$SR time window and also does not affect the nuclear spins. Our results agree with those of Walter et al. [WA92] who performed neutron scattering experiments on $\text{YbCu}_2\text{Si}_2$ and estimated to about $10^4$ GHz (see also the discussion of $\text{YbNi}_2\text{Si}_2$ in Chapter 4.1.5.1.b) the fluctuation rate of the Yb$^{3+}$ electronic moments.

A $\mu$SR spectra recorded at 5 K and fitted with Eq. 4-4 is displayed in Figure 4-21. Since the depolarization rate is small, $\Delta = 0.13$ MHz, the MORE facility at PSI (details in Chapter 3) was employed to check for the minimum and the recovery of the 1/3 term on a longer time scale (without MORE the typical time window is around 10 $\mu$s). The temperature dependence of the depolarization rate $\Delta(T)$ is shown in Figure 4-22. Between 2 K and 130 K $\Delta(T)$ is almost temperature independent. Above 180 K the fast decrease of the depolarization points to the onset of the $\mu^+$ diffusion and the Kubo-Toyabe fit is no longer valid.

The knowledge of the depolarization rate due to the field distribution generated by the randomly oriented nuclear magnetic moments may give some hints about the muon site in the crystallographic unit cell. Due to the Coulomb repulsion from the ions, the muon stops in symmetric interstitial sites (see Table 4-2). In $\text{CeCu}_2\text{Si}_2$, which possesses an identical structure and almost the same lattice parameters, a relaxation rate of $\Delta = 0.135$ MHz was observed [FE95], with a similar temperature dependence. The (1/2,1/2,0) site was chosen as muon site after considering the qualitative information obtained from Knight shift data measured on a single crystal (from the ZF measurements alone it was not possible to distin-
Figure 4-21: μSR signal taken in YbCu$_2$Si$_2$ at 5 K using the MORE facility at PSI. The signal was fitted with Eq. 4-4 (the solid line).

Figure 4-23: The temperature dependence of the relaxation rate $\Delta$ of YbCu$_2$Si$_2$. The fast decrease of $\Delta(T)$ above 180 K points to the onset of the muon diffusion.
guish between the (1/2,1/2,0) and (1/2,0,0) sites for which the calculated \( \mu^+ \) depolarization rate is similar. The same (1/2,1/2,0) site was found for the muon in CeRu\(_2\)Si\(_2\) [AM93], [AM97]. In CeRh\(_2\)Si\(_2\), (1/2,0,0) was identified as the muon site based on the magnetic structure determined by neutron scattering and the ZF \( \mu \)SR measurements in the magnetically ordered phase (see Chapter 5.2 for details). In Ce\(_{0.95}\)La\(_{0.05}\)Ru\(_2\)Si\(_2\) [YA97] the (1/2,0,1/8) muon site was favored among the 11 most probable sites in the ThCr\(_2\)Si\(_2\) structure [MA88], Table 4-2. In U(Pr\(_{1-\delta}\)Fe\(_\delta\))\(_2\)Ge\(_2\) [PO00] the same (1/2,0,1/8) site was again assigned to the muon. For Yb(Cu\(_{1-x}\)Ni\(_x\))\(_2\)Si\(_2\) the muon site could not be determined precisely since no wiggles were observed in the \( \mu \)SR spectra of the magnetic phase. Some hints, however, could be obtained from the different types of \( \mu \)SR experiments (see below).

Knowing \( \Delta \) one can scan the unit cell to search for the muon site. The second moment \( M_2 \) (Eq. 4-5) was mapped in several symmetry planes of the ThCr\(_2\)Si\(_2\) structure. The \( M_{2,i} \) terms \( (M_2 = \sum M_{2,i}) \) were computed separately for each nuclear spin type \( i \). The natural abundance of the isotopes was taken into account by weighing each \( M_{2,i} \) with a probability \( p_i = \) abundance\(_i \) / 100. The values of calculated \( \Delta = \sqrt{M_2/2} \) are presented in Figure 4-23. The gray areas in Figure 4-23 indicate the sites for which 0.12 \( \mu s^{-1} \leq \Delta \leq 0.14 \mu s^{-1} \), as found in the experimental data. The stars/numbers indicate the possible muon sites given in Table 4-2, [MA88]). With A and B we have

<table>
<thead>
<tr>
<th>Nr. (as in Figure 4-23)</th>
<th>Wickoff notation</th>
<th>( \mu^+ ) site (in atomic coordinates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(8g)</td>
<td>0 1/2 1/8</td>
</tr>
<tr>
<td>2</td>
<td>(2b)</td>
<td>1/2 1/2 0</td>
</tr>
<tr>
<td>3</td>
<td>(8f)</td>
<td>1/4 1/4 1/4</td>
</tr>
<tr>
<td>4</td>
<td>(4e)</td>
<td>0 0 1/4</td>
</tr>
<tr>
<td>5</td>
<td>(4e)</td>
<td>1/2 1/2 5/16</td>
</tr>
<tr>
<td>6</td>
<td>(8j)</td>
<td>1/4 1/4 0</td>
</tr>
<tr>
<td>7</td>
<td>(8g)</td>
<td>1/2 0 1/16</td>
</tr>
<tr>
<td>8</td>
<td>(16n)</td>
<td>1/8 1/2 3/32</td>
</tr>
<tr>
<td>9</td>
<td>(16m)</td>
<td>1/4 1/4 5/32</td>
</tr>
<tr>
<td>10</td>
<td>(16m)</td>
<td>1/8 1/8 7/32</td>
</tr>
<tr>
<td>11</td>
<td>(4c)</td>
<td>0 1/2 0</td>
</tr>
</tbody>
</table>

Table 4-2: Possible muon sites in the ThCr\(_2\)Si\(_2\) type of structure (from [MA88])

Figure 4-23: the \( \Delta \) mapping on different crystallographic planes of YbCu\(_2\)Si\(_2\). With stars/numbers the sites described on Table 4-2 are indicated. A and B are possible muon sites in YbCu\(_2\)Si\(_2\) (see text).
denoted the possible muon sites in YbCu$_2$Si$_2$, respectively 8g (1/2,0,0.045) and 4e (1/2,1/2,0.03).

The dependence of the relaxation rate $\Delta$ on the Ni concentration $x$, $\Delta(x)$, computed for the 8g (A, dashed line) and the 4e (B, solid line) sites, is displayed in Figure 4-24 together with the experimental data. Notice that for the B site, for $x = 1$ a value of $\Delta$ of about 0.1 $\mu$s$^{-1}$ should have been measured, which is not the case (see Chapter 4.1.5.1.b ). The experimental data follow closer (Figure 4-24) the $\Delta(x)$ dependence computed for the A site, which appears to be the muon site in YbCu$_2$Si$_2$, than that computed for the site B. We could not exclude, however, the possibility that the muon site (particularly the $z$ component) changes slightly with the increase of the Ni concentration. This is suggested in Figure 4-24 by the dotted line which represents the calculated $\Delta(x)$ dependence for the (1/2,0,0) site.

For the understanding of the $\mu$SR results in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$, in the following subchapter the ZF/LF $\mu$SR data for YbNi$_2$Si$_2$, at the other end of the series, will be presented.
b) YbNi$_2$Si$_2$

The ZF μSR spectra for YbNi$_2$Si$_2$ could be best fitted with an exponential depolarization function for all temperatures above 4 K (Figure 4-25):

$$P(t) = \exp(-\lambda_{ZF} t),$$  \hspace{1cm} (4-6)

where $\lambda_{ZF}$ is the ZF $\mu^+$ relaxation rate due to the Yb$^{3+}$ spin fluctuations. In this case, the exponential depolarization function indicates the relaxation of the muon spin due to the fast fluctuating fields at the place where it comes at rest. $\lambda_{ZF}$ is proportional to the second moment of the field distribution created by the Yb$^{3+}$ electronic moments and inversely proportional to their fluctuation rate $\nu$ (see Chapter 3):

$$\lambda_{ZF,u} = \frac{M_{2,ZF}}{\nu} = M_{2,ZF} \tau_0,$$

for non-correlated fluctuations of the Yb electronic moments (index u). $\tau_0$ is the Yb$^{3+}$ spin fluctuation or correlation time, $\tau_0 = 1/\nu$. The exponential depolarization function is a particular case of the Dynamical Kubo-Toyabe (DKT) function and it's a good approximation of it in the limit of fast fluctuations (see the discussion in Chapter 3).

![Figure 4-25: $\mu^+$ depolarization in YbNi$_2$Si$_2$ at different temperatures above 3.2 K. The lines are fits of Eq. 4-6 to the $\mu$SR spectra.](image)

A power-law depolarization function

$$P(t) = A \exp(-\lambda_{ZF}) \beta$$  \hspace{1cm} (4-7)
was used to fit the ZF $\mu$SR data for YbNi$_2$Si$_2$ below $T_N = 6$ K down to $T_N$ (Figure 4-26). The insert in Figure 4-26 shows the temperature dependence of the parameter $\beta$. The different symbols represent experimental data taken using different instruments.

![Figure 4-26: $\mu$SR spectra for YbNi$_2$Si$_2$ at selected temperatures. The lines are fits using Eq. 4-7. The insert shows the temperature dependence of $\beta$ (see the text; different symbols represent results of measurements using different $\mu$SR spectrometers).](image)

The use of a power-law depolarization function is in general justified in the following cases:

- the transition to a spin glass state [SC85],
- an anisotropy or distribution of the fluctuations rate of the magnetic moments [PI00],
- the distribution of transition temperatures.

The first situation can be excluded since neutron scattering measurements [AN95] have shown that the ground state of YbNi$_2$Si$_2$ is antiferromagnetic (see Chapter 4.1.5.2). On the other hand, we cannot distinguish between the last two possibilities because:

- the fluctuations of the Yb magnetic moments might be anisotropic close to the magnetic phase transition (below $T_N$ the moments are oriented in the a-b crystallographic plane [AN95]).
- the magnetic transition itself is broad (see Figure 4-51), supporting the idea of a distribution of transition temperatures $T_m$ and consequently a distribution of relaxation rates.

**The dynamics of the Yb magnetic moments** was investigated in LF configuration: a field scan ($LF = 0...6000$ G) at 5 K and a temperature scan with $LF = 2000$ G were performed. In both cases, the LF $\mu$SR spectra could be fitted using a strictly exponential depolarization function (Eq. 4-6). The temperature dependence of the relaxation rates is presented in Figure 4-27 together with the fit results of the ZF $\mu$SR measurements. The double logarithmic scale
Figure 4-27: Temperature dependence of the ZF (closed symbols, different symbols indicating results obtained on different $\mu$SR spectrometers) and LF (line + open symbols) $\mu^+$ relaxation rate in YbNi$_2$Si$_2$. The insert represents the results of the longitudinal field scan at 5 K. The line is a guide to the eye.

was used to show the details at low temperatures and to demonstrate the power-law like behavior of $\lambda(T)$ in different temperature regimes. Note the monotonic increase of $\lambda_{ZF}$, measured in ZF, with decreasing temperature, while $\lambda_{LF}$, measured in LF of 2000 G, changes slope below 10 K. The insert in Figure 4-27 depicts the field dependence of the $\mu^+$ LF relaxation rate measured at 5 K, $\lambda_{LF}(5\,K)$.

The field dependence of $\lambda_{LF}(5K)$ shows a fast decrease with the increase of the applied field followed by saturation at fields higher than 1000 G (insert in Figure 4-27). This result will be discussed in detail later. On the other hand, there is almost no dependence of $\lambda_{LF}$ on the applied field above 20 K (Figure 4-27). In the following this behavior will be discussed first. A flat $\lambda(B)$ dependence is expected for fast Yb$^{3+}$ spin fluctuations. Using Eq. 3-17

$$\lambda_{LF,u} = \frac{M_{2}^{ZF} \tau_0}{1 + \omega^2 \tau_0^2},$$

(4-8)

in the limit of fast uncorrelated spin fluctuations ($\omega^2 \tau_0^2 \ll 1$) $\lambda_{LF}$ become field independent,

$$\lambda_{LF,u} = M_{2}^{ZF} \tau_0.$$

(4-9)

In this equation $\omega = \gamma B$, where $B$ is the longitudinally applied magnetic field. Since $M_{2}^{ZF}$ can be calculated using Eq. 3-3 ($M_{2}^{ZF} \approx 3.2 \cdot 10^4$ MHz for the site A, see the discussion in Chapter 4.1.5.1 about the muon site) a value of 112 GHz for the Yb$^{3+}$ spin fluctuation rate
The $\lambda_{\text{LF}}(T)$ dependence (LF = 2000 G) follows a power-law dependence above 15 K (Figure 4-29):

$$\lambda_{\text{LF}}(T) \propto (T)^{-0.56}.$$  

(4-10)

This $\lambda_{\text{LF}}(T)$ dependence (almost $1/\sqrt{T}$ -type) reflects the temperature dependence of the fluctuation rate of Yb$^{3+}$ magnetic moment, $\nu_{4f}(\nu_{4f} \approx 1/\lambda_{\text{LF}} \approx \sqrt{T})$, if the value of the fluctuating moment can be considered temperature independent (which can be the case at high temperatures). Below 10 K $\lambda_{\text{LF}}(T)$ changes slope (Figure 4-27).

The high temperature $\sqrt{T}$ -like dependence of $\nu_{4f}$ is similar to that previously observed in UCd$_{11}$ [BA86], CeNiSn [KA95] and YbAuCu$_{4}$ [BO96] using the $\mu$SR technique and in other Ce, Yb or U Kondo lattices using NMR or inelastic neutron scattering techniques. In an inelastic neutron scattering experiment the quasielastic linewidth, $\Gamma^{Q}$, is a measure of the 4f spin fluctuation rate in the case of a Lorentzian shaped 4f excitation spectrum. In Kondo lattices, $\Gamma^{Q}$ shows a $\sqrt{T}$ dependence at high temperatures ([PA98] and references therein). The 4f spin fluctuation rate $\Gamma^{\text{NMR}}(\Gamma^{\text{NMR}} \propto \nu_{4f})^6$ of some Kondo lattice compounds, computed from the nuclear spin-lattice relaxation measured in NMR experiments, exhibits a similar behavior: it shows a plateau at low temperature, characteristic of a Fermi liquid be-

$\nu_{4f}$ ($\nu_{4f} = 1/\tau_{0}$) at 5 K has been calculated. For the Yb$^{3+}$ magnetic moment, a value of 1.4 $\mu_{B}$ was used in the calculations. This value corresponds to the moment of the CEF ground state of YbNi$_{2}$Si$_{2}$ [BO91] and is a good approximation for the effective magnetic moment, at least up to $\approx 30$ K (see Figure 4-28), when the occupation of the excited CEF levels become important. The product $\omega^{2}\tau_{0}^{2} = \omega^{2}/\nu_{4f}^{2}$, computed for a field of 6000 G, gives a value of $2 \times 10^{-5}$ (i.e. $\ll 1$) which justifies the use of Eq. 4-9 for calculating $\tau_{0}$.

The $\lambda_{\text{LF}}(T)$ dependence (almost $1/\sqrt{T}$ -type) reflects the temperature dependence of the fluctuation rate of Yb$^{3+}$ magnetic moment, $\nu_{4f}(\nu_{4f} \approx 1/\lambda_{\text{LF}} \approx \sqrt{T})$, if the value of the fluctuating moment can be considered temperature independent (which can be the case at high temperatures). Below 10 K $\lambda_{\text{LF}}(T)$ changes slope (Figure 4-27).

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behavior, followed by a shallow minimum around the Kondo temperature $T_K$ and a $\sqrt{T}$ behavior at high temperatures, Figure 4-30 [QA87].

The $\sqrt{T}$ law for the fluctuation rate of the rare earth magnetic moment was predicted by Cox et al. [CO85] within the framework of the degenerate Anderson one-impurity model. The model is derived under the assumptions that

• it applies only to a degenerate ion (does not take into account the CEF splitting) or, in the presence of CEF splitting, is limited to temperatures $k_B T$ away from the values of the CEF splitting,

• it applies only to single rare-earth impurities.

However, there is quite some experimental evidence that single impurity results are relevant also to the magnetic response of Kondo lattice compounds (see also the discussion in Chapter 2) for $T \gg T_0$ (in the theory of Cox et al. by $T_0$ the Kondo temperature is denoted).

For $T > 5T_0$ an approximate analytical expression for $\Gamma^{\text{NMR}}$ is proposed by Cox et al. [CO85] and from Bethe-Ansatz calculations the exact result at $T = 0$ is known [RA84]:

$$\Gamma^{\text{NMR}}(0) = \frac{N}{\pi} e^{-N \Gamma} \left(1 + \frac{1}{N}\right),$$

and for $T > T_0$:

$$\frac{\Gamma^{\text{NMR}}(T)}{T_0} \approx \frac{2.4}{N} \sqrt{\frac{T}{T_0}}.$$

Here $N$ is the ground state degeneracy ($N = 8$ for a full orbital degeneracy of the ground state of Yb$^{3+}$) and $\Gamma$ is the Gamma function. In Figure 4-30 the dashed curve represents the calculation by Cox et al. and the dashed-dotted curve the high temperature asymptote [0.4($T/T_0$)$^{1/2}$, $N = 6$].

Since no maximum was observed in the $\lambda_{12}(T)$ dependence for YbNi$_2$Si$_2$ (i.e. no minimum in $v_{\text{th}}(T)$) the scaling of the YbNi$_2$Si$_2$ data presented in Figure 4-30 is only approximate. However, the value of about 7 K for $T_0$ ($= T_K$) that could be deduced from the $v_{\text{th}}^{\text{SR}}(T)/T_0 = f(T/T_0)$ scaling presented in Figure 4-30, is of the same order of magnitude as the Kondo temperature found in other Yb Kondo lattice systems presenting magnetic ordering at low temperature (see Table 4-3).
4.1 Yb(Cu,\textsubscript{1-x}Ni\textsubscript{x})\textsubscript{2}Si\textsubscript{2}

| YbSi   | 2.5  | 1.6  | [BO89]   |
| YbBiPt | 1-10 | 0.4  | [CA94]   |
| YbBiPd | 8    | <2   | [AL89], [DH88] |
| YbNiAl | 3    | 3    | [SC95], [BR95] |
| YbPdSb | 7    | 1    | [BR95]   |
| YbP    | 10   | 0.7  | [BR93], [DO90] |
| YbN    | 5    | 0.9  | [BR93]   |
| YbNiSn | 0.7  | 5.7  | [BO93]   |
| YbCu\textsubscript{4}Au | 20   | 0.5  | [BO96]   |
| YbNi\textsubscript{2}Si\textsubscript{2} |   7  | 2.1  | [BO91], this work |

Table 4-3: Characteristic temperatures for different Yb compounds.

The deviation from the pure $\sqrt{T}$ law (see Eq. 4-10) and the absence of the minimum in the $\nu_4(T)$ dependence for YbNi\textsubscript{2}Si\textsubscript{2} might be related to the absence of the full orbital degeneracy at low temperatures, i.e. to CEF effects. It was shown ([PA88] and references therein) that no minimum is expected in the $I(T)$ curve for $N = 2$ ($N = 2$ at low $T$ and $N = 6$ at high $T$, for YbNi\textsubscript{2}Si\textsubscript{2}). Bonville et al. [BO96] invoked CEF effects to justify the absence of the minimum in $I^Q(T)$ and $I^\mu$SR($T$) dependence for YbCu\textsubscript{4}Au.

The temperature dependence of the paramagnetic relaxation rate of the Yb\textsuperscript{3+} ion in YbNi\textsubscript{2}Si\textsubscript{2}, measured using the Mössbauer technique [BO91], is presented in Figure 4-31 (triangles) together with our data (circles). Our data were scaled down by a factor of $\approx 6$, to fit the low $T$ Mössbauer data. There are no reliable data above 60 K in the Mössbauer experiment because of the small dynamical line broadening due to the fast spin fluctuation. It is not very clear yet where the difference between the $\mu$SR and the Mössbauer data is coming from (a $2\pi$ factor might have been forgotten in [BO91]). Our calculated value can be influenced by a further reduction of the Yb\textsuperscript{3+} magnetic moment due to the Kondo effect or by the anisotropy of the magnetic susceptibility at low temperatures. These effects could play a role in the reduction of the calculated $\nu_4^{\text{SR}}$ but

![Figure 4-31: Thermal variation of the paramagnetic relaxation rate of the Yb\textsuperscript{3+} magnetic moments measured using Mössbauer (triangles, [BO91]) and $\mu$SR (circles, scaled results) techniques. The dashed line shows a $T$-linear fit (see text). The solid line represents the fit described by Eq. 4-10.](image-url)
do not explain the full difference:

- André et al. [AN95] performed neutron scattering experiments in the magnetic phase of YbNi$_2$Si$_2$ (below 2.1 K) and found an ordered magnetic moment close to the CEF ground state moment, so the Kondo effect reduces only marginally the Yb$^{3+}$ magnetic moment in YbNi$_2$Si$_2$.

- The increase of the anisotropy with decreasing temperature can play a role via the second moment of the field distribution, which is modified if the fluctuations become anisotropic. The effect is large only in a particular case, i.e. for a single crystal where the muon resides in the easy magnetization plane. However, for a polycrystalline sample the effect on the second moment is smaller and further reduced if the muon site is not in the easy magnetization plane, as it seems to be the case for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.

We therefore conclude that the value $\nu_{sf} = 120$ GHz, measured by $\mu$SR, reflects correctly the fluctuation rate of the Yb$^{3+}$ magnetic moment in YbNi$_2$Si$_2$, at 5 K.

Coming back to the ZF/LF results between $T_m < T < 20$ K, an explanation of the difference between the ZF and the LF $\mu^+$ relaxation rate (Figure 4-27) and the behavior of the field dependence of the $\mu^+$ relaxation rate at 5 K (insert in Figure 4-27) is necessary. The field distribution created by the nuclear magnetic moments, $\Delta/\gamma$, should not play a role because its width is at the most 1G in YbNi$_2$Si$_2$ (for a $\Delta_K = 0.09$ MHz). Therefore a longitudinal field of 10 G would be enough to decouple the static contribution to the $\mu^+$ relaxation rate.

We analyze the field dependence of the LF $\mu^+$ relaxation rate in terms of two contributions:

$$\dot{\lambda}_{LF}(B) = \dot{\lambda}_u + \dot{\lambda}_c(B),$$

where $\dot{\lambda}_u$ would be the field independent $\mu^+$ relaxation rate due to the Yb$^{3+}$ spin fluctuations, as described above (Eq. 4-9). The field dependence of $\dot{\lambda}_{LF}$ is due to the second term, $\dot{\lambda}_c$, see Figure 4-32. The second contribution can originate from:

- Induced fluctuations of the nuclear magnetic moments (so called double relaxation) by the fluctuating Yb$^{3+}$ magnetic moments at low temperatures. Since the fluctuation rate of the Yb$^{3+}$ magnetic moments decreases when approaching the magnetic transition, the coupling with the nuclear magnetic moments should increase, i.e. the nuclear magnetic moments can see and
follow the Yb\(^{3+}\) fluctuations, providing a second relaxation channel for the muon ensemble.

- Correlated fluctuations of the Yb\(^{3+}\) moments may have a positive (negative) contribution to the relaxation rate depending on the type, ferromagnetic (antiferromagnetic), of the spin fluctuations and the muon site.

A third possibility will be described when the results in Yb(Cu\(_{1-x}\)Ni\(_x\))\(_2\)Si\(_2\) are discussed (Chapter 4.1.5.1.c).

Fitting \(\lambda_c(B)\) with a field dependence as that described by Eq. 4-8 (the dotted line in Figure 4-32), we obtain \(M_{2c}^{ZF} = 1.24\) MHz\(^2\) and \(\nu_c = 1/\tau_c = 12\) MHz. From the fit results, the double relaxation mechanism is excluded since it requires a value of the second moment of the nuclear field distribution more than an order of magnitude higher that the experimental/calculated one.

If we consider the second case, the situation can be viewed as follows: at high temperatures, the spins fluctuate completely uncorrelated and cause statistically independent contributions to the components of the fluctuating hyperfine fields at the muon site. With decreasing temperature, the paramagnetic spins develop parallel (antiparallel) correlations like in ferromagnets (antiferromagnets). One can use a modified Eq. 4-8 ([P100] and references therein) to describe the relaxation rate due to the correlated fluctuations:

\[
\lambda_c = \frac{2}{3} \frac{\gamma_\mu^2 B_c^2 \tau_c}{1 + \omega^2 \tau_c^2}, \tag{4-11}
\]

and therefore

\[
\lambda_{LF}^{ZF}(B) = M_{2c}^{ZF} \tau_0 + \frac{2}{3} \frac{\gamma_\mu^2 B_c^2 \tau_c}{1 + \omega^2 \tau_c^2}, \tag{4-12}
\]

with \(B_c\) the amplitude of the correlated part of the local fluctuating magnetic field and \(\tau_c\) its fluctuation time \((\omega = \gamma_\mu B)\). In YbNi\(_2\)Si\(_2\), the Yb\(^{3+}\) magnetic moments show helical order below \(T_m\). The magnetic structure (see Chapter 4.1.5.2) can be described as ferromagnetic a-b planes rotated along the c direction. Increasing spin-spin correlations increase the value of \(B_c\) since both possible muon sites are close to the a-b plane and contain a second order symmetry axis for the Yb structure, i.e. the magnetic fields produced by the in-plane ferromagnetic arrangement of the Yb\(^{3+}\) magnetic moments add constructively. From the fit of Eq. 4-11 to the \(\lambda_c(B)\) data (Figure 4-32), a value of around 16 G for \(B_c\) and 12 MHz for \(\nu_c\) \((= 1/\tau_c)\) were obtained. Within this model we would describe the fluctuations of the Yb\(^{3+}\) magnetic moment as follows:

- At high temperatures the Yb magnetic moments perform uncorrelated fluctuations. The average field at the muon site is zero. \(B_c\) is zero too.
- Correlated fluctuations of the Yb magnetic moments develop at low temperatures, i.e. along certain axes or in some planes the average field \((B_c)\) is no more zero. \(B_c\) has a fluctuation time \(\tau_c\) that is larger than \(\tau_0\).
- Notice also that the difference between the ZF and the 2000 G LF \(\mu^+\) relaxation rates become significant below 10 K, i.e. the temperature at which essentially only the CEF
ground state is populated. A similar dependence of the LF relaxation rate, observed in CePt$_2$Sn$_2$ by Luke et al. [LU97], was also related to the depopulation of the excited CEF levels. Unfortunately, the authors do not present/discuss the field dependence of the measured $\mu^+$ relaxation rate.

- In principle, in Eq. 4-12 the second moment that appears in the first term should be smaller than $M^2_{ZF}$ since part of the Yb$^{3+}$ moments are correlated (i.e. do no more contribute to the uncorrelated fluctuations). Since $B_c$ is small, the corresponding value of the correlated moments is also small and Eq. 4-12 remains valid.

The value of $\lambda_{ZF}(T) - \lambda_{LF,0}(T)$ increases with decreasing temperature towards $T_m$ (see Figure 4-27), indicating a corresponding increase of $B^2_c \tau_c$. The value of $B_c$ increases from zero (uncorrelated fluctuations) to a value of the order of kG (the local field in the magnetic phase, see Chapter 4.1.5.2) for fully correlated fluctuations of the magnetic moments. With $B_c = 16$ G, at 5 K, the magnetic correlations between the Yb$^{3+}$ moments are weak.

Clearly, other explanations of the $\lambda_{LF}(B)$ dependence are possible. Eq. 4-8, on which the field dependence of the LF relaxation rate is based, is derived under the assumption that the local fields are fluctuating with the auto-correlation function

$$\frac{\langle B(0)B(t) \rangle}{\langle B(0)^2 \rangle} = e^{-\Delta t}$$

(see for example [UE99]).

Its Fourier transformation gives the Lorentz-type dependence of $\lambda_{LF}(B)$ described by Eq. 4-8. This expression is valid in the fast fluctuation limit ($\nu \Delta >> 1$), i.e. when the relaxation is predominantly caused by spin flipping. It might not be a good approximation for the $\lambda_{LF}(B)$ dependence when phenomena like anisotropic field fluctuations, magnetic clustering (expected to occur close to the magnetic transition) or inter-site spin-spin correlations are involved. More theoretical/experimental work should be performed to check for the different possibilities and, eventually, to include in the above equation terms describing the fluctuation anisotropy, the magnetic cluster size distribution or the spin-spin correlation length.
c) Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$

**ZF-LF measurements in the paramagnetic regime ($T > T_m$):**

**Experimental results**

As stated above, for Ni concentrations $x > 0$, the dynamics of the Yb$^{3+}$ magnetic moments affect the $\mu^+$ polarization. Since the static (nuclear moments) and dynamic depolarization channels are independent, a product of a Kubo-Toyabe function with a power law (power Kubo-Toyabe, PKT) was selected to fit the ZF $\mu$SR spectra for $x > 0$ at $T \geq T_m$ where $T_m$ is the magnetic transition temperature,

$$P(t) = \left( \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) e^{-\frac{x_{\mu+}^2}{2}} \right) \exp(-\lambda_{ZF} t) \beta. \quad (4-13)$$

In Eq. 4-13 $\Delta$ describes the contribution to the $\mu^+$ depolarization arising from the static nuclear magnetic moments (see Table 4-1) while $\lambda_{ZF}$ reflects the dynamics of the Yb$^{3+}$ magnetic moments in zero applied field. The values of $\Delta$ for different Ni concentrations are displayed in Figure 4-24. They show a monotonous decrease with the increase of the Ni concentration $x$, in agreement with the Monte-Carlo simulations. The $\Delta(x)$ dependence indicates that the muon should be close to the $(1/2,0,0)$ site (site #7 or site A in Figure 4-23).

![Figure 4-33: ZF $\mu$SR spectra for Yb(Cu$_{0.875}$Ni$_{0.125}$)$_2$Si$_2$ at different temperatures below and above the magnetic transition ($T_m = 0.5$ K). Notice the Gaussian shape of the depolarization at high temperatures. The lines are fits of the $\mu$SR spectra (see text).](image)

In Figure 4-33 several $\mu$SR spectra for Yb(Cu$_{0.875}$Ni$_{0.125}$)$_2$Si$_2$ at different temperatures above and below the magnetic transition ($T_m = 0.5$ K) are displayed. Their shape is typical for the
Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples. Notice the Gaussian shape of the depolarization function at 100 K. For comparison see the μSR spectra measured above $T_m$ in YbNi$_2$Si$_2$, Figure 4-25. The temperature dependence of the exponent $\beta$ is presented in Figure 4-34 for the sample with $x = 0.75$. This $\beta(T)$ dependency is also typical for all concentrations $0 < x < 1$: it is constant and equals one down to 10 K; below $\approx 10$ K $\beta$ decreases with decreasing temperature. In general, a power law depolarization function indicates the existence of a distribution of the fluctuation rates at that temperature, but it says nothing about the shape or the origin of the fluctuation rate distribution. Some of the effects that might produce the observed power law relaxation rate were discussed on Page 53. It is still not possible to distinguish between the following two effects:

- The disorder induced by the chemical substitution which can lead to
  - magnetic clustering formation close to the magnetic transition temperature, leading to a distribution of relaxation rates related probably to the cluster dimension, the value of the fluctuating moment, etc.
  - a distribution of Kondo temperatures $T_K$ reflected also in a distribution of transition temperatures $T_m$. The relaxation rate distribution, in this case, is given by the distribution of $(T-T_m)$ at each value of $T$.

- The anisotropy of the relaxation rate (due to anisotropic fluctuations of the 4f-moments), as described on Page 53. μSR measurements on single crystals are needed to understand the role of this effect. In YbNi$_2$Si$_2$, the anisotropic fluctuations of the 4f-moments can be investigated by checking the difference between the μSR spectra collected with the $a$-$b$ plane of the tetragonal structure parallel with the muon spin and the spectra recorded with the muon spin perpendicular to the $a$-$b$ plane.

As it will be shown below, the disorder induced by the chemical substitution plays an important role in establishing the ground state of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. It is therefore conceivable that it also affects the distribution of relaxation rates above the magnetic transition tempera-
The magnetism in these compounds is strongly related with the neighbor arrangement of the Yb ions, i.e. with the chemical substitution $x$.

The temperature dependence of $\lambda_{ZF}$ for different Ni concentrations $x$ is presented in Figure 4-36 in a double logarithmic plot. At high temperatures (region I in Figure 4-36) $\lambda_{ZF}(T)$ has the same $1/\sqrt{T}$-like dependence as described for YbNi$_2$Si$_2$, in agreement with the model of Cox et al. [CO85] presented in Chapter 4.1.5.1.b (Figure 4-30). At low temperatures $\lambda_{ZF}(T)$ changes the slope first around 20 K and secondly below 2 K. The first slope change might be related to the depopulation of the excited CEF levels as the temperature is decreased. The slope change below 2 K is due to the slowing of the Yb$^{3+}$ spin fluctuations while the magnetic transition temperature $T_m$ is approached from above (region III). This effect is evidenced in Figure 4-35 where the data for Yb(Cu$_{0.25}$Ni$_{0.75}$)$_2$Si$_2$ are displayed on a semilogarithmic scale.

The results of the LF $\mu$SR measurements are presented in Figure 4-37. The temperature scan in a longitudinal field configuration (LF = 2000 G) are presented together with the ZF data to show the effect, on the $\mu^+$ relaxation rate, due to the correlation between the Yb$^{3+}$ magnetic moments. For a better display, the data in Figure 4-37 are shifted vertically (see the legend in Figure 4-37). The continuous increase of the difference between $\lambda_{ZF}$ and $\lambda_{LF}$ with decreasing temperature can be ascribed, as in YbNi$_2$Si$_2$, to the increase of the correlated fluctuations of the CEF ground state Yb magnetic moments (see also Figure 4-27, Figure 4-33 and the discussion in Chapter 4.1.5.1.b).
In Figure 4-38 the ZF and the LF (2000 G) relaxation rates at 5 K are displayed for different Ni concentrations x.

\( T_K(x) \) for \( \text{Yb(Cu}_{1-x}\text{Ni}_x\text{)}_2\text{Si}_2 \) \((T_K = \text{Kondo Temperature})\)

To check the scaling presented in Figure 4-30 (the model of Cox et al. [CO85]) which would allow the estimation of the characteristic temperature \( T_0 \) \((= T_K)\), we should compute the temperature dependence of the Yb-spin relaxation rate for all Ni concentrations x. For this purpose, the value of the second moment of the field distribution, arising from the electronic moments of Yb\(^{3+}\), is needed.

We assume that the main contribution to the increase with x of the LF \( \mu^+ \) relaxation rate (see Figure 4-38) is due to the decrease of the fluctuation rate \( v_{af} (\lambda_{af} = M_2 \tau_0, \text{with} \tau_0 = 1/v_{af}) \) of the Yb\(^{3+}\) magnetic moments. In other words, we consider that the second moment remains unchanged, at least for x \( \geq 0.5 \). Since the difference between \( \lambda_{ZF} \) and \( \lambda_{LF} \) (which can be related, for example, to the Yb\(^{3+}\) spin-spin correlation) presented in Figure 4-38 is almost unchanged above x = 0.5 at 5 K (see also
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Figure 4-37), we can argue that the effect of the correlated fluctuations is also basically the same for \( x \geq 0.5 \) (a similar effect was observed in YbCu_{5-x}Al_x, see Chapter 4.2).

Considering that the muon site does not change with the Ni concentration \( x \) it is expected that correlated fluctuations have the same effect for different Ni concentrations if the magnitude of the magnetic moments involved in the fluctuations are similar. Since this implies that the second moment of the field distribution at the muon site does not vary with \( x \), it supports our previously made approximation. No assumption was made, up to now, about the strength of the magnetic correlation or the correlation time/length which, as it was discussed at the end of Chapter 4.1.5.1.b, might lead to a modified field auto-correlation function.

In Figure 4-39a, the \( (\nu_{d}(x)/T_0(x)) = f(T/T_0(x)) \) scaling is presented for different Ni concentrations \( x \) (see also Figure 4-30). The scaling is less satisfactory for \( x \leq 0.375 \), due probably to the fact that the approximation of an \( x \)-independent second moment might fail for small \( x \).

The scaling presented in Figure 4-39a allows the estimation of the \( T_0(x) \) dependence, which is displayed in Figure 4-39b. It is in qualitative agreement with the \( \theta_p(x) \) dependence (\( \theta_p \) is the paramagnetic Curie temperature) presented, for comparison, in the same figure. Our results point to the decrease of the Kondo temperature with the increase of the Ni concentration \( x \).

Dalmas de Réotier et al. [DA96] have challenged a similar scaling procedure performed for CeNiSn by Kalvius et al. ([KA94], [KA95]). Surely, the scaling procedure is not free of errors since it neglects the influence of the CEF fields (it led to an extremely low \( T_K \), \( \leq 0.1 \) K, for CeNiSn). However, in our case, the values of the Kondo temperatures are in good agreement: for YbCu_{2}Si_{2} (\( x = 0 \)) with that obtained from macroscopic measurements by Tomala et al. [TO99] and for YbNi_{2}Si_{2} with that of similar Yb compounds (see Table 4-3). This might be explained by the fact that in our case the scaling occurs at high temperatures, i.e. where the CEF splitting does not play a major role.

**Figure 4-39a:** \( (\nu_{d}(x)/T_0(x)) = f(T/T_0(x)) \) scaling for Yb(Cu_{1-x}Ni_x)_{2}Si_2. See also Figure 4-30.

**Figure 4-39b:** \( T_0(x) \) for Yb(Cu_{1-x}Ni_x)_{2}Si_2 as obtained from the scaling presented in Figure 4-39a. For comparison, the \( \theta_p(x) \) data are also presented. \( T_0(0) \) is from Tomala et al. [TO90].
$[J_{4f}N(E_F)](x)$ for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$

In the temperature region where a deviation from the $1/\sqrt{T}$ dependence of the LF relaxation rate $\lambda_L(T)$ was observed, but above $T_m$, the fluctuation rate of the 4f magnetic moments $v_{4f}(T)$ is linear in temperature (see Figure 4-40) and is believed to be a signature of a Fermi-liquid phase. A linear $v_{4f}(T)$ dependence is measured for relaxation rates governed by the Korringa and the RKKY (precursor of the magnetic phase below $T_m$) relaxation mechanisms (see below).

The RKKY relaxation mechanism, due to inter-ionic exchange, represents a temperature independent contribution (as long as the excited CEF levels are negligibly populated) to the Yb$^{3+}$ relaxation rate:

$$v_{\text{RKKY}} = c' |\theta_p|$$

(see [HA86] and references therein), where $c'$ is a constant and $\theta_p$ is the paramagnetic Curie temperature (see Figure 4-41).

The Korringa relaxation rate

$$v_{\text{Korr}} = C_K T$$

represents the relaxation rate of the Yb magnetic moments due to the interaction of the Yb magnetic moments with the conduction electrons. $C_K$ is the Korringa constant, proportional to the second power of the product $J_{4f}N(E_F)$. This product, according to the Dioniach phase diagram (see the discussion on Chapter 2), controls the low temperature properties in our compounds:

$$C_K \propto (J_{4f} \cdot N(E_F))^2$$

where $J_{4f}$ is the 4f electron - conduction electron exchange integral, $N(E_F)$ is the
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Conduction electron density of states per spin at the Fermi energy.

From a fit of the form

$$\nu_{hf} = \nu_{\text{RKKY}} + C_K T$$

(4-14)

to the experimental data (see Figure 4-40) the coefficients $\nu_{\text{RKKY}}$ and $C_K$ are obtained. They are displayed in Figures 4-41 and 4-42. The decrease of $\nu_{\text{RKKY}}$ with the increase of the Ni concentration (see Figure 4-41) is in agreement with the observed decrease of $|\theta_p|$ and $T_0$ (see Figure 4-39b).

As shown, the Korringa constant $C_K$ provides a direct measure of $J_{hf} N(E_F)$. A decrease of $J_{hf} N(E_F)$ with the increase of the Ni concentration (which coincides also with the increase of the lattice pressure on the Yb ions) in the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ compounds, is suggested by the Doniach phase diagram (see the discussion on Chapter 2 and Figure 2-2). It indicates the approach toward a magnetic ground state of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ with the increase of the Ni concentration $x$. This result will be further confirmed by μSR measurements at low temperature.

In Ce compounds, the decrease of $J_{hf} N(E_F)$ when approaching the magnetic phase was proved by Amato [AM98] for CeCu$_{1-x}$Al$_x$. The $J_{hf} N(E_F) = f(x)$ dependence was obtained from the coupling constant $A_c$ (see Chapter 3.5) determined in a TF measurement.

**Correlations between the Yb$^{3+}$ magnetic moments**: $B_c(x)$ and $v_c(x)$

Field scans, in longitudinal field configuration at 5 K, were performed for all Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples (see, for example Figure 4-27). The field dependence of the $\mu^+$ relaxation rate, $\lambda_{\text{LF,SK}}$, could be fitted for different Ni concentrations $x$ using Eq. 4-12:

$$\lambda_{\text{LF}}(B) = M_T^2 \tau_0 + \frac{2}{3} \frac{\gamma^2 B^2 \tau_c}{1 + \omega^2 \tau_c^2}.$$
The same model as for YbNi$_2$Si$_2$, see Page 59, with uncorrelated and correlated Yb$^{3+}$ spin fluctuations, was considered. The $x$-dependencies of the fitted correlated field value ($B_c$) and fluctuation rate ($v_c = 1/\tau_c$) are depicted in Figure 4-43 and Figure 4-44, respectively. If the model described by Eq. 4-12 is correct, then $B_c$ increases with $x$ (chemical pressure), and the same happens to $v_c$. While the increase of $B_c$ can be related with the increase of the average correlated moment, the increase of $v_c$ with the chemical pressure is not yet understood. The reader should keep in mind that $v_0 (= 1/\tau_0)$, the fluctuation rate of the electronic moments in the absence of spin-spin correlations, decreases with the increase of the chemical pressure. Striking are also (like in the case of YbNi$_2$Si$_2$) the small values of $B_c$ and $v_c$.

4.1.5.2 ZF measurements in the magnetic phase ($T < T_m$).

The low temperature $\mu$SR measurements were performed using the GPS (down to 1.8 K) and the LTF (down to around 40 mK) spectrometers at PSI. Some of the measurements on the $x = 0.125$ sample were performed, down to around 300 mK, using a He$^3$ cryostat at the EMU beam line at ISIS, UK. The $\mu$SR measurements at low temperatures indicate that magnetic order occur in all samples with $x \geq 0.125$. The signature of the magnetic order is a fast relaxing Gaussian-like component in the $\mu$SR spectra (Figure 4-45). Since no spontaneous oscillations were observed we conclude that either the average field at the muon site is zero or the field distribution is very broad. In the case of a zero average field at the muon site, a dynamical Kubo-Toyabe depolarization function would be appropriate to fit the magnetic contribution to the $\mu$SR spectra close to the magnetic transition. In the case of a non-zero average field at the muon site, no oscillation is observed in the $\mu$SR spectra only if the depolarization rate is very large, i.e. the $\mu^-$ polarization is lost before that the muon spin rotates by $\pi$. In Figure 4-46 simulated $\mu$SR spectra are displayed to show the effect of Gaussian field distributions around a nonzero average magnetic field (20 G in our example, i.e. 0.27 MHz). A simple case was con-
sidered in our simulation: a field perpendicular to the muon polarization (for more general situations see [KO91], [PI99] and [LA00]), therefore no 1/3 term appear in the µSR spectra, as it should when the field can take all orientations in space. Note that for large field distributions, a Gaussian depolarization function represents a good fit of the µSR data. However, one should keep in mind that the value of the depolarization rate $\Delta$, when fitting the data with a Gaussian, is overestimated [KO91].

The magnetic structure of YbNi$_2$Si$_2$ was investigated using the neutron diffraction techniques [AN95]. In the neutron diffraction pattern at 1.43 K one observes peaks of magnetic origin which were indexed with the wave vector $k = (0, 0, 0.8025)$. The magnetic structure is helical with the Yb$^{3+}$ magnetic moment lying in the a-b plane of the tetragonal crystal structure (see Figure 4-47). The value of the ordered moment at 1.35 K is around 1.47 $\mu_B$ [AN95].

Assuming the magnetic structure as deduced from the neutron data one can compute the dipolar fields at different possible muon sites, see Chapter 4.1.5.1.a (in the magnetic unit cell, crystallographic equivalent muon sites can be magnetically inequivalent). We find that the field seen by the muon is nonzero for all selected muon sites (see Figure 4-24). Since that no wiggles were observed in the µSR spectra, the field distribution at the muon site has to be very large (see the discussion on Page 68 and Figure 4-46). We will discuss the origin of the large field distribution, calculate it for the (1/2, 0, 1/16) site (# 7 in Figure 4-23), and justify a fit of the µSR spectra at $T < T_m$ in the magnetic phase, without a wiggling term.

An intrinsic field distribution arises from the helical magnetic structure of YbNi$_2$Si$_2$ (see Appendix C - the particular case discussed at the end of the appendix, and the discussion in Chapter 3.3.1.4.4).

The field distribution generated by a known distribution of magnetic moments is simulated by calculating the dipolar fields at the possible (magnetic equivalent) muon sites. As shown in Appendix C, for the particular case of the helical structure of YbNi$_2$Si$_2$, the fields at different muon site describe an ellipse as in the case of a single-$k$ sine-
modulated magnetic structure. Both Eq. C-1 or Eq. C-2 can be used to generate the field distribution but:

- Eq. C-1 should be used only if the \( k \)-vector is commensurate (finite number of fields on the ellipse, given by the value of the \( k \)-vector).
- The calculation of a too small number of fields (by using Eq. C-1) can lead to incorrect field distributions (see Figure 4-48, and Figure 4-49).
- Eq. C-2 is correct for (nearly) incommensurate helical structures (large number of fields on the ellipse, Figures 4-49 and 4-50).

In Figure 4-48 the fields at the muon site, computed for the magnetic unit cell presented in Figure 4-47, are displayed. The site \#1 from Figure 4-47 (site A from Figure 4-23) was considered. The parameter \( n \) indicates the number of crystallographic unit cells in the magnetic unit cell. A calculation for a \( n = 162 \) magnetic unit cell is presented in Figure 4-49. In both cases, Eq. C-1 was used.

![Figure 4-48](image)

**Figure 4-48:** Magnetic fields at the muon site for a magnetic unit cell made of 5 structural unit cells.

Figure 4-50 shows the equivalence between Eq. C-2 and C-1 when a large number of fields is considered. For comparison, the field distribution obtained from Figure 4-48 is also shown, using the same field bining.

Several conclusions can be drawn from Figure 4-50:

- A sufficiently large number of fields should be generated to simulate correctly the field distribution.
- In YbNi\(_2\)Si\(_2\), the width of the field distribution at the assumed muon site is broad. This intrinsic field distribu-
tion is further broadened by lattice defects: dislocations, missing ions, etc. Therefore it is justified, as discussed on Page 68, to use the Gaussian depolarization function to describe the \( \mu^+ \) depolarization below \( T_m \).

In the transition temperature region the \( \mu \)SR spectra were fitted with

\[
AP_z(t) = A_{\text{para}} \left( \frac{1}{3} + \frac{2}{3} \left( 1 - \frac{\Delta^2 t^2}{2} \right) e^{-\frac{\Delta^2 t^2}{2}} \right) e^{-\left(\lambda t\right)^2} + A_{\text{mag}} \left( \frac{1}{3} e^{-\lambda_m t} + \frac{2}{3} e^{-\frac{\sigma_m^2 t^2}{2}} \right),
\]

(4-15)

where \( A_{\text{para}} + A_{\text{mag}} = A \) is the full asymmetry (obtained from fits of the \( T > T_m \) \( \mu \)SR spectra). The first term in Eq. 4-15 describes the paramagnetic part of the sample and is identical to that given by Eq. 4-13. The second term accounts for the magnetic phase: \( \lambda_m \) represents the \( \mu^+ \) relaxation rate while \( \sigma_m \) (see the discussion above) is the depolarization rate due to the field distribution created by the electronic moments, in that phase. The ratio \( A_{\text{mag}}/A \) indicates the fraction of the sample that is subject to magnetic ordering. The temperature dependence of \( A_{\text{mag}}/A \) for different Ni concentrations \( x \) is presented in Figure 4-51. The lines are fits to a phenomenological function of the form

\[
\frac{A_m}{A}(T, x) = \frac{a(x)}{1 + e^{b(x)(T-T_m(x))}} \quad (4-16)
\]

which was chosen to define a transition temperature. As can be seen, the fits are remarkably good. The meaning of the different terms in Eq 4-16 is the following: \( a(x) \) represents the magnetic fraction of the sample, \( T_m(x) \) the transition temperature. \( b \) is a fit parameter that can be used to describe the width of the transition (by changing the value of \( b \), the slope of the transition is changed).

Notice that the magnetic correlations develop in a fraction of the sample which depends on \( x \). This fraction increases with the increase of the Ni concentration, and for \( x = 0.5 \) almost the entire sample is magnetic below \( T_m \) [\( T_m = f(x) \)]. Recall that in the discussion presented in Chapter 4.1.1,
from the correspondence between the chemical and the external pressure a critical concentration \( x_c \approx 0.5 \) was calculated, a value close to the concentration at which the full sample is magnetic at low temperatures.

It was found [AN99] that the fraction of the sample that becomes magnetic scales well with the probability for a Yb ion to have at least two Ni ions as nearest neighbors. To explain this finding let us assume for a magnetic ion of type A a nearest neighbors coordination number \( N \) with neighbors of type \( B \) or \( C \) (see the example presented in Figure 4-52, where \( A = \text{Yb}, N = 8, B = \text{Cu} \) and \( C = \text{Ni} \)). Suppose that the A ions order magnetically only when surrounded by at least \( n \) of the type-C ions. In Figure 4-52 the probability, \( P_B(n,x) \), for the Yb ion to have a number \( n \) of Ni neighbors in a \( \text{Yb(Cu}_{1-x}\text{Ni}_x)_{2}\text{Si}_2 \) compound is given by

\[
P_B(n,x) = \frac{N!}{n!(N-n)!} x^n (1-x)^{N-n},
\]

and the probability to have at least \( n \) Ni neighbors can be easily calculated by summation:

\[
P_B(\geq n,x) = \sum_{i=n}^{N} \frac{N!}{i!(N-i)!} x^i (1-x)^{N-i}.
\]

The probability of an Yb ion to have \( n = 1, 2 \) and 3 Ni nearest neighbors, for different Ni concentrations \( x \), is displayed in Figure 4-53 together with the measured fraction of the sample that displays magnetic ordering, \( \frac{A_{mag}}{A} \).

![Figure 4-53: Probability for an Yb ion to have at least \( n \) Ni ions as nearest neighbors.](image)

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**Figure 4-53:** Probability for an Yb ion to have at least \( n \) Ni ions, function of the Ni concentration \( x \) in \( \text{Yb(Cu}_{1-x}\text{Ni}_x)_{2}\text{Si}_2 \) (lines). On the same graph, the fraction of the sample that presents magnetic ordering at low temperatures, \( \frac{A_{mag}}{A} \) is represented (●).
A similar scaling procedure was used by Jaccarino and Walker [JA65] to describe the discontinuous occurrence of localized moments in some alloys. They assumed that the distinction between different impurity ions is based on the nature of their local environment in the disordered alloy and considered that in some environments they are unmagnetized and in all others they have their full magnetic moment. Then the model to describe the different environments is similar to that presented above. However, an important distinction needs to be made between the two approaches although the mathematical procedure is the same:

- In the Jaccarino-Walker model the occurrence of the magnetic moment on the respective ion is determined by its environment, while in our case the Yb ions have a magnetic moment and the environment sets the necessary condition for the Yb ions to order magnetically.

The cluster like type of magnetic ordering for the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples with $x < 0.5$, emerging from the above model, supports the use of Eq. 4-15 to fit the $\mu$SR data in the magnetic transition region.

In Figure 4-54 the Ni concentration dependence of the transition temperatures $T_m$ is plotted. The magnetic transition temperature could be determined from macroscopic measurements (resistivity) only for YbNi$_2$Si$_2$ (the other samples had a too large residual resistivity). $T_m$ is also not well defined microscopically. The reason may be a distribution (disorder induced) of Kondo temperatures leading to a distribution of magnetic transition temperatures in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The gradual increase of $T_m$ (considered as the center of the assumed distribution of $T_m$) indicates the gradual change, with the increase of $x$, of the balance between the Kondo and the RKKY interaction in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The results confirm those obtain by macroscopic measurements (Chapter 4.1.2-4) and the ZF and LF $\mu$SR data described in Chapter 4.1.5.1. The dotted line in Figure 4-54 is to guide the eye. Its zero value around
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$x = 0.1$ was suggested by a test measurement on a $x = 0.08$ sample which does not show any sign of magnetic ordering down to the lowest attained temperature of 40 mK.

The temperature dependence of the depolarization rate due to the electronic moments in the magnetic phase, $\sigma_m$, is reported in Figure 4-55 in a double logarithmic plot. A clear increase with the increase of the Ni concentration of $\sigma_m$ is observed (see also Figure 4-56). The increase of $\sigma_m$ is exponential with the increase of the Ni concentration $x$.

As stated, the depolarization rate $\sigma_m$ in the magnetic phase reflects the second moment of the field distribution arising from the Yb 4f moments. The fast increase of $\sigma_m$ with $x$ can be related to the increase of the ordered moment due to the change in the balance of the Kondo and the RKKY interactions. At low Ni concentrations a cluster type of magnetic ordering occurs, with reduced magnetic moments due to the Kondo effect. The size of the clusters should not play a significant role in the $\sigma_m(x)$ dependence since no slope-change was observed around $x = 0.5$, the Ni concentration at which, the magnetism occurs in the entire volume of the sample (see Figure 4-53). To the contrary, two distinct regimes are observed in the $T_m(\sigma_m)$ dependence presented in Figure 4-57. A fast increase of the $T_m$ in the range of small Yb moments ($\sigma \approx \mu_{Yb}$), related to the cluster-type of magnetic ordering presented above is followed by a slope change above $x = 0.375$. For both regions, a linear $T_m(\mu_{Yb})$ dependence appears to be a good approximation.

**Discussion of the low $T$ results**

In the literature, two main models deal with the disorder effects on the low-$T$ physical properties of heavy fermion (HF) systems: the Kondo disorder model [M96] and the Griffiths phase model [CA98]. They explain some of the observed ([ICA98] and references therein) non-Fermi-liquid (NFL) behavior of the low-$T$ thermodynamic and transport properties. Even though the NFL behavior was not seen in the temperature dependence of the electrical resistivity in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ (perhaps due to the high residual
resistivity of the $x > 0$ samples), the discussion of the mentioned models in relation with our data is worthwhile.

In the first model, a broad distribution of Kondo temperatures $T_K$ is expected to originate from the disorder due to the different environment of the magnetic ions (for example in the case of chemical substitution). The distribution of the Kondo temperatures $P(T_K)$ is generated by a random distribution of the Kondo coupling constant $N(E_F)J$ and takes a nonzero value at $T = 0$ (see Figure 4-58). The RKKY interaction is not included in this model. The argument is that if the $P(T_K)$ is broad enough, the fraction of the spins which remain unquenched at low temperatures is small (dashed area in Figure 58), forming a dilute system of spins in which the RKKY interaction is less effective.

The scaling proposed by MacLaughlin et al. [MA96] to check for the applicability of the Kondo disorder model (cooperative disorder-driven) to Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ could not be performed due to the small number of points in our $K(T)$ data (not shown) and of the low-$T$ impurity contribution to the magnetic susceptibility (see Chapter 4.1.4). In the equation above $a^*$ is an effective $\mu^*/\ell$ - ion dipolar coupling and $K$ is the Knight shift. However, as pointed out from the discussion of our experimental data:

- The RKKY interaction plays an important role in the physical properties of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and therefore should be taken into account in the theory.
- We have considered the distribution of the Kondo temperature only as an argument to explain the width of the magnetic transition in the Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ samples. In UCu$_{5-x}$Pd$_x$, where the Kondo disorder model (vs. the Griffiths phase model) was used to discuss the $\mu$SR and NMR data [MA00], the broad $P(T_K)$ distribution was indicated also by the small value ($\beta \sim 0.4 - 0.7$) of the exponent of the power-law fit of the ZF and LZ $\mu$SR data. In Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$, the
ZF-LF μSR spectra were correctly fitted using an exponential depolarization function (or power law with $\beta$ close to 1, see Chapter 4.1.5.1.c).

- It should be mentioned that both models lead to power-law time dependencies of the $\mu^+$ polarization with rather small values of the parameter $\beta$, which have not been observed in our data.

The Griffiths phase model incorporates both the disorder and the competition between the RKKY and the Kondo effect. The presence of disorder is considered to lead to the coexistence of a metallic paramagnetic phase (with magnetic moments reduced by the Kondo interaction) and a granular magnetic ordered phase (dominated by the RKKY interaction) equivalent to the Griffiths phase of dilute magnetic systems [GR69]. For the $\mu^+$ relaxation rate it predicts [MA00]:

$$\lambda(B) \propto B^{-\frac{\beta}{1+\beta}},$$  \hspace{1cm} (4-17)

i.e. a power-law dependence of the LF relaxation rate on the applied field. $\beta$ is a model parameter and should be smaller than one to insure the divergence of the magnetic susceptibility at zero temperature [CA98]. As it is seen in the test plot presented in Figure 4-59 a power-law dependence for the $\mu^+$ relaxation rate vs. the longitudinal field cannot be totally excluded. However, several features of the Griffiths phase model are not found in our data:

- The model does not predict the slope change of $\lambda_{LF,SK}(B)$ at high fields (see Figure 4-59) and its field independence after the slope change (we have associated the field independence of $\lambda_{LF,SK}$ to fast uncorrelated fluctuations, see Chapter 4.1.5.1.c).

- The Griffiths phase model, in its original form, was discussed in relation with a quantum critical point, i.e., for a disordered system, close to a critical concentration at which the magnetic order appears. It predicts, for the paramagnetic phase, the existence of a distribution of (finite) magnetic clusters but does not discuss the possible short/long range ordering of those clusters for which some conditions (e.g. cluster size, fluctuation rate or a neighboring condition, as for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$) are fulfilled.

- The cluster formation in the paramagnetic regime implies a power law $\mu^+$ depolarization function reflecting the differences in size, moment and fluctuation rate between these clusters. However, as specified above, the ZF μSR data for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ were well fitted with a power law with a value of $\beta$ close to one, and for the LF data an exponential depolarization function was successfully used.

We should not close this section without mentioning the following: by increasing the Ni concentration in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ the lattice pressure, as we have seen in Chapter 4.1.1, increases. The condition for the magnetic ordering in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ seems to be related to a specific nearest neighbor configuration of the Yb ions. However, the lattice pressure in the part of the sample for which the specific configuration is not present also increases with the increase of the Ni concentration. We speculate that, in principle, for a certain value of the Ni content $x$ two magnetic transitions can be found in the system, one for which the neighborhood configuration matters, and another one, in the remaining fraction of the sample, for which the critical pressure condition is fulfilled. In Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ the “critical lattice pressure” (obtained from the correspondence between the external and chemical substitution) should be around $x = 0.5$. The fact that at this value of the Ni concentration the magnetic ordering occurs in almost the entire sample volume (due to the neighborhood condition) might explain why a second magnetic transition was not observed in our samples.
4.2 YbCu$_{5-x}$Al$_x$

The YbCu$_{5-x}$Al$_x$ system was intensively studied during the last years, due to its peculiar magnetic properties when the Al concentration is $x = 1.5$ (NFL behavior, [BA99] and references therein). The Al/Cu substitution in YbCu$_{5-x}$Al$_x$, like the Ni/Cu substitution in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ - see Chapter 4.1, allows one to study the evolution of the Yb ion ground state from a nonmagnetic $4f^{14}$ state in YbCu$_4$Al toward a magnetic $4f^{13}$ state in YbCu$_3$Al$_2$ ($T_m = 2$ K [BA99]). The magnetic ground state of YbCu$_3$Al$_2$, determined by neutron diffraction, is antiferromagnetic. It is described by a propagation vector $k = (1/2,1/2,0)$ [BA97]. The ordered magnetic moment at 10 mK is parallel to the $c$ axis and has a value of $\mu_{Yb} = 2.1 \mu_B$.

The YbCu$_{3.5}$Al$_{1.5}$ compound is close to a quantum critical point (QCP) and its low-$T$ physical properties show non-Fermi-liquid (NFL) behavior. A NFL behavior, associated to the closeness to the QCP is induced in YbCu$_4$Al (FL at low $T$) by external pressure ($p = 15$ kbar) as evidenced by the linear temperature dependence of the electrical resistivity measured below 30 K [BA97]. The Al/Cu substitution drives the system towards a magnetic ground state, see the discussion in Chapter 4.2.1, even if the unit cell volume increases.

ZF and LF $\mu$SR experiments have been performed [AN01] on the $x = 1, 1.5$ and 2 samples. The goal was to follow the evolution of the Yb-spin dynamics as a function of the Al concentration in YbCu$_{5-x}$Al$_x$ and to obtain some information on the Yb-spin dynamics close to the QCP.

4.2.1 Macroscopic properties

All the investigated YbCu$_{5-x}$Al$_x$ samples ($x = 1, 1.5$ and 2) crystallize in the hexagonal CaCu$_5$ type of structure, space group P6/mmm [IA71] (see Figure 4-60).

![Figure 4-60: Position of the atoms in the hexagonal unit cell of YbCu$_{5-x}$Al$_x$.](image)

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7 The samples were produced and characterized by macroscopic measurements at the Technical University of Vienna, by the groups of Prof. E. Bauer and Prof. G. Wiesinger.
The position of the atoms in the hexagonal unite cell are:

Yb in 1a: (0, 0, 0),
Cu in 2c: (2/3, 1/3, 0) and (1/3, 2/3, 0),
Cu and Al in 3g: (1/2, 0, 1/2), (0, 1/2, 0) and (1/2, 1/2, 1/2).

The Al/Cu substitution takes place in the \( z = 1/2 \) plane (see Figure 4-60), i.e. the Al atoms occupy preferentially the 3g sites [BA93]. This situation is identical with that observed in CeCu_{5-x}Al_x [KJ91]. In both series, the 3g sites are randomly occupied by the Cu and Al ions.

X-ray diffraction experiments on YbCu_{5-x}Al_x revealed a continuous increase of the lattice parameter \( a \) and a slight decrease of \( c \), Figure 4-61, with the increase of the Al concentration \( x \). Notice the increase of the unit cell volume with the increase of the \( x \), Figure 4-61, which suggests a decrease of the (lattice) pressure on the Yb ions. This result, combined with the fact that the Al/Cu substitution drives the YbCu_{5-x}Al_x system towards a magnetic ground state is at variance, at a first sight, with the results obtained in Yb(Cu_{1-x}Ni_x)_2Si_2 where it was the increase of the (lattice) pressure which stabilized the magnetic ground state. Two possible explanations are given on the next page.

The temperature dependence of the normalized electrical resistivity \( \rho/\rho_{273K} \) is displayed in Figure 4-62 for different Al concentrations (data and notations from Bauer et al. [BA99]). The position of the \( \rho(T) \) maximum \( T_{\rho,max} \) (insert in Figure 4-62) decreases with the increase of the Al concentration. The reduction, with the increase of the Al concentration \( x \), of \( T_{\rho,max} \), is often related either with the reduction of the CEF splitting upon the Al/Cu substitution or with the reduction of the Kondo temperature (see the discussion in Chapter 4.1.2). In YbCu_{5-x}Al_x, a reduction of the Kondo temperature with the increase of the Al concentration is expected, because the Al/Cu substitution drives YbCu_{5-x}Al_x towards a mag-

![Figure 4-61: Concentration-dependent variation of the lattice parameters a, c, and the volume V of YbCu_{5-x}Al_x (from Bauer et al. [BA99]).](image1)

![Figure 4-62: Temperature-dependent electrical resistivity \( \rho \) of YbCu_{5-x}Al_x for various concentrations x. The insert shows the concentration-dependent variation of T_{\rho,max} [BA99].](image2)
namic ordered ground state. A similar behavior follows also from the external pressure response of $T_{p, \text{low}}^{\text{max}}$ [BA99], i.e. with increasing external pressure $T_{p, \text{low}}^{\text{max}}$ decreases.

The fast increase of the residual resistivity with the Al/Cu substitution, (Figure 4-62) is related to the growing crystallographic disorder induced by the chemical substitution.

At first analysis the chemical substitution and the external pressure lead to opposite results:

- The Al/Cu substitution in YbCu$_{4}$Al (which corresponds to a decrease of the lattice pressure if the lattice pressure is associated with a pure volume effect) drives this system towards a magnetic ground state ($T_K(x)$ decreases with the increase of $x$, [BA99]).
- The applied external pressure on YbCu$_{4}$Al drives it towards a magnetic ground state ($T_K(p)$ decreases with the increase of $p$, [BA99]).

Since the external pressure can be considered as a pure volume effect (see the discussion in Chapter 4), these results have to be clarified. The explanation refers either to the special type of volume change in YbCu$_{5-x}$Al$_x$ or to the difference between the external pressure and the chemical substitution:

- The volume of the unit cell of YbCu$_{5-x}$Al$_x$ increases with the increase of the Al concentration, but the lattice parameter $c$ decreases slightly (see Figure 4-61). Since the lattice parameter $c$ determines primarily the Yb-Yb distance in the hexagonal unit cell, a decrease of $c$ is equivalent to an increase of the pressure in the $c$ direction. However, the reduction of $c$ with the increase of the Al concentration is very small, Figure 4-61.
- As shown in Chapter 4, the effect of the chemical substitution is not exclusively a volume change (as the external pressure is) but it also introduces lattice disorder and electron doping. Both these secondary effects modify the density of states at the Fermi level, $N(E_F)$, thus changing the balance between the Kondo and the RKKY interaction via the $J_{K}N(E_F)$ product (see Chapter 2). If we consider that a volume change should have the same effect on the $J_{K}$ parameter irrespective of whether it arises from chemical substitution or external pressure, then the observed $T_K$ decrease with increasing Al concentration must originate from a decrease of the density of states at the Fermi level.

The optical conductivity of the YbCu$_{5-x}$Al$_x$ indicates that the number of free carriers has a tendency to decrease upon an increasing Al content ([BA99] and references therein). As a
consequence the electronic density of states at the Fermi energy $N(E_F)$ is expected to decrease, thus providing an explanation for the observed $T_K(x)$ dependence.

Non-Fermi-liquid (NFL) behavior was observed in the temperature dependencies of the specific heat, electrical resistivity and magnetic susceptibility [BA99] of the YbCu$_{5-x}$Al$_x$ samples for $x$ around 1.5 (see Figure 4-63). The observed NFL behavior, i.e. a logarithmic term in the temperature dependence of the specific heat below $\simeq 2$ K (see also [SE00]), non-quadratic terms in the temperature dependence of the electrical resistivity at low temperatures (below $\simeq 2$ K) and a $T^{-2/3}$ dependence of the magnetic susceptibility, was ascribed to the closeness of YbCu$_{5-x}$Al$_x$ to a quantum-critical phase transition (i.e. at $T = 0$) for $x = 1.5$. In these systems enhanced spin fluctuations are supposed to cause the breakdown of the Fermi-liquid ground state [MI93].

Since the $\mu$SR technique is sensitive to spin fluctuations, via the relaxation rate of the $\mu^+$ polarization, we have performed $\mu$SR measurements on three YbCu$_{5-x}$Al$_x$ samples with $x = 1$ (paramagnetic-FL), $x = 1.5$ (QCP) and $x = 2$ (magnetically ordered).

### 4.2.2 $\mu$SR results

The $\mu$SR measurements were performed between 40 mK and 300 K in zero- (ZF) and longitudinal-field (LF) configurations.

The ZF $\mu$SR spectra were fitted using the following function for the muon spin polarization (identical to that used for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$):

$$AP_z(t) = A_{\text{para}} \left[ \frac{1}{3} + \frac{2}{3} \left( 1 - \Delta^2 t^2 \right) e^{-\frac{\Delta^2 t^2}{2}} \right] e^{-(\lambda t)^\beta}. \quad (4-18)$$

Eq. 4-18 is a product of a Kubo-Toyabe with a power law (see Chapter 3.3.1.4.2) describing a two-channel depolarization of the muon spin. The first channel ($\Delta$) arises from the field distribution at the muon site created by the surrounding nuclear magnetic moments (Yb$^{171,173}$, Cu$^{63,65}$ and Al$^{27}$) and the second, of dynamic origin (the exponential term $\lambda$), originates from the fluctuations of the Yb electronic moments.

### Muon site

$\mu$SR spectra of YbCu$_4$Al taken at 0.9 K and 30 K are displayed in Figure 4-64. The lines in Figure 4-64 are fits of Eq. 4-18 to the $\mu$SR signal. The exponent $\beta$ is close to one for the entire temperature range. The temperature dependence of the muon depolarization rate, $\Delta$, is displayed in Figure 4-65. The fitted value of $\Delta$, about 0.21 MHz (corresponding to a field width of $\Delta B = 2.5$ G) for the YbCu$_4$Al sample, increases slightly with the Al concentration $x$, in agreement with Monte-Carlo calculation results (see below).
Figure 4-64: $\mu$SR spectra for $\text{YbCu}_4\text{Al}$ at 0.9 K and 30 K. The solid lines are fits of Eq. 4-18 to the data. The parameter $\Delta$ was found to be the same at both temperatures (see Figure 4-65).

Figure 4-65: Temperature dependence of $\Delta_{\text{nuc}}$ for $\text{YbCu}_4\text{Al}$. The insert shows the experimental (solid squares) and calculated (solid circles, see text) dependence of $\Delta$ on the Al concentration in $\text{YbCu}_{5-x}\text{Al}_x$. The lines are guides to the eye.
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The value of $\Delta$ can be obtained from the second moment of the field distribution (see Chapter 2) if the muon site is known. No clear muon site assignment is known for compounds that crystallize with the CaCu$_5$ type of structure. In CeCu$_5$Al$_x$, for example, the $1b$ site (0,0,1/2) was ascribed to the muon by Wiesinger et al. ([WI94], [WI95]). The same muon site was also found in UPd$_2$Al$_3$ ([AM92], [FE95]). On the other hand, for UNi$_2$Al$_3$ the wave function of the implanted muon is not localized but extends over a hexagonal ring of interstitial lattice sites $m$ or $k$ surrounding the highly symmetrical site $b$ [AM00]. In GdNi$_5$ (see [MU00] and references therein) a different and more complicated situation occurs: above 80 K the muon localizes at the $3f$ site (1/2, 0, 0) while below 80 K also the $6m$ site (0.13, 0.26, 1/2) becomes populated (hopping is allowed between the $3f$ and the $6m$ sites). The $6m$ site is one of the five location of deuterium in LaNi$_5$D$_x$ [PE93].

Among the value of $\Delta$ calculated for different possible muon sites, values closed to $\Delta = 0.21 \mu s^{-1}$, see the insert in Figure 4-65, were obtained for the (0,0,1/2) crystallographic site (site $1b$), like for CeCu$_5$Al$_x$ or UPd$_2$Al$_3$. The Monte-Carlo calculations were performed assuming a statistical distribution of the substituted Al atoms among the 3g sites [BA93]. The slightly smaller calculated $\Delta$ values compared to the experimental ones might originate from slight displacements of the muon from the assumed $1b$ site (i.e. towards Cu or Al atoms). For the $3f$ and the $6m$ sites ([AM00], [MU00]) the computed depolarization rates $\Delta$ are about two times larger than the measured one, which excludes these sites for the muon in YbCu$_5$Al$_x$.

**Zf/Lf $\mu$SR experimental results**

$\mu$SR spectra taken at different temperatures for YbCu$_{3.5}$Al$_{1.5}$ and YbCu$_3$Al$_2$ are presented in Figures 4-66 and 4-67, respectively (the lines are fits of Eq. 4-18 to the experimental data, 

![Figure 4-66: $\mu$SR spectra for YbCu$_{3.5}$Al$_{1.5}$ measured at different temperatures. The lines are fits of Eq. 4-18 to the experimental data.](image1)

![Figure 4-67: Zf-$\mu$SR spectra for YbCu$_3$Al$_2$ at different temperatures. The fast contribution at early times for T < 2.1 K is due to the occurrence of the magnetic ordering of the Yb moments (for the fit equation, see text).](image2)
except for the spectra of YbCu$_3$Al$_2$ at 1.4 K). Notice that for both samples, the almost Gaussian depolarization at 30 K reflects the nuclear contribution to the depolarization rate. The effect of the Yb spin-fluctuations on the $\mu^+$ relaxation is observed at low temperatures (see also Figure 4-69) where the $\mu$SR spectra have an exponential-like shape. The depolarization functions remain exponential down to the lowest attained temperature 0.044 K for YbCu$_{3.5}$Al$_{1.5}$, while for YbCu$_3$Al$_2$ another component, of Gaussian form, sets in below around 2 K. The Gaussian component, with a large relaxation (see Figure 4-67, the measurement was made at 1.44 K), originates from the field distribution created by the electronic moments and indicates a magnetic phase transition. It was fitted by adding the term

$$A_{mag} = \left( \frac{1}{3} e^{-\lambda_2 m^2} + \frac{2}{3} e^{-\frac{\lambda_4 m^2}{2}} \right)$$

(4-18a)

to Eq. 4-18.

In Figure 4-68, the temperature dependence of the power-law exponent $\beta$ for YbCu$_{3.5}$Al$_{1.5}$ and YbCu$_3$Al$_2$ is plotted (see Eq. 4-18). $\beta$ is constant and equals one for YbCu$_{3.5}$Al$_{1.5}$ for $T > 10$ K (30 K for YbCu$_3$Al$_2$) then decreases to a value of about 0.85 (0.8) at lower $T$. For YbCu$_{3.5}$Al$_{1.5}$ $\beta$ is roughly constant below 3 K. Notice the similar temperature dependence of $\beta$ for both compounds.

The temperature dependencies of the ZF and ZF/LF (2000 G) muon relaxation rate are displayed respectively in Figures 4-69 (in a log-log plot) and 4-70 (semi-logarithmic plot, to show the details at low temperatures).

Similar features, for all investigated compounds, were observed in the $\lambda_{ZF}(T)$ dependencies, i.e., an increase with decreasing temperature (region I), then a change of the slope (region II), see Figure 4-69. The slopes corresponding to the regions I and II are the same in all compounds, indicating similar relaxation mechanisms. However, while for YbCu$_{3.5}$Al$_{1.5}$ and YbCu$_3$Al$_2$ the slope change at around 30 K could be attributed to CEF effects (the first excited CEF level

\[ \text{Figure 4-68: Temperature dependence of the parameter } \beta \text{ from Eq. 4-18, for YbCu}_{3.5}\text{Al}_{1.5} \text{ and YbCu}_3\text{Al}_2. \text{ The lines are guide for the eye. The } \mu\text{SR spectra for YbCu}_3\text{Al}_2 \text{ were well fitted by an exponential damped Kubo-Gauss depolarization function (i.e. } \beta = 1).} \]

\[ \text{Figure 4-69: Temperature dependence of the zero field relaxation rate } \lambda \text{ (see Eq. 4-18) for different Al concentration } x \text{ in YbCu}_{5-x}\text{Al}_x. \text{ The dashed line (region I) indicates a linear } \lambda_{ZF}(T) \text{ dependence while the dotted line (region II) a } \lambda_{ZF}(T) \propto T^{-1/2} \text{ dependence (see text). In region III different } \lambda_{ZF}(T) \text{ behaviors were observed (see text). The solid line is a guide for the eye.} \]
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is at about 100 K for YbCu₃Al₂ [BA97]), this cannot be the case for YbCu₄Al for which the CEF splitting is higher while the slope-change occurs at a lower temperature (∼2 K). The temperature at which the \( \lambda_{ZF}(T) \) changes slope in YbCu₃.₅Al₁.₅ and YbCu₃Al₂ coincides with the temperature at which the value of the power law exponent \( \beta \) from Eq. 4-18 starts to decrease, see Figure 4-68. Region II is characterized by a \( \lambda_{ZF}(T) \propto T^{-1/3} \) dependence (dotted line in Figure 4-69). Notice that the similarity between the temperature dependencies of the muon spin relaxation rate in the YbCu₅₅Al₁.₅ samples is lost in region III. Interestingly, the deviation from the \( \lambda_{ZF}(T) \propto T^{-1/3} \) law observed in Region III has totally different origins for all three investigated compounds. It results from:

- The saturation of the muon spin fluctuation rate below \( T_{sat} \) in YbCu₄Al, see Figure 4-69 (μSR measurements at lower temperatures are needed to confirm this result).
- The occurrence, below \( T_{in} \), of a quasistatic spin-glass-like ground state in YbCu₃.₅Al₁.₅. We describe this ground state as formed by slow fluctuating Yb moments (or small magnetic clusters) embedded in a sea of fast fluctuating Yb magnetic moments (see the discussion on page 87). \( T_{in} \) is roughly equal with the temperature (1.2 K) below which a logarithmic dependence of the specific heat coefficient \( c(T)/T \) was found in YbCu₅₅Al₁.₅, indicating NFL behavior at low temperature [BA97].
- The slowing of the fluctuation of the Yb magnetic moments in YbCu₃Al₂ below \( T_{slow} \) (see also the \( \lambda_{LF}(T, 2000 \text{ G}) \) results presented in Figure 4-70), close to a magnetic ordering transition temperature. In YbCu₃Al₂ magnetic ordering occurs below \( T_N = 2 \text{ K} \).

The \( \lambda_{LF}(T, 2000 \text{ G}) \) rates were obtained from a fit of a power low depolarization function to the μSR spectra with an exponent equal to that of the ZF measurements (Figure 4-68). For the YbCu₃.₅Al₁.₅ and YbCu₃Al₂ samples \( \lambda_{LF}(T, 2000 \text{ G}) \) is almost temperature independent (below \( \approx 50 \text{ K} \) for YbCu₃.₅Al₁.₅ and below \( \approx 20 \text{ K} \) for YbCu₃Al₂) and is ascribed to the uncorrelated fluctuations of the Yb ions. The ZF relaxation rate is strongly temperature dependent. One should also mention that the \( 1/\sqrt{T} \)-like \( \lambda_{ZF}(T, 2000 \text{ G}) \) dependence, as found for the Yb(Cuₓ₋ₓNiₓ)₂S₆ samples, may also be seen in the LF data in YbCu₅₅Alₓ, but could not clearly be confirmed due to the small number of data points at high temperatures.

![Figure 4-70: The temperature dependence of the ZF (full symbols) and LF = 2000 G (open symbols) relaxation rates for YbCu₃.₅Al₁.₅ (•, □) and YbCu₃Al₂ (▲, △).](image-url)
The dynamics of the Yb magnetic moments

To get more insight in the dynamics of the Yb magnetic moments, field scans in LF configuration were performed at selected temperatures: for YbCu$_3$Al$_2$ at 5 K (region II) and for YbCu$_{3.5}$Al$_{1.5}$ at 44 mK (region III).

For YbCu$_3$Al$_2$ a power law depolarization function (Eq. 4-7) with $\beta = 0.8$ (i.e. the ZF value) provided a correct fit for the LF $\mu$SR spectra. This was not possible for YbCu$_{3.5}$Al$_{1.5}$ (see below). Remember that for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ an exponential depolarization function fitted the LF scans at 5 K (i.e. $\beta = 1$, as for the ZF spectra). In Figure 4-71 the $\lambda_{LF}(B, 5 \text{ K})$ dependence for YbCu$_3$Al$_2$ is displayed. It is similar to that of YbNi$_2$Si$_2$ and could be fitted using the same equation, Eq. 4-12:

$$\lambda(B) = M_2^{ZF} \tau_0 + \frac{2 \gamma_\mu^2 B_c^2 \tau_c}{3 \left(1 + \omega^2 \tau_c^{-2}\right)}.$$

The two terms on the right side of the equation denote the contribution from respectively the uncorrelated and the correlated parts of the fluctuations of the Yb magnetic moments to the muon relaxation rate. A fit of Eq. 4-12 to the $\lambda_{LF}(B, 5 \text{ K})$ dependence is displayed in Figure 4-71. The values of the fit parameters, $B_c \approx 10 \text{ G}$ and $\nu_c = 1/\tau_c = 4 \text{ MHz}$, are similar with those obtained for YbNi$_2$Si$_2$ (see Chapter 4.1.5.1.b). For the $M_2^{ZF} \tau_0$ product a value of 0.087 MHz was found. However, the characteristic time $\tau_0$ could not be determined due to the lack of information concerning the value of the fluctuating Yb magnetic moment. The uncorrelated fluctuations are fast, as proved by the field independence of the corresponding muon spin relaxation rate (see $\lambda(B, 5 \text{ K})$ for $B > 500 \text{ G}$).

We conclude that in YbCu$_3$Al$_2$, or by generalization in YbCu$_{3-x}$Al$_x$ (region II in Figure 4-69), correlations develop between fast fluctuating Yb magnetic moments, as in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The effect of these correlations on the muon spin relaxation rate can be suppressed by applying a longitudinal field. The reduction of the ZF relaxation rate by the applied LF is identical for YbCu$_{3.5}$Al$_{1.5}$ and YbCu$_3$Al$_2$, as shown in Figure 4-72, where the difference $\lambda_{ZF}(T)-\lambda_{LF}(2 \text{ kG}, T)$ is plotted as a function of temperature, for both compounds. If one assumes that $\lambda_{LF}(2 \text{ kG}, T)$ describes the uncorrelated (fast) fluctuations, then the identical effect of the LF on $\lambda_{ZF}(T)$ indicates that the mechanism driving the correlated fluctuations of the Yb moments is independent of the amplitude and the fluctuation rate of the un-
correlated Yb magnetic moments. It would be interesting to search the existence of a similar behavior for intermediate values of the applied LF.

A completely different picture emerges from the field dependence of the muon spin relaxation rate measured at 0.044 K for YbCu$_{3.5}$Al$_{1.5}$ (region III in Figure 4-69). It will be shown that the low temperature physical properties of YbCu$_{3.5}$Al$_{1.5}$ are determined by a spin-glass like quasistatic distribution of either fluctuating Yb magnetic moments or small ferromagnetic-correlated Yb clusters, embedded in a sea of uncorrelated Yb magnetic moments.

The µSR spectra recorded for YbCu$_{3.5}$Al$_{1.5}$ at 44 mK in different longitudinal fields are displayed in Figure 4-73. The spectra were best fitted with a phenomenological depolarization function,

\[ P(t) = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t}. \]  

(4-19)

We discuss two possible interpretations of these fits:

- We can interpret the LF data using a model, discussed in [PI00] for a similar behavior of $\lambda(B,T)$ in Nd$_{1.4}$Ce$_{0.2}$Sr$_{0.4}$CuO$_{4.8}$, which takes into account the correlated fluctuations of the magnetic moments. Within this model, the excitation of an Yb ion from a correlated ($\lambda_1$) into an uncorrelated ($\lambda_2$) state (two level system) should be understood as a breaking of the inter-site correlation of the ion with the surrounding moments, while the correlation between the surrounding moments is not affected. The model considers that the distribution of the relaxation rates is centered on two values, $\lambda_1$ and $\lambda_2$. To insure the convergence of the fits, $\lambda_1$ was kept fixed in the fit procedure to the constant value ($\lambda_1 = 0.04$ MHz) found in the LF (2000 G) temperature scan, see Figure 4-70. Fits of the µSR spectra (recorded for YbCu$_{3.5}$Al$_{1.5}$ at 0.044 K) with Eq. 4-19 are displayed in Figure 4-73 (solid lines).
The fitted values of $A_1(B)$ and $\lambda_2(B)$ are displayed, respectively, in Figures 4-74 and 4-75. Within this model, the increase of $A_1$ with the increase of the applied magnetic field reflects the change of the fraction of the Yb spins that are involved in uncorrelated fluctuations. The field independent value of $\lambda_2$, Figure 4-75, indicates (see the discussion in Chapter 4.1.5.1.b) that the correlated moment fluctuations are fast, i.e. the formula

$$\lambda_2 = \frac{2}{3} \gamma_n^2 B^2 \tau_c$$

should be used to calculate the correlated field and the fluctuation rate.

No information was found in the literature about the value of the fluctuating moments. Therefore, we cannot make estimates regarding neither the value of the correlated field nor its fluctuation rate. A crucial cross check for the applicability of the model to our data is given by the $A_1(B)$ dependency, which should follow an $(1-c)\exp(-B/d)$ dependency [PI00], where $c$ and $d$ are parameters describing the energy difference between the two levels. The best fit is presented in Figure 4-74 (dashed line). Notice that while the fitted $\lambda_2$ is (roughly) field independent, as the model predicts, the measured $A_1$ values at large fields are overestimated.

- The second possibility is to consider that the observed field dependence of the $\mu$SR spectra originates from the decoupling from a quasistatic field distribution. This field distribution should have a Lorentzian shape in order to lead to the observed exponential-like $\mu$SR spectra. This type of distribution would imply, as described in Chapter 3.3.1.2, that dilute and large moments originate from the formation of magnetic clusters. Since a pure Kubo-Lorentz depolarization function (KL, Chapter 3.3.1.4.2) alone does not fit the ZF $\mu$SR spectra, a second contribution should be taken into account, which could arise from the slow fluctuations of these magnetic clusters suppressing the $1/3$-term in Eq. 3-12a in ZF.

The LF relaxation function in Lorentzian fields is given by the equation ([UE81], [UE85])

Figure 4-74: Field dependence of the fraction of the sample with uncorrelated Yb-spin fluctuations ($A_1$ from Eq. 4-19, circles). The lines are fits according to the models mentioned in the text.

Figure 4-75: $\lambda_2(B)$ dependence (see Eq. 4-19). Its constant value function of the applied LF indicates that the correlated fluctuations are fast.
Chapter 4  Experimental results: chemical substitution

\[ P(t, H_L) = 1 - (\lambda / \omega_L) j_1(\omega_L t) \exp(-\lambda t) - (\lambda / \omega_L)^2 \left[ j_0(\omega_L t) \exp(-\lambda t) - 1 \right] \]
\[ - \int_0^t \left( \frac{(\lambda / \omega_L)^2}{1 + (\lambda / \omega_L)^2} \right) \frac{\lambda}{\omega_L t} \exp(-\lambda t) \, dt , \]

and the asymptotic behavior \((t \gg 0)\) of \(P(t, B)\) can be calculated:

\[ P(t \gg 0, B) = \left[ 1 + (\lambda / \omega_L)^2 \right] [1 - (\lambda / \omega_L) \arctg(\omega_L / \lambda)] , \tag{4-20} \]

using

\[ \int_0^\infty e^{-px} \frac{\sin qx}{x} \, dx = \arctg \frac{q}{p} . \]

In these equations \(j_0\) and \(j_1\) denote spherical Bessel functions, \(\lambda / \gamma_0\) is the half-width at half maximum of the Lorentzian field distribution. \(\omega_L\) describes the muon spin precession around the applied field, \(B = \omega_L / \gamma_0\). This behavior can now be compared to the behavior of \(A_1(B)\) extract from the phenomenological fit using Eq. 4-19. A fit of Eq. 4-20 to the \(A_1(B)\) dependence, presented in Figure 4-74 (dotted line) gives \(\lambda = 0.34\) MHz. As stated above, the Lorentzian field distribution arises from a dilute distribution of quasi-static magnetic moments (clusters), a picture similar with that describing dilute spin glasses \([GI84]\). Following this analogy, the width of the field distribution can be written as

\[ \lambda = K \rho \epsilon \gamma_0 < m > , \tag{4-21} \]

where \(K\) is a constant (= 4.54 for randomly oriented spins), \(\rho\) is the number of Yb sites per unit volume, \(c\) the fraction of these sites carrying magnetic moment and \(< m >\) is an average magnetic moment of the Yb ions. From the measured value of \(\lambda\) follows \(c < m > = 26 \times 10^{-3}\). If we use for \(c > m\) the value corresponding to the saturated magnetic moment of the Yb ions in YbCu$_3$Al$_{1.6}$ (which orders magnetically below 0.25 K \([B099]\)), \(\mu_{Yb} = 0.1 \mu_B\), the lower limit of \(c\) can be calculated: \(c > 26\%\). This value is too large for a diluted spin system. Two possible explanations are given below:

- The magnetic ordering in YbCu$_3$Al$_{1.6}$ takes place, as for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$, only in a fraction \(f\) of the sample \((f < 1)\). In this case the magnetic moment per Yb ion should be calculated as \(\mu_{Yb} = 0.1/f\), giving a larger value for \(\mu_{Yb}\) and, correspondingly, a smaller value for \(c\). \(\mu\)SR measurements on the YbCu$_3$Al$_{1.6}$ sample are necessary to verify this hypothesis, which, would confirm this peculiar behavior also for the YbCu$_{3-x}$Cu$_x$ series.
- The anomaly below 0.25 K, observed for YbCu$_3$Al$_{1.6}$ in magnetic susceptibility measurements and ascribed to the magnetic ordering, is of ferromagnetic origin \([B099]\). If we assume that ferromagnetic correlations between the Yb magnetic moments are present also in YbCu$_3$Al$_{1.5}$, then \(< m >\) represents the average magnetic moment of the magnetic clusters \((= n \mu_{Yb}\) with \(n\) the average number of the Yb ions in one cluster), which again will push down the value of \(c\). This picture resembles that of a superparamagnet. Again, further investigations are necessary to confirm this hypothesis.

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4.2 YbCu$_{3.5}$Al$_{1.5}$

The second model suits better the LF results for YbCu$_{3.5}$Al$_{1.5}$ as shown by the fit of Eq. 4-20 to the $A_1(B)$ dependence. This is so despite the fact that we have used in the fits the LF behavior of the asymptotic dependence of a Kubo-Lorentz depolarization function instead of a Dynamical Kubo-Lorentz function as suggested by our data (the fluctuations of the moments yielding the Lorentzian field distribution are quasistatic). In this model a spin-glass like distribution of quasistatic Yb moments (or ferromagnetic magnetic clusters embedded in a sea of magnetic moments which fluctuate uncorrelated) is responsible for the muon spin relaxation rate.

- This behavior could be precursor of a spin-glass freezing ground state, similar to that observed by Vollmer et al. [VO00] in the NFL compound UCu$_4$Pd. From specific heat measurements, a peak at $\approx 0.2$ K in the temperature dependence of the specific heat coefficient, which follows a power-law dependence at higher temperatures (NFL behavior) in UCu$_4$Pd, was interpreted as a spin-glass freezing of the U magnetic moments. These results were challenged by the µSR measurements of MacLaughlin et al. [LA00], who did not observed the freezing of the U magnetic moments at 0.2 K. However, both authors invoked the Griffiths phase model to explain their results above 0.2 K.

- One should also mention the similar behavior observed in CeAl$_3$ (a stoichiometric compound) by µSR and NMR measurements ([BA87a], [SC93], [AM95], [GA95]). Below 3K two magnetic phases coexist:
  - a paramagnetic phase with fluctuating Ce magnetic moments (the spin-lattice relaxation, measured using the NMR technique, follows a Korringa-type variation below 0.6 K)
  - a second phase characterized by static correlations between the Ce magnetic moments as evidenced by the oscillations observed in the µSR spectra below 0.7 K.

Different from YbCu$_{3.5}$Al$_{1.5}$, the phase separation in CeAl$_3$ was related with the existence of large internal stress, which would favor the paramagnetic ground state.

Within the Griffiths phase model, proposed by Castro Neto et al. [CA98], the NFL behavior in $f$-electron systems may be attributed to the existence of Griffiths singularities close to the quantum critical point. Magnetic clusters are formed in the paramagnetic phase due to the competition between the RKKY and Kondo interactions in the presence of disorder. Despite the fact that the assumptions of the Griffiths phase model seem to coincide with our findings, the power law dependence of the specific heat coefficient predicted by the model was not observed in YbCu$_{3.5}$Al$_{1.5}$ (a logarithmic dependence is found [BA99]). On the other hand, another model dealing with disorder-induced NFL, the Kondo disorder model of Miranda et al. [MI96], predicts a logarithmic dependence for the specific heat coefficient as well as for the magnetic susceptibility, a dependence which was not observed in our sample. The magnetic susceptibility of YbCu$_{3.5}$Al$_{1.5}$ has a power-law dependence, $\chi(T) \propto T^{2/3}$ [BA99].

Our µSR data are not completely supported by any of the models discussed above. Further development of current theories of disorder-driven NFL is required to understand NFL behavior in YbCu$_{3.5}$Al$_{1.5}$. However, the LF results point to the formation of rare and slowly fluctuating magnetic clusters as described within the Griffiths phase model. The cluster dimension should be small compared to the average distance from the muon to the center of the cluster, i.e., the fraction of the muons that stops in these clusters should fit the high field $P_L(B)dB$ fraction of a Lorentzian $P_L(B)$ field distribution. It is not the case for YbCu$_3$Al$_2$, where magnetic ordering sets in below 2 K. The signature of this ordering in the µSR spectra
is a fast relaxing signal, see Figure 4-67 - the run at 1.4 K, which could be described by Eq. 4-18a. As for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ ($x > 0$), no oscillations were observed in the μSR spectra below $T_N$, although the computed local field at the muon site is different from zero. For YbCu$_3$Al$_2$ the local field at the (0,0,1/2) site (see Page 82) is 9 kG, which together with the lattice defects create the large field distribution seen by the muon.

4.3 Conclusions

In this chapter we have presented the effect of the chemical substitution on the physical properties of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and YbCu$_{5-x}$Al$_x$. For both series the chemical substitution leads to a change of the magnetic ground state, from nonmagnetic in YbCu$_2$Si$_2$ and YbCu$_{4-x}$Al$_x$ to magnetic in YbNi$_2$Si$_2$ and YbCu$_3$Al$_2$.

Macroscopic measurements in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ have shown the increase of the effective Yb magnetic moment upon the Ni/Cu substitution and a decrease of the absolute value of the paramagnetic Curie temperature $|\theta_p|$ with the increase of the Ni concentration $x$ (chemical pressure), equivalent to the reduction of the Kondo temperature.

From the ZF/LF μSR measurements in the paramagnetic phase of Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$:

- A $(\nu_0(x)/\theta_0(x)) \approx (T/T_0(x))$ scaling was found for the fluctuation rate of the Yb moments, from which the dependence of the Kondo temperature $T_0$ on the Ni concentration could be extracted. The decrease of the Kondo temperature with the increase of the Ni concentration observed in the $\theta_0(x)$ dependence agrees well with the $\theta_p(x)$ dependence of the paramagnetic Curie temperature.
- By determining the Korringa constant, we have a direct measure of $J_{hf}N(E_F)$. Its decrease with the increase of the Ni concentration is in agreement with the Doniach phase diagram for Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$.
- The effect of the Yb spin-spin correlations was evidenced in LF scans at selected temperatures. A model to describe the correlated fluctuations of the Yb ions was presented, from which the values of the correlated moment and the fluctuation rate could be determined. As expected, an increase of the average correlated moment with the increase of the Ni concentration was observed by LF scans at 5 K. However, the similar increase of the correlated moment fluctuation rate with the increase of $x$ is not yet fully understood.

The effect of the disorder introduced by the chemical pressure is evidenced by the unusual occurrence of magnetic order in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$. The fraction of the sample which becomes magnetic scales well with the probability of an Yb ion to have at least two Ni ions as nearest neighbors. A similar behavior should not be excluded for the YbCu$_{5-x}$Al$_x$ samples at intermediate concentrations between $x = 1.5$ and 2.

As for the Ni/Cu substitution in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$, the Al/Cu substitution in YbCu$_{5-x}$Al$_x$ has a similar effect on the magnetic properties, i.e. it drives the system towards a magnetic ground state. YbCu$_{3.5}$Al$_{1.5}$ is close to a quantum critical point, as evidenced by transport, magnetic and thermodynamic measurements. Correlations between the Yb magnetic moments develop
at low temperatures in YbCu$_{5-x}$Al$_x$ (region II in Figure 4-69). The strength of the magnetic interaction between the Yb magnetic moments increases with the increase of the Al concentration $x$ leading to a magnetic phase transition at $T_m=2$ K for $x=2$. No slowing of the uncorrelated fluctuations of the Yb magnetic moments, as observed for YbCu$_3$Al$_2$ close to its magnetic transition temperature, was found for YbCu$_{3.5}$Al$_{1.5}$ down to the lowest attained temperature of 0.044 mK. In YbCu$_{3.5}$Al$_{1.5}$ the fast increase of $\chi_T$ with the decrease of the temperature (region III in Figure 4-69) is associated with a quasistatic spin-glass-like distribution of Yb magnetic moments (ferromagnetic clusters).

From the contribution of the nuclear magnetic moments to the muon depolarization rate, the muon site could be identified in the YbCu$_{5-x}$Al$_x$ series and constraints on the possible muon site in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ were obtained.
5 Experimental results: external pressure

The pressure is an important steering parameter in the study of heavy fermion systems. The external pressure (obtained using a pressure cell), as opposed to the chemical pressure (chemical substitution), is a clean way to bring a substance near a phase transition in order to study its physical properties. Pressures of around 35 kbar are obtained [WA99] using non-magnetic clamped cells while several hundreds of kbar are obtained using diamond anvil cells ([JA83] and references therein). For μSR measurements one is only interested in pressure cells made out of nonmagnetic materials.

The maximum pressure one can reach with a pressure cell depends strongly on the type of the experiment and on the particular sample environment. In the first part of this chapter, I will discuss the design, materials, characteristics and limitations of the pressure cell that we have built and used in our μSR experiments. The second part is dedicated to the discussion of the pressure effect on the magnetic properties of CeRh$_2$Si$_2$.

Before starting, we should mention the existence of a gas pressure cell at PSI ([BU86], [KR94]) using a He compressor to generate the pressure. Our goal was to offer an alternative, i.e. a pressure cell that is easier to handle, free from all the security requirements implied by a gas-cell device, and working at low temperatures in a commercial cryostat.

5.1 The pressure cell

General considerations

Since in a pressure μSR experiment the muons are stopped both in the pressure cell walls and the sample, a clamped type of pressure cell (see below) was adopted because it provides the optimal sample/pressure cell signal ratio. Roughly, the sample/pressure-cell signal ratio is equal to the ratio of sample/pressure-cell cross section perpendicular to the muon beam, where the muons come to rest (see Figure 5-1). The signal from the pressure cell represents a background sig-

\[ S = S_1 + S_2 \]
\[ A = A_1 + A_2 \]

\[ A \frac{S_1}{S} = \frac{S_2}{S} \]

\[ S_1 : \text{sample} \]
\[ S_2 : \text{pressure cell} \]

Figure 5-1: Sample/pressure cell signal ratio. $A_1$ and $A_2$ are the amplitudes of sample and cell μSR signals.
nal (remember that the total amplitude of the μSR signal is constant). In Figure 5-1, by $A$ is denoted the total asymmetry ($S$: cross section of the muon beam) and by $A_1$ and $A_2$ the corresponding asymmetries of the sample and the pressure cell ($S_1$ and $S_2$).

The μE1 beam line of PSI was used (high energy muon beam, see Chapter 3 for a description). The $μ^+$ momentum was adjusted using the bending magnets until the optimum signal/pressure-cell ratio was obtained (see below).

A large sample space (i.e. large inner diameter of the pressure cell) is needed for a good sample/cell signal ratio while a large pressure demands that the ratio between the outer and the inner diameters is large (i.e. a small sample space for a given diameter of the pressure cell). The outer diameter $D_1$ of our pressure cell was dictated by the inner diameter of the sample-chamber of our cryostat, JANIS SuperTran - VP, which is 27.5 mm. We have chosen 24 mm for the outer diameter of the pressure cell, leaving around 0.6 mm on each side for the coils used to measure the pressure (see below) and the rest for the He flow. Independent of the type of clamped cell or of the pre-machining treatment, from Figure 5-2 ([DA70], [ER93]) we can see that the maximum achievable pressure tends to saturate for a diameter ratio (DR) higher than 3. For safety reasons, even if the gain is not remarkable, high values of DR are preferred. Since the value of the outer diameter of the pressure cell is determined by the dimension of the cryostat, a DR = 3 was used for our tests.

Computer simulations, see Figure 5-3, indicated that for a DR of 3, more than half of the total asymmetry arises from the sample (See Figure 5-4). We have assumed that, for a given muon momentum, all the muons stop in a plane that is at a distance $D$ from the surface of the cell (Figure 5-3). The sample/pressure-cell signal ratio is
given, roughly, by the ratio of the lengths of the dashed/full lines in Figure 5-3, situated at a distance D from the surface of the pressure cell. For the computer simulation a muon beam with a Gaussian profile was considered. The full width of the Gaussian distribution (the beam spot diameter), which was measured (not shown here) using a scintillator that scanned the plane perpendicular to the beam, is 1 cm. In Figure 5-3, D is the penetration depth, related to the muon momentum (see Figure 5-4). The experimental points were obtained using a pressure cell made of copper-beryllium (see below for the choice of the materials). A single crystal of Ni was used as sample (see Figure 5-1). The shape of the single crystal was cylindrical with the dimensions: diameter 8 mm and length 20 mm. We have chosen Ni because of its clear $\mu$SR signal (Figure 5-11 and 5-12) which allows a correct determination of the signal amplitude of the sample alone.

**Design**

A typical clamped cell is presented in Figure 5-5. Our cell was made after a design used by the group of Prof. Sierra at the University of Geneva. The pressure is held by use of the upper screw after the pressure was applied. The teflon cup and the extrusion ring prevent the leakage of the cell (see below). The teflon cup gets deformed and protects from leakage in the low-pressures regime while the extrusion ring (Cu-Be) stops the leaks that might occur at high pressures. Notice also the system of coils, used to measure the pressure (see below).

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8 obtained from Dr. J. Major, University of Stuttgart
A second limitation (after the outer diameter was fixed at 24 mm) for the pressure cell design is the distance, 27 mm, between the bottom of the cryostat and the center of the beam. With a sample of 20 mm length and 3 mm distance from the bottom of the cryostat to the pressure cell, the bottom bolt should be at most 14 mm long, which is too short to sustain a maximum envisaged pressure of 17 kbar. Several tests showed that the threads on the bottom bolt could not support more than 12 kbar. Moreover, when the pressure is applied, since the entire sample space is filled with the sample, the lateral deformation of the teflon cup might lead to unwanted inhomogeneities in the applied pressure. These effects, together with the fact that the teflon gives a quite large signal (see below), forced us to search for a new design in which we still use a teflon cup to solve the leak problems but we keep it away from the sample space. It is also important to limit to one, if possible, the number of background μSR signals (i.e. background materials). The new design is presented in Figure 5-6. The bottom bolt was discarded and a new compartment, where the pressure is applied, was introduced. A problem with this design might be the extraction of the sample after releasing the pressure. Since no direct contact exists between the sample and the teflon cup, the sample should not, in principle, get stuck. The pressure cell was tested at 17 kbar at room temperature. At low temperature, however, only 10 kbar remained due to the large width of the teflon cup walls (1 mm) used during the first tests. Some tests with thinner teflon cup walls are still under way. The gasket has a double role: it prevents leakage by squeezing the teflon cup when the pressure is applied and allows the extraction of the teflon cup (its hole has threads) after releasing the pressure.

Figure 5-6: The design of the new pressure cell for μSR measurements. Only the most important elements are displayed.

Materials

The choice of materials is essential for a μSR experiments since, as already mentioned, a large fraction of the μSR signal arises from the pressure-cell walls. A material with a strong temperature dependent relaxation rate will complicate the separation of the sample/cell signals in the μSR spectra. For the body of the pressure-cell we used copper-beryllium (CuBe 25 1/2HT). This is one of the most employed materials for building non-magnetic piston-cylinder-type of pressure cells subject to large tensile stresses. Another remarkable property of this alloy is the increase of its tensile strength with the decrease of the temperature, which makes it suitable for cryogenic applications (see also [WA99] and [ER96]).
The μSR signal of Cu-Be 25, Figure 5-7, can be fitted with the following function (see Appendix D for details about the background (Bck)):

\[
P(t) = \frac{1}{3} + \frac{2}{3} \left( 1 - \Delta^2 t^2 \right) e^{-\frac{\Delta^2 t^2}{2}} + Bck,
\]

(5-1)

the already known Kubo-Toyabe depolarization function (see Chapter 3). The \(\mu^+\) depolarization \(\Delta\) is due to the \(\text{Cu}^{63}\), \(\text{Cu}^{65}\) and \(\text{Be}^{9}\) nuclear moments. The temperature dependence of the \(\mu^+\) depolarization rate \(\Delta\) arising from the Cu-Be cell is displayed in Figure 5-10. Above 40 K, the decrease of \(\Delta\) with increasing the temperature is due to \(\mu^+\) diffusion and a fit of the μSR spectra with Eq. 5-1 is no more correct. Since we intend to use the pressure cell only in the low temperature regime (below 30 K) we are not affected by that problem. Because \(\Delta\) is temperature independent up to around 40 K (see Figure 5-8, \(\Delta = 0.345(2)\ MHz\)), it can be fixed in the fit procedure.

More recently we have tested another material, the so called MP35N Co-Ni alloy, already used for a double layer pressure cell [WA99]. The material has the composition 35% Co, 35% Ni and 20% Cr and 10% Mo (by weight). Despite of its composition, the material is nonmagnetic. The μSR spectra obtained in a ZF μSR temperature scan on a MP35N sample (obtained from Dr. Walker) were satisfactorily fitted by Eq. 5-1. This behavior indicates, as seen above, that nuclear moments, \(\text{Co}^{59}\), \(\text{Ni}^{61}\), \(\text{Cr}^{53}\) and \(\text{Mn}^{55}\), contribute to \(\mu^+\) depolarization. The \(\Delta(T)\) dependence for the MP35N sample is displayed in Figure 5-9.
Interestingly, the values of $\Delta$ in Cu-Be 25 ($\Delta = 0.345(2)$ $\mu$s$^{-1}$) and MP35N ($\Delta = 0.341(2)$ $\mu$s$^{-1}$) are very close. This is an important point if a double layer cell is used because the signal from the two layers of the body of the pressure cell could be fitted using a single depolarization function. Further ZF-LF $\mu$SR measurements should be performed to record the response of MP35N to the applied field. Without entering into details, I should also mention that our tests indicate a missing asymmetry in the $\mu$SR signal, the origin of which should be further investigated.

The piston of the pressure cell is made out of tungsten carbide due to its high compressive yield strength ([ER96] and reference therein). The $\mu$SR spectra of the piston material, fitted with a power law function,

$$P(t) = e^{-\lambda t^\beta} + \text{Bck.},$$

is presented in Figure 5-10 ($\beta = 0.6$ and $\lambda = 1.5$ MHz). Notice the fast depolarization.

As discussed in Chapter 3 a fast relaxing signal in the $\mu$SR spectra is often the sign of a magnetic transition. To avoid confusion with a signal arising from the sample, the piston should be far away from the muon beam. During tests performed with the pressure-cell having the piston in the maximum load position (i.e. closest to the beam axis), no signal from the piston was detected in the $\mu$SR spectra.

A typical $\mu$SR spectrum measured at 20 K with a Ni single crystal in the pressure cell is displayed in Figure 5-11. The details of the fit at early times are displayed in Figure 5-12.
5.1 The pressure cell

Figure 5-11: μSR spectra recorded at 30 K for a Cu-Be pressure cell with a Ni s.c. sample. The thin line is a fit of the μSR spectra with Eq. 5-1a (only the first two terms are shown). The thick line represents the contribution from the pressure cell. The experimental points do not follow the high frequency because the binning is 60.125 ns in this display (binning = number of added histogram channels).

The thin line in both figures indicates the fit of the μSR spectra to:

\[ P(t) = A_1 \cdot P_{KT}(t) + A_{Ni} \cdot \cos(2\pi \cdot v_{Ni} \cdot t + \phi_{Ni}) \cdot e^{-\lambda_{Ni} t} + Bck \]  

(5-1a)

where the first term is the Kubo-Toyabe term from the Cu-Be cell and the second one the oscillating signal arising from the Ni single crystal (at the working temperatures Ni is magnetically ordered). The muon stops at a site where the local field is around 1500 G (v_{Ni} = 20.3 MHz). By \( A_{Ni} \), \( v_{Ni} \), \( \phi_{Ni} \) and \( \lambda_{Ni} \) we have denoted the asymmetry (see also Figure 5-4), frequency, initial phase and the relaxation rate (0.47 MHz) of the Ni single crystal μSR signal.

Figure 5-12: μSR spectra and fit of Figure 5-11 at short times on an expanded scale. Binning of the experimental points: 2-1.25 ns.
As pressure transmitting media a 1:1 mixture of n-pentane and isoamyl alcohol (from Fluka Chemie AG) was used. The seal is provided by the teflon cup, the BLA element and the extrusion ring. When the pressure is applied, the bottom part of the teflon cup gets squeezed between the BLA element and the cell’s wall (see Figure 5-6). The extrusion ring is deformed by the upper part of the teflon cup and therefore acts as a supplementary seal. Since the volume of the liquid mixture is reduced by a factor of about 2 at maximum pressure if a sample smaller than 20 mm is used, a spacer should be added in order to reach the maximum pressure for the full travel of the piston and to avoid that the pistons gets too close to the sample space. We have used copper-beryllium disks since they do not add an additional signal in the μSR spectrum. Teflon should not be used because of its peculiar μSR signal, see Figure 5-13 (the μSR spectrum was measured at 30 K). We discovered this fortuitously, actually by using teflon as spacer.

Since the μSR signal of teflon was not known up to now, it’s worthwhile to present our results. Moreover, because of its characteristic signal, teflon could be used for asymmetry calibration purposes when Ni single crystals are not available.

Teflon is a polymer of tetrafluoroethylene (C₂F₄, see Figure 5-14). The organic compound C₂F₄ is made up of two carbon atoms with one π and one σ bond between them forming a double bond. Two fluorine atoms are attached to each carbon atom by a single-σ

![Figure 5-13: μSR spectra for teflon at 30 K. The solid line is a fit with Eq. 5-2.](image)

![Figure 5-14: Chemical structure of tetrafluoroethylene (C₂F₄ i.e. teflon).](image)
5.1 The pressure cell

bond. Teflon is formed by breaking the π bond between the carbon atoms and linking it to another tetrafluoroethylene, and so on. From a structural point of view, it is amorphous. In fluorine ionic crystals (LiF, NaF, CaF$_2$ and BaF$_2$, [BR86]) a kind of hydrogen-type bonded F$i$F model was used to describe the μSR spectra. We have used the same idea to describe the $P(t)$ dependence of the muon polarization in teflon. In this model, the muon stops at the center of the line joining two F$_{19}^-$ nuclei. A calculation of $P(t)$ considering a static collinear geometry of μ$^+$ and the two fluorine nuclei and only the μ$^+$ - F$_{19}^-$ dipole-dipole interaction leads to

$$
P(t) = \frac{1}{6} \left[ 3 + \cos(\sqrt{3} \cdot 2\pi \cdot t) + \left(1 - \frac{1}{\sqrt{3}}\right) \cos\left(\frac{3 - \sqrt{3}}{2} \cdot 2\pi \cdot t\right) + \left(1 + \frac{1}{\sqrt{3}}\right) \cos\left(\frac{3 + \sqrt{3}}{2} \cdot 2\pi \cdot t\right) \right] e^{-\lambda t} \tag{5-2}
$$

where $\nu$ is the dipolar interaction frequency, related with the $\mu^+$-F$_{19}^-$ distance by

$$
h\nu = (\chi_0 \cdot \gamma_0) / \mu^3 \tag{5-3}
$$

In Eq. 5-2 $\lambda$ is the $\mu^+$ relaxation rate. A fit of Eq. 5-2 to the μSR spectra measured in teflon is presented in Figure 5-13. The value $\nu = 0.192(3)$ MHz obtained from the fit is compatible with the values of $\nu$ in the fluorine ionic crystals. We do not discuss further the results, since it is not the topic of this thesis. However, if teflon needs to be used for asymmetry calibration purposes in μSR experiments, it is worthwhile to study the problem further (using the MORE option at PSI for a larger time window). Moreover, the similarities between our μSR results in an amorphous compound (teflon) and those measured in single crystalline fluorine samples by Brewer et al. [BR86] are surprising and merit further consideration.

Applying and measuring the pressure

Several precise but not complicated steps should be followed to use the pressure cell. They are presented in detail in Appendix E.

The two external coils shown in Figure 5-5 belong to the pressure measurement system. Our manometer is a piece of lead, i.e. we measure the pressure dependence of the superconducting transition temperature of lead, $T_{c, P_0}(p)$. The decrease of $T_{c, P_0}(p)$ with $p$ is well known [BI88]: $\Delta T_{c, P_0} / \Delta p = 0.0364$ K/kbar.

The pressure measurement made use of a standard technique. It consists of applying a small alternating magnetic field to the sample (a small disk of lead, see Figure 5-15) by means of a primary coil and detecting, with a system of two secondary coils (pick-up coils), the variation of flux due to the changes of the magnetic properties of the sample. The pick-up coils are oppositely wounded and connected in series to compensate for the direct induced potential from the induction coils. The lead should be located in the center of one of the pick-up coils. Below the temperature of the superconducting transition of lead, the two pick-up coils get unbalanced and a net signal is observed via a phase difference between the input signal and the pick-up coil output signal (measured using a lock-in amplifier). An estimate of the
expected signal from the transition of a perfect superconductor is given (in SI units, [WE76]) by

$$U = \pi f B V [1/(1-D)](N/R),$$

where $f$ is the frequency of the applied ac-field $B$, $V$ the sample volume, $D$ the demagnetization factor and $N/R$ the number of windings divided by the radius for the pick-up coil. It is assumed that no signal is induced by the superconducting transition of lead on the second pick-up coil, which is far away from the lead manometer. For the values $f = 83$ Hz, $V = 2$ mm$^3$ (a disk of Pb, $\Phi = 3$ mm, $h = 0.3$ mm), $D = 0.8$ [SA89], $B = 2$ G, $N = 400$, $R = 12$ mm of the parameters we used, an induced voltage $U = 20 \mu$V is expected.

Figure 5-15: Circuit scheme for measuring the superconducting transition of Pb.

Figure 5-16: Typical signal showing the superconducting transition of lead.

The circuit scheme is displayed in Figure 5-15. An ITHACO DYNATRAC 391 A lock-in amplifier was used to generate the input signal in the induction coils ($v = 83$ Hz, 1V PP) and to record the signal of the pick-up coils. The sensitivity scale was 30 nV. A typical recorded signal is displayed in Figure 5-16.

**Temperature stability**

Since the variation of $T_c$ with the pressure is small, the temperature inside the pressure cell should be known with high precision. A schematic configuration of the disposition of the temperature sensors and the heaters in our cryostat is shown in Figure 5-17. Because we have no temperature sensors inside of the pressure cell (to avoid wire-breaking problems due to the large volume of our samples) several tests were performed to find which one of the temperature sensors (sample stick or diffuser) could be used to give the temperature inside the cell pressure cell. For this purpose, a third sensor was inserted into the sample space of an empty pressure cell and glued to its bottom bolt.
During normal μSR runs without the pressure cell the temperature is controlled in a two-loop mode, i.e. at the diffuser and at the sample-stick (see Figure 5-18). In first tests it was observed that due to the particular position of the sample stick heater and the large mass of the pressure cell, the temperature inside the cell did not follow a change of the sample-stick temperature (see Figure 5-19). In other words, with this configuration, the pressure cell temperature is solely controlled by the diffuser temperature.
The cryostat was therefore used in a single loop mode, with the temperature controlled only by the diffuser. To show that the sample stick sensor can be used to measure the temperature inside the pressure cell (provided that one waits for temperature stabilization), we have plotted in Figure 5-20 the difference between the temperatures indicated by the sample stick sensor and the sensor inside the sample space. Notice that the difference oscillates around zero in the milli-Kelvin range. When the superconducting transition of lead is measured, the pick-up coils signal is monitored while changing slowly the temperature in both directions, across the transition.

### 5.2 Pressure effects on CeRh$_2$Si$_2$

CeRh$_2$Si$_2$ has a body-centered tetragonal structure of the ThCr$_2$Si$_2$-type (space group I4/mmm). It is an antiferromagnet with two magnetic transitions, at 36 K ($T_N^1$) and 25 K ($T_N^2$) [GR-84]. A hydrostatic pressure of about 13 kbar suppresses the antiferromagnetism and gives rise to superconductivity below 0.4 K [MO-96]. CeRh$_2$Si$_2$ has the highest magnetic transition temperature among the Ce Kondo lattice compounds and the largest $\delta T_N/\delta p$ rate, resulting in suppression of magnetism ($T_N$) under applied pressure ($p$). Neutron scattering experiments under pressure [KA00] have shown that the cerium moment decreases linearly with the pressure, which is surprising in view of its high Néel temperature. Previous $\mu$SR experiments on CeRh$_2$Si$_2$ ([DA90], [YA00]) have detected an oscillating contribution to the $\mu$SR signal below $T_{N_2}$ indicating a finite field at the muon site, i.e., a direct measure of the Ce magnetic moment. With these magnetic properties CeRh$_2$Si$_2$ became an ideal test material for our pressure cell.

The $\mu$SR measurements were performed using the GPD instrument on the $\mu$E4 high energy muon beam (see Chapter 3) at PSI. A commercial Janis cryostat was employed between 1.6 K and 300 K. The sample was a polycrystalline cylinder of 7.4 mm diameter and 20 mm length obtained from Dr. G. J. Nieuwenhuys from Kamerlingh Onnes Laboratory, Leiden University, Holland.

In the paramagnetic regime of CeRh$_2$Si$_2$ the $\mu$SR spectra are almost flat, i.e. the nuclear contribution (Si$^{29}$, Rh$^{103}$) to the depolarization rate is very small while the Ce-spin fluctuation rate is very high and therefore invisible in the $\mu$SR time window, as in YbCu$_2$Si$_2$. The muon relaxation rate of CeRh$_2$Si$_2$ in the paramagnetic phase is estimated to be about 0.01 $\mu$s$^{-1}$ [YA00]. No slowing of the 4f-spin fluctuations close to the magnetic transition, as seen in Yb(Cu$_{1-x}$Ni$_x$)$_2$Si$_2$ and YbCu$_{5-y}$Al$_y$, was observed in CeRh$_2$Si$_2$. Therefore, we have limited our investigation to the evolution of the magnetic ground state under pressure.

### The magnetic phase of CeRh$_2$Si$_2$ at zero pressure

The nature of antiferromagnetism of CeRh$_2$Si$_2$ was intensively studied during these last years. Grier et al. [GR84] have determined the $k$-vectors describing the magnetic structure in the two antiferromagnetic phases by using powder neutron diffraction techniques. Below $T_{N_1}$ they observed Bragg reflections representing a magnetic modulation with $k_1 = (1/2,1/2,0)$. 


A second Bragg reflection with \( k_2 = (1/2,1/2,1/2) \) was observed below \( T_{N2} \). The \( k_1 \) reflection is not replaced completely by the \( k_2 \) reflection (below \( T_{N2} \)), but both coexist with comparable intensities at low temperatures. These results were also confirmed for a single crystalline sample by Kawarazaki et al. [KA95b].

Actually, the principal subject of debate is the magnetic structure of CeRh\(_2\)Si\(_2\) below \( T_{N2} \). The two modulations described by \( k_1 \) and \( k_2 \) could reflect either a multidomain type of magnetic ordering, i.e. each modulation is specific to its own domain, or a combination of modulations which pertains to a single magnetic structure over the crystal (multi-q structure). Grier et al. [GR84] and Kawarazaki et al. [KA95b] have both favored a single-domain double-\( k \) magnetic structure with magnetic moments varying from 1.7 \( \mu_B \) to 2.4 \( \mu_B \). Quite different was the cerium magnetic moment predicted from NMR measurements (\( = 0.3 \mu_B \), [KA98]). This disagreement was explained [KA98] by the difference between the characteristic time of observation in NMR and neutron diffraction (see also Figure 3-1).

A neutron-diffraction experiment under pressure performed by Kawarazaki et al. [KA00] gives yet another interpretation of the observed Bragg peaks and their pressure dependence. They consider a 4-\( k \) magnetic structure with a value of the ordered moment around 1.4 \( \mu_B \). The results of a \( \mu \)SR experiment [YA00] agreed with this value of the moment but could not distinguish between the 4-\( q \) single domain magnetic structure and the multidomain magnetic structures. Our interpretation of the \( \mu \)SR results measured at \( T < T_{N2} \) is at variance with the interpretation of the similar \( \mu \)SR data given by Yamamoto et al. [YA00]. The pressure dependence of the ordered moment, as presented in the work of Kawarazaki et al. [KA00] was not observed in our data. For clarity, in the following the discussion of the results is divided in two parts: \( T_{N2} < T < T_{N1} \) and \( T < T_{N2} \).

The magnetic ordered phase for \( T_{N2} < T < T_{N1} \)

It is generally accepted that the magnetic structure of CeRh\(_2\)Si\(_2\) in this temperature interval is described by a modulation vector \( k = (1/2,1/2,0) \), see Figure 5-21 (the different symbols - open circles and full circles - represent Ce ions situated respectively in the corners and in the center of the crystallographic unit cell). No oscillations but some rather fast relaxation was observed in the \( \mu \)SR spectra, indicating that either the average field at the muon site is zero or the field distribution is large (see Figure 5-22).
There are different possibilities to fit the \( \mu \)SR spectra but for all of them the sum of two depolarization functions have to be employed in order to obtain satisfying fits. This implies either two crystallographically inequivalent muon sites or one crystallographic site containing two magnetically inequivalent sites. One of the muon stopping sites appears to be the (1/2,0,0) site (4\( c \) in Wickoff notation), see the discussion of the \( T < T_{N2} \) data. According to the magnetic structure presented in Figure 5-21 all the 4\( c \) sites are magnetically equivalent and therefore responsible for one of the two component of the \( \mu \)SR signal. Therefore, the second component of the \( \mu \)SR spectra should arise from muons stopping at another muon site. One should keep in mind that this discussion is valid only assuming that the proposed magnetic structure is correct and that the compound is single-phased.

In all the two component fits that we have tried (Figure 5-22), one component has a small relaxation rate (around 0.5 MHz) while the relaxation rate of the other component is several times larger (= 2-5 MHz). Moreover, it appears clearly that one of the fit functions has to be a Kubo-Lorentz function, which is ascribed to the muons stopping at the 4\( c \) sites, see below. From the magnetic structure presented in Figure 5-21 one observes that the field at the 4\( c \) site is zero, since these sites are center of inversion for the magnetic structure. It will be shown below that the relaxation rate corresponding to the 4\( c \) sites is the smaller one. Therefore, we shall look for a second site, which gives the large relaxation rate. However, from the fits to our data, we could not precisely decide about the ratio between the asymmetries corresponding to the two sites. The reasons are presented below (we present here only one of these fits, the discussion is similar for the other ones).

One can use two KL depolarization functions to fit the \( \mu \)SR spectra,

\[
AP(t) = A_1 \left[ \frac{1}{3} + \frac{2}{3}(1-\lambda_1 t) e^{-\lambda_1 t} \right] + A_2 \left[ \frac{1}{3} + \frac{2}{3}(1-\lambda_2 t) e^{-\lambda_2 t} \right],
\]

(5-4)
see Figure 5-22(a). For comparison, the same µSR spectra fitted with a single KL and with a single exponential depolarization function are displayed in Figure 5-22(b) and 5-22(c) respectively. The shortcomings of these latter fits are evident.

From a free fit of Eq. 5-4 to the µSR spectra, we obtain a value of ≈ 1.3 for the ratio between the asymmetries of the two fit components, \( A_1/A_2 \) (see Figure 5-24). The term with the higher asymmetry is associated with the \((1/2,0,0)\) site, as will be shown later. This asymmetry ratio is close to 4/3. Since there are four \((1/2,0,0)\)-type sites in the unit cell, the second site should have a multiplicity three, which is impossible within the I4/mmm space group to which CeRh\(_2\)Si\(_2\) belongs. For the possible muon sites in CeRh\(_2\)Si\(_2\), see Table 4-2 on page 50.

Since it is possible that the fit does not yield the correct asymmetries (due to low statistics, non-ideal Lorentzian field distribution or because that the second depolarization function is not a KL), we will discuss different possibilities for the \( A_1/A_2 \) ratio:

- **4/4 = 1**: in this case, since there is only one site of multiplicity 4 available for the muon, the \( 4c \) site, it would mean that half of them are magnetically inequivalent i.e. the magnetic structure should be different from the one presented in Figure 5-21. One possibility is that the two sublattices, the one described with open circles and the one described with full circles in Figure 5-21, have different ordered moments. One should mention that a similar magnetic structure was proposed by Grier et al. [GR84], but in relation to the magnetic structure below \( T_{N2} \), not \( T_{N1} \).
- **4/2 = 2**: quite far apart from the 1.3 value found in our fits, it is one of the limited combinations allowed by the crystal structure of CeRh\(_2\)Si\(_2\). In this case 2/3 of the muons stop at the \( 4c \) site and 1/3 of them at the \( 2b \) site.
- **We should not neglect the possibility that \( A_1/A_2 = 1.3 \) amounts in fact to \( = 1.3 \) (i.e. the fit described by Eq. 5-4 is correct), in which case we would rather think that the sample consists of two magnetic phases. µSR measurements in TF configuration might help to solve this problem.

**The magnetic ordered phase for \( T < T_{N2} \)**

Below \( T_{N2} \) a slowly relaxing oscillating component shows up in the µSR spectra, denoting a fraction of the muons that stop at a site with a non-zero average field. The spectra were best fitted using

\[
AP(t) = A_1 \left[ \frac{1}{3} + \frac{2}{3} (1 - \lambda_1 t) e^{-\lambda_1 t} \right] \\
+ A_2 \left[ \frac{1}{3} + \frac{2}{3} (1 - \lambda_2 t) e^{-\lambda_2 t} \right] \\
+ A_3 \left[ \frac{1}{3} + \frac{2}{3} e^{-\lambda_3 t} \cos(2\pi \nu t) \right] 
\]

(5-5)

**Figure 5-23:** Fit of Eq. 5-2 to the 10 K µSR spectra of CeRh\(_2\)Si\(_2\).
where the first two terms have the same meaning as in Eq. 5-4 and the third term describes an oscillating component. $\lambda_3$ is the $\mu^+$ depolarization rate at the corresponding muon site and $\nu$ is the $\mu^+$ precession frequency

$$\nu = \gamma_\mu B/2\pi$$

with $B$ the average local field at the muon site. A fit of Eq. 5-5 to a $\mu$SR spectrum is displayed in Figure 5-23.

The temperature dependence of the fitted $A_i$ coefficients is plotted in Figure 5-24. Notice that while $A_2$ remains roughly constant down to $\approx 15$ K, the asymmetry of the oscillating component, $A_3$, grows at the expense of the $A_1$ term until both reach the same amplitude. The muon sites responsible for the first term in Eq. 5-4, the 4c sites, are no longer magnetically equivalent below $T_{N2}$. For half of them the average field sensed by the muon is still zero - the first term in Eq. 5-5 - and has the same field distribution as above $T_{N2}$ since no significant change of $\lambda_1$ was observed at $T_{N2}$, see Figure 5-25. For the other half of the 4c muon sites, the average field at the muon site has a finite value and is therefore associated with the third component in Eq. 5-5.

Below 15 K $A_2$ starts to increase, interestingly, up to the high temperature value of $A_1$, while the values of $A_1$ and $A_3$ decrease correspondingly. More points at $T < 5$ K are needed to confirm this behavior. Moreover, the temperature at which $A_2$ starts to increase corresponds to the temperature at which an unusual increase in $\lambda_3(T)$ is observed, Figure 5-26. Notice also the large values of $\lambda_2$ compared to $\lambda_1$ and $\lambda_3$. The $\lambda_1(T)$ dependence has a Brillouin-like behavior, and saturates below $\approx 24$ K (see Figure 5-25). The further increase of $\lambda_1(T)$ and $\lambda_2(T)$ below 15 K is not fully understood. It is surely not re-
lated with changes of the value of the ordered moment since the value of the Ce magnetic moment remains constant down to 5 K, as shown by the \( v(T) \) dependence in Figure 5-27.

\( \lambda_3(T) \), the relaxation rate of the oscillating component is roughly temperature independent below 25 K in agreement with the temperature behavior of the ordered moment. We should also mention that measurements of the static susceptibility for CeRh\(_2\)Si\(_2\) [GO84], have shown an anomaly in the \( \chi(T) \) dependence at 5.2 K, but which was not confirmed by other macroscopic or microscopic measurements.

We will discuss in the following the origin of the finite field at the muon site below \( T_{N2} \), in relation with the magnetic structure proposed by Kawarazaki et al. [KA00], displayed in Figure 5-28. Remember that for \( T_{N2} < T < T_{N1} \) the magnetic structure is modulated with \( k = (1/2,1/2,0) \): the D\(^+\) magnetic structure presented in Figure 5-28(a). We will ignore, for the following discussion, the fact that the muon site that describes the second component in Eq. 5-4 and Eq. 5-5 is not yet known. We will come back later to this point.

The origin of the finite field at the muon site should be related with the observation of the \( k_2 = (1/2,1/2,1/2) \) peaks in the neutron diffraction spectra below \( T_{N2} \). Since the intensities of

\[ \begin{align*}
&\text{(a) D}^+ \\
&\text{(b) S} \\
&\text{(c) 4-}k
\end{align*} \]

*Figure 5-28: Proposed magnetic structures for CeRh\(_2\)Si\(_2\) [KA00a]: (a) D\(^+\) structure, \( k_1 = (1/2,1/2,0) \), (b) S structure, \( k_2 = (1/2,1/2,1/2) \) and (c) 4-\( k \) structure, \( k = (1/2,1/2,1/2) + (-1/2,1/2,0) + (1/2,1/2,1/2) \).
the reflections corresponding to the $k_1$ and $k_2$ modulations are similar, the discussion is whether each modulation develops in its own domain, like the D' and the S structures in Figure 5-28, or they form a multiple-$k$ structure, as that presented in Figure 5-28(c).

First, we should calculate the field at the 4c sites for all the magnetic structures presented in Figure 5-28:
(a) It was shown before that the average field is zero at all the 4c sites for the magnetic structure D', due to the fact that the 4c sites are inversion centers for the magnetic moments of the Ce ions.
(b) The average field is nonzero at all the 4c sites of the S structure because they are no more inversion centers for the Ce magnetic moments. In fact, they are for the first nearest neighbors, but not for the second nearest neighbors.
(c) For the 4-k magnetic structure the average field is zero at half of the 4c sites, the sites between two "black" Ce ions, Figure 5-29(a), while at the other 50% of 4c sites, the average field is nonzero see Figure 5-29(b).

If the value of the Ce magnetic moment is the same for the S and the 4-k magnetic structures, the nonzero value of the local field should be the same for both structures. From the value of the muon precession frequency, $\nu = 1.66(2)$ MHz, the average field at the muon site could be calculated, $B \approx 122$ G. With the given magnetic structure, a dipolar field calculation lead to the measured value of the average field if the Ce magnetic moment is 1.46 $\mu_B$. This value agrees with $\mu_{Ce} = 1.38 \mu_B$ obtained by Kawarazaki et al. [KA00] from neutron scattering measurements and is identical with that measured by Yamamoto et al. [YA00] in a µSR experiment. Notice that the contact field contribution to the local field is zero for all magnetic structures.

At first sight, from the µSR measurements one cannot decide which of the D' + S or the 4-k magnetic structures are formed since in both cases half of the 4c sites change from sites with zero average field, between $T_{N1}$ and $T_{N2}$ into sites with $122$ G average field below $T_{N2}$. The same conclusion emerges also from [YA00]. This behavior is best reflected in the temperature dependence of $A_1$ and $A_3$, respectively the non-wiggling and the wiggling components in the µSR signal corresponding to the 4c sites, shown in Figure 5-24.
5.2 Pressure effects on CeRh$_2$Si$_2$

Notice that in the above discussion we did not touch on either the problem of the muon site corresponding to the second signal in Eq. 5-4 and Eq. 5-5 or its temperature behavior across the magnetic transition $T_{N2}$. In fact, these problems do not appear in the $\mu$SR results of Yamamoto et al. [YA00]. Their fit function contains only the equivalent of the first and the third term in Eq. 5-5. The temperature dependence of their fitted $A_1$ and $A_3$ is identical to that presented in Figure 5-24. $A_1$ from [YA00] is shown in Figure 5-30. Their sample seems to have a better quality than ours do since they fitted a zero $A_3$ relaxation rate for the wiggling component. Is the $A_2$ term sample dependent or is it due to a foreign phase showing up only in our sample? We shall show in the following that neither of these cases apply.

- It is difficult to understand, from Figure 5-30, why $A$ increases below $T_{N2}$ while the magnetic moment that generates it saturates. This fact suggests a missing component in the fit function and is also supported by the fact that:
  - a reduced asymmetry was observed below $T_{N1}$,  
  - Yamamoto et al. [YA00] have approximated the KL function with an exponential which introduces a supplementary reduction of the asymmetry
- another argument in favor of our interpretation is given by earlier measurements, at 22.5 K, on a CeRh$_2$Si$_2$ sample, presented in [DA90]. They found a value of 0.32 for the fraction of the muons that precess around the nonzero local field, which is in agreement with our results, see Figure 5-23. They have also detected a fast relaxing signal, accounting for around 0.45 of the total asymmetry, which also agrees well with our results.
- Notice the abrupt increase of $A$ below 10 K in Figure 5-30, similar with that observed in our sample

In conclusion, we consider that the second signal observed in our $\mu$SR measurements is intrinsic to CeRh$_2$Si$_2$. Its origin is still unclear for the moment but, as stated above, TF measurements might help to discern between the different possibilities.

The difference between the given possible magnetic structures above and below $T_{N2}$ is quite small. The magnetic moments in two planes change the orientation if one goes from the D' to the S magnetic structures while only the moments in one plane change the orientation if one goes from D' to the 4-k magnetic structure. We will argue that one cannot explain the reduced value of the relaxation rate for the wiggling component, $A_3$, compared to $A_1$, see Figure 5-26, if a 4-k magnetic structure is considered. This raises the question of the cor-

![Figure 5-30: Temperature dependence of the relaxation rate for CeRh$_2$Si$_2$. Data from [YA00].](image)
rectness of the magnetic structure presented in [KA00]. The answer to this question might represent the solution to our second signal problem.

It was shown that the finite field at the muon site below $T_{N2}$ is a second nearest neighbor effect. If the 4-$k$ structure is realized below $T_{N2}$, Figure 5-28(c), the magnetic field at the 4c sites between two “white” Ce ions is nonzero, see Figure 5-29(b), due to the change of the orientation of Ce magnetic moments in the upper “black” plane. As one can notice from Figure 5-25 - $\lambda(T)$, the reorientation of the Ce magnetic moments in the “black” plane reduces the width of the field distribution at the 4c sites between the “white” Ce ions (which are second nearest neighbors for the “black” ions). A similar effect should have been observed, in principle, also for the 4c sites between the “black” ions which are first nearest neighbors of the ions that changed orientation. Since no change of the widths of the field distribution (relaxation rate) was observed (see the temperature dependence of $\lambda$ displayed in Figure 5-25 we conclude that if one had to decide between the multi-domain magnetic structure and the 4-$k$ magnetic structures presented in [KA00] we would rather favor the former one.

CeRh$_2$Si$_2$ under pressure

The $\mu$SR under pressure experiments were performed using the experimental setup and the instruments presented in detail in Chapter 5.1. The measurements were performed in the temperature range $1.6 \text{ K} < T < 300 \text{ K}$ and up to $\approx 7 \text{ kbar}$, see Figure 5-31 where the Lock-in signals recorded during the pressure measurement are displayed. Notice, in Figure 5-31, the similar slope in the transition region of all curves, indicating the homogeneity of the pressure (at least for the Pb manometer).

We have measured the pressure dependence of the magnetic transition temperatures $T_{N1}$ and $T_{N2}$. The sign of the magnetic transition in the $\mu$SR spectra is a fast relaxing signal at $T < T_{N1}$ and the observation of an oscillating signal for $T < T_{N2}$. In addition, due to the clear signature on the $\mu$SR spectra of the magnetic phase below $T_{N2}$, the pressure dependence of the Ce magnetic moment was also determined.

We shall show that, since the value of the muon precession frequency does not change with the applied pressure, the value of the Ce magnetic moment remains unchanged, at least for the low-pressure regime, i.e. up to $\approx 5 \text{ kbar}$, where it was possible to detect wiggles in the recorded $\mu$SR spectra.

![Figure 5-31: Lock-in signals recorded during the pressure measurement see Chapter 5.1 for details.](image-url)
A typical μSR spectrum recorded at 10 K is displayed in Figure 5-32. To fit the μSR spectra, a sum of Eq. 5-5, for the CeRh$_2$Si$_2$ signal, and Eq. 5-1, for the signal arising from the Cu-Be pressure cell signal (see Chapter 5.1), was used.

The pressure dependence of the magnetic transition temperatures of CeRh$_2$Si$_2$, $T_{N1}$ and $T_{N2}$, is displayed in Figure 5-33 together with similar results obtained from macroscopic measurements [GR97]. While both the $T_{N1}(p)$ dependencies presented in Figure 5-33 are similar, this is not the case for the pressure dependence of $T_{N2}$. The difference might arise from the way the transition temperatures were determined: a slope change in the $\rho(T)$ dependence in [GR97]; the observation of the muon precession, in our μSR experiment.

![Figure 5-32: Typical μSR spectra recorded at 10 K, for a CeRh$_2$Si$_2$ sample in a Cu-Be pressure cell. The lines are fits, see the text, of the μSR spectra.](image)

![Figure 5-33: Pressure dependence of the magnetic transition temperatures $T_{N1}$ and $T_{N2}$ of CeRh$_2$Si$_2$: full symbols = data from [GR97], open symbols = our results. The lines are guides for the eye.](image)

![Figure 5-34: Temperature dependence of the frequency of the oscillating signal in CeRh$_2$Si$_2$ for different applied pressures. Notice that $\nu$ does not vary with pressure in the indicated pressure range. The dotted line indicates the value of $\nu$ at 4 kbar calculated from the results of [KA00].](image)
The suppression of the transition temperature by the applied pressure in CeRh$_2$Si$_2$ fits well the Doniach phase diagram, see Chapter 2. The reduction of the unit-cell volume due to the applied pressure should increase the Kondo temperature and reduce the magnetic transition temperature, through the increased hybridization between the 4f electrons and the conduction electrons. The situation is, however, more complicated since CeRh$_2$Si$_2$ exhibit a superconducting transition at low temperatures for pressures close to the critical pressure. The critical pressure, around 11 kbar, was not reached in our experiment.

The fitted $v(T)$ dependencies for different applied pressures are displayed in Figure 5-34. The solid lines indicate the magnetic transition temperatures. Notice that:

- The value of $v$ is almost pressure independent, $v(P = 4 \text{ kbar}) = 0.97 v(P = 0 \text{ kbar})$. The dotted line in Figure 5-34 represents the value of $v(P = 4 \text{ kbar})$ as calculated from the experimental data of [KA00].
- The magnetic phase below $T_{N2}$ involves almost saturated values of the Ce magnetic moments as observed from their temperature dependence, see Figure 5-34.

Kawarazaki et al. [KA00], in a neutron scattering experiment under pressure on CeRh$_2$Si$_2$, have found a linear dependence of the Ce magnetic moment on the magnetic transition temperature $T_{N1}$, see Figure 5-35 - full circles, from which they concluded that the character of the magnetic order is itinerant. Our results are at variance with the linear $\mu_{Ce}(T_{N1})$ dependence found in [KA00] and indicate that the magnitude of the Ce magnetic moment in CeRh$_2$Si$_2$ is, within the error bars, pressure independent up to 4 kbar (see Figure 5-35, open circles). This result suggests that Ce has a well-localized magnetic moment and is consistent with the large transition temperatures of CeRh$_2$Si$_2$. Notice, however, the faster decrease of the magnetic transition temperature $T_{N1}$ measured by Kawarazaki et al. [KA00] compared to our results ($\mu$SR) and those of Grosche et al. [GR97] obtained from the temperature dependence of the electrical resistivity.

![Figure 5-35: The saturated Ce magnetic moment shown as a function of the transition temperature $T_{N1}$: open circles - our data, full circles - data from [KA00]. The moment and the transition temperature are normalized at the ambient pressure.](image)
5.3 Conclusions

We have made a systematic study of some of the materials that can possibly be used to build a pressure cell suited for μSR experiments. From the μSR measurements on these materials,

- we found that MP35N, with remarkable tensile properties - proposed by [WA99] for double layered pressure cells for macroscopic measurements, is also suitable for μSR pressure cells because of its μSR signal, similar to that of Cu-Be.
- we found an unexpected oscillating signal in teflon (C2F4). It arises from muons stopping between two fluorine atoms. Due to its specific μSR signal, teflon could be used for asymmetry calibration purposes in μSR experiments (instead of the Ni single crystal currently use).

The magnetic structures of CeRh2Si2 proposed by Kawarazaki et al. [KA00] from neutron scattering experiments under pressure are at variance with our μSR results both below $T_{N1}$ and $T_{N2}$. At temperatures between $T_{N1}$ and $T_{N2}$ the origin of one of the two contributions to the μSR signal cannot be explained by the proposed magnetic structure. Below $T_{N2}$ the interpretation of our results points to a double domain magnetic structure, in contrast with the single domain 4-k magnetic structure proposed in [KA00]. The magnetic structure of CeRh2Si2 remains a subject of debate.

The suppression of the magnetic transition temperature $T_{N1}$ by the increase of the applied pressure indicates a change of the balance between the RKKY interaction and the Kondo interaction in favor of the latter one, in agreement with the Doniach phase diagram. However, the magnetic moment of the Ce ions does not vary, within the error bars, up to around 4 kbar. This result, which suggests a well localized Ce magnetic moment, at least in the low pressure range, is compatible with the high transition temperature in CeRh2Si2. The reduction of the Ce magnetic moment with the increase of the applied pressure found in neutron scattering measurements by Kawarazaki et al [KA00] is intriguing. Similarly, the faster reduction of the magnetic transition temperature $T_{N1}$ measured by the same authors appears incompatible with the results obtained in μSR experiments and electrical resistivity measurements [GR97].
Appendix A

Computing the $\mu$SR spectra for a $\delta$-function field distribution at the muon site

This is the starting point for almost all $\mu$SR spectra simulations. We will restrict the discussion to the static case. One can consider that we use a perfect single domain single-crystal with one muon site.

Let's consider the $xyz$ laboratory frame as in Figure A-1. It is assumed that the magnetic field $B = B \cdot 1_B$, the initial muon spin polarization $P(0) = 1_{p0}$ and the direction of the detector is given by $1_r$ where the $1_i$ are unit vectors in the mentioned directions. We compute the $P_i(t)$ dependence as seen by the detector. Since the life-time of the muon is not taken into account, (like if the muons would continuously emit positrons), the simulated spectra resembles the usual $\mu$SR spectra.

![Figure A-1: The orientation of $P(0)$, $B$ and $1_r$ in the laboratory reference frame.](image)

The detector will record the projection $P_i(t)$ of the $P(t)$ vector along the $1_r$ direction and it can be computed as follows:

$$P_i(t) = P(t) \cdot 1_r$$

Since $P$ rotates around $B$ with the angular speed $\omega = \gamma B$, the easiest way to calculate $P(t)$ is to separate it in two components: a component parallel with $B$ and another one perpendicular to $B$: 

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\[ P(t) = P_{||B} + P_{\perp B}(t) \]

where \( P_{||B} \), the component of \( P(t) \) along the \( B \) direction, is time independent.

\[ P_{||B} = (l_{P0} \cdot 1_B) 1_B. \]

To illustrate the rotation of \( P_\perp(t) \) in the plane perpendicular to \( B \) we need two unit vectors in that plane. Since we know \( P(0) \), one of the vectors could be

\[ x_1 = P(0) - P_{||B} = 1_{P0} - P_{||B} = 1_{P0} - (l_{P0} \cdot 1_B) 1_B. \]

The first unit vector will then be \( 1_{x1} = x_1 / x_1 \). The second vector, \( y_1 \) can be constructed as being perpendicular on both \( B \) and \( x_1 \):

\[ y_1 = 1_{y1} = 1_B \otimes 1_{x1} \]

\[ P_{\perp B}(t) = x_1 \cdot \cos(\omega t) \cdot 1_{x1} + x_1 \cdot \sin(\omega t) \cdot 1_{y1} \]

or

\[ P_{\perp B}(t) = x_1 \cdot \cos(\omega t) + (1_B \otimes x_1) \cdot \sin(\omega t) \]

Finally:

\[ P_r(t) = P(t) \cdot 1_r = P_{||B} \cdot 1_r + P_{\perp B}(t) \cdot 1_r \]

\[ P_r(t) = (l_{P0} \cdot 1_B)(1_B \cdot 1_r) + (x_1 \cdot 1_r) \cdot \cos(\omega t) + ((1_B \otimes x_1) \cdot 1_r) \cdot \sin(\omega t) \]

As an example the \( P_r(t) \) dependence as seen in the back detector (z direction) is computed. The muon beam is considered fully polarized along the z direction and the orientation of the magnetic field at the muon site is described by the direction cosines \((\cos \alpha, \cos \beta, \cos \gamma) = (B_x/B, B_y/B, B_z/B)\).

\[ \mathbf{1}_B = (\cos \alpha, \cos \beta, \cos \gamma), \quad \mathbf{1}_r = 1_z = (0, 0, 1), \quad l_{P0} = (0, 0, 1) \]

Figure A-2: The orientation of \( P(0) \), \( B \) and \( 1_r \) in the laboratory reference frame for the example given in the text.
\[ x_1 = 1_{p0} - (1_{p0} \cdot 1_B) 1_B = (0,0,1) - \cos \gamma (\cos \alpha, \cos \beta, \cos \gamma) \]
\[ = (-\cos \gamma \cos \alpha, -\cos \gamma \cos \beta, 1 - \cos^2 \gamma) \]

\[ 1_B \otimes x_1 = \begin{pmatrix} i & j & k \\ \cos \alpha & \cos \beta & \cos \gamma \\ -\cos \gamma \cos \alpha & -\cos \beta \cos \gamma & 1 - \cos^2 \gamma \end{pmatrix} \]
\[ = (\cos \beta, -\cos \alpha, 0) \]

up to now all calculated terms are independent of the detector position. Since:

\[ P(t) = (1_{p0} \cdot 1_B)(1_B \cdot 1_i) + (x_i \cdot 1_i) \cdot \cos (\omega t) + ((1_B \otimes x_1) \cdot 1_i) \cdot \sin (\omega t) \quad (A-1) \]

we obtain:

\[ P(t) = P_0(t) = \cos^2 \gamma + \sin^2 \gamma \cos (\omega t) + 0 \quad (A-2) \]

The corresponding \( \mu \)SR fit would be \( P_0(t) = A_1 + A_2 \cos (\omega t) \) where \( A_1 \) and \( A_2 \) are the amplitudes of the non-wiggling and wiggling component. Therefore when the use of Eq. A-2 to fit the \( \mu \)SR spectra is possible, one obtains information about the magnitude \( (B = \omega / \gamma) \) and orientation \( (\gamma) \) of the local magnetic field at the muon site. The \( A_2/A_1 \) ratio is the tangent of the angle between the magnetic field and the direction of the observation.

There is a more intuitive way to compute the \( P(t) \), by examining attentively the Figure A-2 right, and computing correctly the projections. The \( P(t) \) dependencies for the other directions could be computed using Eq. A-1. Of course, for the -r direction, \( P_r(t) = -P_i(t) \).

If the spectra have been recorded also in a perpendicular direction, the angle between \( B \) and another axis can be found and therefore the orientation of the magnetic field in the laboratory coordinates can be determined (see for example [SC98]).

Care should be taken when the \( \mu \)SR spectra is simulated for multi-domains single crystals. In that case we are close to the polycrystalline case.

The results described above remain valid also when relaxation processes are involved.
Appendix B

The dipolar fields, at the muon site, created by a double-\( k \) incommensurate magnetic structure

It was shown, in Chapter 3, that the magnetic field at the muon site \((r_\mu)\) generated by an ordered distribution of magnetic moments described by a single \( k \) vector can be written as:

\[
B_{\text{dip}}(r_\mu) = \mathcal{S}_{\text{cos}} \cos(2\pi k \cdot r_\mu) - \mathcal{S}_{\text{sin}} \sin(2\pi k \cdot r_\mu).
\]

\(\mathcal{S}_{\text{cos}}\) and \(\mathcal{S}_{\text{sin}}\) are lattice sums described in Eq. 3-8 and are identical for magnetically equivalent muon sites. We recall that if the structure is incommensurate, one can use a continuous variable \( \alpha (\alpha = 0...360) \) instead of \(2\pi k \cdot r_\mu\) in the above equation, which simplifies the calculations.

It is easy to generalize this formula for a magnetic structure described by a double-\( k \) vector:

\[
B_{\text{dip}}(r_\mu) = \mathcal{S}_{1\text{cos}} \cos(2\pi k_1 \cdot r_\mu) - \mathcal{S}_{1\text{sin}} \sin(2\pi k_1 \cdot r_\mu) \\
+ \mathcal{S}_{2\text{cos}} \cos(2\pi k_2 \cdot r_\mu) - \mathcal{S}_{2\text{sin}} \sin(2\pi k_2 \cdot r_\mu). \tag{B-1}
\]

Eq. B-1 was obtained for:

\[
m_i = M_1 \cos(2\pi k_1 R_i + \phi_i) + M_2 \cos(2\pi k_2 R_i + \phi_2),
\]

with the same notations as in Figure 3-9. We could not found an easy way for generating the field distribution for the general case of two incommensurate \( k \) vectors being arbitrarily oriented (i.e. without the necessity to compute the field at each muon site but by using an \( \alpha \) parameter, see above). However, using the notations: \( k_2 = k_1 + \Delta k \) and \( 2\pi \Delta k \cdot r_\mu = \phi(\mu) \) we can transform Eq. B-1 into:

\[
B_{\text{dip}}(r_\mu) = \mathcal{S}_{1\text{cos}} \cos(2\pi k_1 \cdot r_\mu) - \mathcal{S}_{1\text{sin}} \sin(2\pi k_1 \cdot r_\mu) \\
+ \mathcal{S}_{2\text{cos}} \cos(2\pi k_1 \cdot r_\mu + \phi(\mu)) - \mathcal{S}_{2\text{sin}} \sin(2\pi k_1 \cdot r_\mu + \phi(\mu)). \tag{B-2}
\]

It is still correct to consider, as in Chapter 3.3.1.3, that for an incommensurate magnetic structure the product \(2\pi k_1 \cdot r_\mu\) takes all the values (\( \alpha \)) between 0-360 deg. The only difficulty in obtaining an equation similar to Eq. 3-8a is that the \( \phi(\mu) \) term might be different for each \( \alpha \) implying that the calculations should be done, in principle, separately for all muon sites. However, by a careful analysis of each particular case some further simplifications can be found.

For example, the magnetic structure of CeAl\(_2\) is described as a double-\( k \) structure with \( k_1 = (1/2, 1/2 - \delta, 1/2 + \delta) \) and \( k_2 = (-1/2, 1/2 - \delta, 1/2 + \delta) \) [FO90] with \( \delta = 0.112 \). For
this case $\Delta k = (-1, 0, 0)$ resulting that $\varphi(r_\mu) = \varphi(r_{\mu 0})$ is independent of $r_\mu$. This is because $\Delta k$ is a lattice vector in the reciprocal space while the difference between two $r_\mu$'s is a lattice vector in the direct space i.e. their scalar product is an integer.

Therefore Eq. B-2 becomes:

$$B_{\text{dip}} = S_1 \cos \alpha - S_1 \sin \alpha$$
$$+ S_2 \cos (\alpha + \varphi(r_{\mu 0})) - S_2 \sin (\alpha + \varphi(r_{\mu 0})).$$

(B-3)

and should be calculated only for the inequivalent muon sites in one crystallographic unit cell.
Appendix C

The dipolar fields, at the muon site, created by an incommensurate helical magnetic structure

We will present here a way of computing the field distribution for an incommensurate helical magnetic structure (one \( k \) vector). The starting point/notations are presented in the following:

- \( \mathbf{k} \) is the modulation vector. It is assumed that the magnetic moment rotates around \( \mathbf{k} \).
- The arrow describing the magnetic moment lies on the surface of a cone which has the axis parallel with \( \mathbf{k} \) (Figure C-1). The magnetic moment vector can be separated in two components: one parallel to \( \mathbf{k} \), \( m_{||} \) (identical for all ions), and one perpendicular to \( \mathbf{k} \), \( m_{\perp} \). The orientation of \( m_{\perp} \) with respect to that of a reference ion \( m_{\text{ref},\perp} \) is described by the angle \( \alpha \) (see Figure C-1).
- The rotation angle \( \alpha_i \) can be written as: \( \alpha_i = 2\pi k(\mathbf{R}_i - \mathbf{R}_{\text{ref}}) \) where \( \mathbf{R}_i \) and \( \mathbf{R}_{\text{ref}} \) are the position vectors for the \( i \)th magnetic moment and respectively the reference (initial) magnetic moment. The magnetic moments have the same orientation if located in the same plane perpendicular on \( \mathbf{k} \) i.e. the model describes the helical stacking of ferromagnetic planes.
- \( \mathbf{m}_i \) can be written as: \( \mathbf{m}_i = \mathbf{m}_{\parallel} + \mathbf{m}_{\perp} \). \( m_{\parallel} = m_i \cos \theta \) and \( m_{\perp} = m_i \sin \theta \) where \( \theta \) is the angle (constant) between the magnetic moment and the propagation vector.

![Figure C-1: Orientation of the magnetic moment in a helical magnetic structure (see text).](image1)

![Figure C-2: Graphical representation of the different vectors used in the dipolar field calculation.](image2)
The dipolar field at the muon site can be calculated using (see Figure C-2):

$$\vec{B} = \sum \frac{3(\vec{m}_i \cdot \vec{r}_i \vec{r}_i - \vec{m}_i)}{r_i^3}$$

We can write:

$$\vec{m}_{\perp} = m_{\perp} \cos \alpha \cdot \vec{a} + m_{\perp} \sin \alpha \cdot \vec{b}$$

with \(\vec{a}\) and \(\vec{b}\) being unity vectors in a plane perpendicular on \(\vec{k}\). The dipolar field can be therefore rewritten as:

$$\vec{B} = m_{\perp} \sum \frac{3(\vec{a}_i \vec{r}_i \vec{r}_i - \vec{a}_i)}{r_i^3} + m_{\perp} \sum \cos \alpha \left[ \frac{3(\vec{a}_i \vec{r}_i \vec{r}_i - \vec{a}_i)}{r_i^3} \right] + m_{\perp} \sum \sin \alpha \left[ \frac{3(\vec{b}_i \vec{r}_i \vec{r}_i - \vec{b}_i)}{r_i^3} \right]$$

Using \(\vec{R}_i = (\vec{r}_i + \vec{r}_\mu)\) (Figure C-2) and developing the sine and the cosine one obtains:

$$\alpha_i = 2\pi \vec{k} \left( \vec{r}_i + \vec{r}_\mu - \vec{R}_{ref} \right)$$

$$\cos \alpha = \cos(2\pi \vec{k} \vec{r}_\mu) \cos(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref})) - \sin(2\pi \vec{k} \vec{r}_\mu) \sin(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref}))$$

$$\sin \alpha = \sin(2\pi \vec{k} \vec{r}_\mu) \cos(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref})) + \cos(2\pi \vec{k} \vec{r}_\mu) \sin(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref}))$$

Therefore:

$$\vec{B} = m_{\perp} \sum \frac{3(\vec{a}_i \vec{r}_i \vec{r}_i - \vec{a}_i)}{r_i^3} +$$

$$+ m_{\perp} \cos(2\pi \vec{k} \vec{r}_\mu) \sum \cos(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref})) \left[ \frac{3(\vec{a}_i \vec{r}_i \vec{r}_i - \vec{a}_i)}{r_i^3} \right] +$$

$$+ m_{\perp} \sin(2\pi \vec{k} \vec{r}_\mu) \sum \cos(2\pi \vec{k} (\vec{r}_i - \vec{R}_{ref})) \left[ \frac{3(\vec{b}_i \vec{r}_i \vec{r}_i - \vec{b}_i)}{r_i^3} \right]$$

(C-1)

Finally, the above equation can be rewritten as:

$$\vec{B} = \vec{A} + \vec{B} \cdot \cos \alpha + \vec{C} \cdot \sin \alpha , \quad (C-2)$$

meaning that the magnetic fields at the muon lie on the surface on an inclined conical pyramid (see Figure C-3). The basis of the pyramid is an ellipse described by the last two terms of equation (C-2).

The \(\vec{B}\) and \(\vec{C}\) terms from, Eq. C-2 should be computed for all magnetically inequivalent muon sites.

Figure C-3: The distribution of fields for an incommensurate helical magnetic structure.
Particular case:

If \( \vec{k} \parallel \vec{c} \) and \( \vec{m} \) in the a-b plane (i.e. \( a'=a, b'=b, c'=c, m_l = 0 \)), as it is the case in \( \text{YbNi}_2\text{Si}_2 \) for example, the distribution of the magnetic fields is similar to that obtained in the case of an incommensurate magnetic structure, see Chapter 3.3.1.3 since the first term in Eq. C-2 is zero. Therefore all the results obtained for the incommensurate modulated single-\( k \) structure can be used without restrictions.
Appendix D

The background signal for a high-energy muon beam

In a high-energy muon beam, the muons are generated in bunches at a rate given by the frequency of the accelerator (50.63 MHz at PSI). The bunch structure is diluted during the transport of the beam to the sample region but is still visible in the μSR spectra. The only effect of the beam structure is that it gives an oscillating accidental background (see Figure D-1). Because the muons are counted independently, one by one, the muon beam structure does not affect the μSR signal arising from muon stopped into the sample. Since the background in the fit function is usually treated as time independent (see Chapter 3), in the present situation its time dependency should be taken into account by an additional term.

The μSR spectra should be fitted using:

\[ A \cdot P(t) = A_1 \cdot P_{\text{sample}}(t) + A_2 \cdot e^{0.455t} \cos(2\pi \cdot 50.63 \cdot t + \phi_2) \]

\[ + A_3 \cdot e^{0.455t} \cos(2\pi \cdot 101.26 \cdot t + \phi_3) + \ldots + \text{BG} \]  

where the first term represents the signal from the sample (see e.g. Chapter 5). The following terms fit the oscillating background while the last term is the usual time independent background. The positive relaxation (0.445 = 1/τμ, with τμ the muon lifetime) compensates for the muon decay in the fitting procedure. The frequencies are the accelerator frequency and harmonics of it. These frequencies are clearly observable in a Fourier transform of the μSR spectra, see Figure D-2.
Appendix E

Applying the pressure

The steps that should be followed while preparing and using the pressure cell (Figure 5-6) are described below:

- Verify that the space for the teflon cap (STC) is clean and not rough. It can be polished using diamond paste. A rough STC may increase, due to friction, the difference between the applied pressure and the pressure inside the cell.
- A small disk of Pb (around 3 mm diameter and 0.3 mm thickness) is first inserted in the bottom of the cell. It will serve as manometer for determining the pressure (see below).
- Introduce the sample. If the sample is too short, add some extra disks of Cu-Be up to the edge of the sample space.
- Fill the sample space with the transmitting pressure liquid.
- Fill the teflon cup with liquid and close it with the gasket (!! it is assumed that the length of the teflon cup + gasket is 2 mm smaller than the STC).
- Insert the teflon cup + gasket in its position. It is recommended to test this operation firstly by using a cylinder of the same inner diameter like that of the STC but open at both ends.
- Insert the extrusion ring, the piston and the other elements, like in Figures 5-5 and 5-6.
- Mount the cell on its support for applying the pressure (Figure E-1). The pressure-cell support is made in such a way that the cell cannot get stuck inside.

![Figure E-1: Pressure cell on its support, before applying pressure.](image-url)

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• A micrometer (travel dial indicator) measures the travel of the piston (see Figure E-1) when applying pressure. We have used a manual hydraulic press to apply the pressure. During each push, the movement of the micrometer’s needle should be followed carefully. If it keeps moving continuously, after your push, it mean that either there is some leak in the system or there is some plastic deformation of the screws. If you are in the small pressure region (2-3 kbar) you might be in the first situation and increasing the pressure might help might to solve the problem (the extrusion ring get deformed and stops the leakage). If the pressure is high, think twice (but fast), before continuing. Be attentive at all noises that might indicate to you that something is going wrong.

• Close the upper nut, remove the cell from its support, mount-it on the sample stick, insert the coils (taking care that the piece of lead which is inside the cell is more or less positioned in the center of one of the pick-up coils).

• Insert the sample stick into the cryostat. The stick position should be adjusted in such a way that the beam hits the center of the sample. Then you can cool the system and start measuring.
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