Iron based pnictide and chalcogenide superconductors studied by muon spin spectroscopy

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Abstract

In the present thesis the superconducting properties of the Iron-based \( \text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2 \) arsenides, and \( \text{A}_x\text{Fe}_{2-y}\text{Se}_2 \) (\( \text{A} = \text{Cs, Rb, K} \)) chalcogenides are investigated by means of Muon Spin Rotation Spectroscopy. The temperature and pressure dependence of the magnetic penetration depth is obtained from \( \mu \text{SR} \) experiments and analyzed to probe the superconducting gap-symmetries for each samples. The \( \text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2 \) system is described within the multi-gap s+s-wave scenario and results are discussed in the light of the suppression of inter-band processes upon hole doping. Due to the lowered upper critical field \( B_{\text{c2}} \) and reduced \( T_c \), a large section of \( B - T - p \) phase diagram is studied for the hole-overdoped \( x = 1 \) case. By applying hydrostatic pressure, the \( \text{RbFe}_2\text{As}_2 \) system exhibits a classical BCS superconducting characteristics. The \( \text{A}_x\text{Fe}_{2-y}\text{Se}_2 \) chalcogenide represents a system containing magnetically ordered and superconducting phases simultaneously. In all investigated chalcogenide samples, about 90% of the total volume show the strong antiferromagnetic phase and 10% exhibit a paramagnetic behavior. Magnetization measurements reveal a 100% Meissner effect, while \( \mu \text{SR} \) clearly indicates that the paramagnetic phase is a perfect superconductor. Up to now, there is no clear evidence whether the antiferromagnetic phase is also superconducting. The microscopic coexistence and/or phase separation of superconductivity and magnetism is discussed. Moreover, a new hydrostatic double-wall pressure cell is developed and produced, satisfying the demands of \( \mu \text{SR} \) experiments. The designs and characteristics of the new pressure cell are reviewed in the present thesis.
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Symbols, Abbreviations and constants

Symbols

$\pi$  pi-meson
$\mu^-$  Negatively charged muon
$\mu^+$  Positively charged muon
$B$  Magnetic field
$E$  Electric field
$H$  Magnetic flux density
$A$  Vector potential
$\nabla$  Partial derivative operator
$T_c$  Superconducting transition temperature
$B_{c1}$  First critical field in superconductors
$B_{c2}$  Second critical field in superconductors
$j_c$  Critical current
$\lambda$  Magnetic penetration depth
$\xi$  Coherent length
$\Delta$  Superconducting energy gap
$n_s$  Superconducting carrier concentration
Contents

Abbreviations

$\mu$SR  Muon Spin Rotation, Relaxation, or Resonance
NMR  Nuclear Magnetic Resonance
EPR  Electron Paramagnetic Resonance
FLL  Flux Line Lattice
SC  Superconductor
HTSC  High temperature superconductor
BCS  Bardeen-Cooper-Schrieffer theory of superconductivity
GL  Ginzburg-Landau theory of superconductivity
ARPES  Angle-resolved photoemission spectroscopy
STM  Scanning tunneling microscope
LEED  Low-energy electron diffraction
SDW  Spin Density Wave

Constants

Boltzmann constant $k_B = 1.3806488(13) \cdot 10^{-23} \text{ J K}^{-1}$
Planck constant $h = 6.62606957(29) \cdot 10^{-34} \text{ J s}$
Elementary charge $e = 1.602176565(65) \cdot 10^{-19} \text{ C}$
Gyromagnetic ratio of muon $\gamma_\mu = 2\pi \times 135.5378 \text{ MHz T}^{-1}$
Magnetic flux quantum $\Phi_0 = 2.067833758(46) \cdot 10^{-15} \text{ Wb}$
Bohr magneton $\mu_B = 927.400968(20) \cdot 10^{-26} \text{ J T}^{-1}$
1. Introduction

1.1. A brief overview of superconductivity

The discovery of the way to liquify helium by Kamerlingh Onnes, in 1908, gave the opportunity to carry out experiments at extremely low temperatures. This technological progress opened the way to many interesting explorations and led to some of the greatest discoveries of 20th century physics, such as superconductivity. The first low temperature resistivity experiment on a superconductor, which was carried out again by Kamerlingh Onnes [63], was performed on mercury. He observed that the electrical resistivity of Hg went down to 0 below a certain temperature $T_c = 7.2$ K. He also found that above certain values of the external magnetic field $B_{ext} \geq B_c$ and the current $j \geq j_c$, the substance recovers its normal physical properties. He refereed the new phenomenon as superconductivity; the substances exhibiting such a phenomena: superconductors; and $T_c$, $B_c$ and $j_c$: the critical values of temperature, field and current, respectively. Later, many other elements of the periodic system have been found to be superconductive. Their critical temperatures are of the order of a few Kelvin.

The main characteristic of superconductivity is not only the infinite conductivity, but also the so called Meissner effect (perfect diamagnetism) observed first in 1933. Unlike perfect metals, superconductors expel a weak magnetic field from their interior, no matter whether they are cooled below the critical temperature $T_c$ in a magnetic field $B_{ext} < B_c$, or whether the magnetic field is applied after cooling. The Meissner effect was explained by the fact that the surface of the sample begins to run persistent currents, producing the magnetic field which fully compensates the external magnetic field. The density of these persistent currents inside a superconductor decays exponentially as a function of the distance from the surface. The
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characteristic length of this decay is called the magnetic penetration depth $\lambda$. The value of $\lambda$ ranges from hundreds to thousands of Ångstroms and becomes infinite at $T > T_c$, that is, when the field completely penetrates the sample. Thus, for all superconductors there is a condition when both resistivity and the magnetic field are zero. In other words, superconductors are perfect diamagnets. It should be noted that the Meissner-effect is fundamentally a new phenomenon which is impossible to be described by classical electrodynamics, even assuming a perfect conductor.

The first attempt of a theoretical explanation of superconductivity appeared in 1935 by the London brothers [85]. According to London theory, the microscopic electric and magnetic fields are described by two basic equations:

$$\vec{E} = \Lambda \frac{\partial \vec{j}_s}{\partial t}$$

(1.1)

$$-\frac{1}{\Lambda} \vec{B} = - \text{curl} \vec{j}_s$$

(1.2)

where $\vec{E}$ is electric field vector; $\vec{B}$ is the magnetic induction; $\vec{j}_s$ is the superconducting current density. $\Lambda = \lambda^2 \mu_0$ is a phenomenological parameter. The London theory gave some quantitative explanation of superconductivity but there was not a sufficient agreement with experiment. In 1957, the microscopic theory was proposed by Bardeen, Cooper and Schrieffer, now shortly called the BCS theory [8]. The main argument was proposed by Cooper in 1956 [31] he demonstrated that an arbitrary small attractive potential between electrons, will result in a bound state (Cooper pairs) with an energy gain with respect to the Fermi level. The BCS theory shows that the electron pairs form a highly coherent state: the condensate. To break this condensate a finite energy is required. Hence, an energy gap $\Delta$ for the condensate excitations appears, which is related to the critical temperature $2\Delta(0) = 3.528 k_B T_c$. In the BCS theory, the weak attractive interaction between electrons is caused by electron-phonon interaction, leading to the formation of Cooper pairs with equal and opposite momentum and spin occupying the ground state.

The perfect agreement between theory and experiments in the case of classical superconductors stimulated the wide acceptance of the BCS theory and the authors
1.1. A brief overview of superconductivity

won the Nobel price. Despite of this big success, the BCS theory was unable to explain some phenomena, in particular when the energy gap is not constant in space. For such situation, the GL theory is much more appropriate. Seven years before BCS, in 1950, V.L. Ginzburg and L. Landau introduced their theory (GL theory) \[79\] by generalizing the Landau’s theory of second-order phase transitions with a complex pseudo wave-function $\psi$ as an order parameter. By applying the Ginzburg-Landau theory for superconductors one can extract two characteristic length scales: (i) the Landau penetration depth for external magnetic fields $\lambda$ (see above); and (ii) the Ginzburg-Landau coherence length $\xi$. This length defines the distance over which $\psi$ can vary.

At the beginning the GL theory was not appreciated and later it was shown by Gor’kov \[49\] that GL theory is a limit of BCS theory valid near $T_c$. The distance $\xi$ can be associated to the spatial extension of the Cooper pairs. The superconductors where $0 < \lambda / \xi < 1 / \sqrt{2}$, that is $\xi \gg \lambda$, are called the Type-I superconductors; and those with $\lambda / \xi > 1 / \sqrt{2}$ Type-II superconductors. In the Type-II superconductors, external magnetic fields above a first and below a second critical field $B_{c1} < B_{ext} < B_{c2}$ destroy the Meissner state and penetrate into the superconductor forming a regular array of flux tubes, the so called Abrikosov Flux Line Lattice (FLL). Each flux carries a quantum flux $\Phi_0 = \frac{hc}{2e}$ \[3\].

During the following decades many experimental and theoretical work were devoted to superconductivity. In particular, many experimental groups were searching for superconductors with a high $T_c$.

In this respect, the discovery by Bednorz and Müller in 1986 was a big step forward opening the way to a broad range of practical applications for superconductors \[9\]. They discovered superconductivity in the complex, layered structure La-Ba-Cu-O ceramics. This discovery is considered as the beginning of a new era, the so-called high-temperature superconductivity (HTSC). In the following years, many HTSC were synthesized and the critical temperature raised rapidly. In all these cases the copper-oxide plane was the main ingredient in the structure of the superconductors. These systems are shortly referred to as cuprates. The discovery raised also the hope for the existence of room-temperature superconductors. The investigation of HTSC brought up more puzzling questions and the exact mecha-
nism governing the superconductivity is not yet clear.

The cuprate HTSCs belong to the class of unconventional superconductors. This means that the pairing mechanism is most probably not arising from phonons and that the symmetry of the energy gap is lower than the symmetry of the underlying Fermi surface. They are characterized by a layered structure which become superconducting under electron or hole doping of the copper-oxide planes. In the undoped state cuprates are in an antiferromagnetic (AF) phase. However, when doped (replacing some of the ions with other elements with different electronic configuration) it first turns into a reasonable conductor exhibiting the pseudo-gap phase. This phase is generally a conductor but with different properties from usual metallic conductors. At some level of doping cuprates become superconducting and the region where a maximum $T_c$ is observed is called the optimally doped region. Nowadays the cuprates are considered as one of the best studied family of complex materials and more than several hundred thousand research papers are devoted to them. Despite the efforts, the main problems are still unsolved. The microscopic mechanism governing the superconductivity is unknown and the origin and nature of the different phases is generally not yet understood. Many review articles are devoted to the cuprate HTSCs (see for example [74, 131, 13]).

The next generation of high-temperature superconductors are the iron-based superconductors containing conducting layers made of iron and a pnictide or chalcogenide element. The era of the iron-based superconductors, often referred as iron age, started in 2006 with the discovery of superconductivity in LaFePO [64], though the critical temperature was only 4 K. In early 2008, the discovery of superconductivity in Fe-containing fluorine-doped lanthanum oxygen iron arsenide LaO$_{1-x}$F$_x$FeAs [65] attracted an renewed attention of physicists and chemists worldwide. The discovery was somewhat surprising as $T_c = 26$ K is rather high despite the presence of iron in the system. Physicists are trying to understand the superconductivity and in particular search for possible similarities between cuprates and Fe-based SCs. Both classes show critical temperatures which may exceed 50 K, and have a layered crystal structure. In both classes superconductivity emerges upon carrier doping starting from antiferromagnetically ordered parent compounds. Despite some similarity there exist many differences, especially
1.1. A brief overview of superconductivity

Figure 1.1.: Conductive layers in cuprate and Fe-based HTSCs. Small arrows indicate the direction of magnetic moments in the undoped state. The graph is taken from [28]

in their electronic configuration. Undoped cuprates are insulators, more specific “Mott-insulators”. Mott-insulators are fundamentally different from a conventional insulator. The electrons are frozen on their respective positions due to strong on-site repulsion energy $U$ and only virtual hopping occurs between the sites. On the other side, most Fe-based SCs behave in the normal state as a semimetal with a tendency towards antiferromagnetic Spin Density Wave (SDW) transitions [18, 88]. The pairing mechanism in these systems is still unknown. Some measurements point to a coupling through magnetic spin fluctuations. A comparison of the phase diagrams of cuprates and Fe-based SC reveals that at low doping level they all show magnetic order. The superconducting phase occurs at some doping level where the magnetic ordering disappears [179]. That is, in all these systems magnetism must be suppressed prior to form a bulk superconducting phase.

It is noticeable that for the iron based systems, the Fe-As-Fe bond angle decreases systematically with increasing $T_c$ and reaches its maximum value for the ideal FeAs tetrahedral angle. Obviously, any distortion from the ideal FeAs tetrahedron is critical and must be taken into account to understand the mechanism of high-Tc superconductivity in these Fe-based materials. So far, five basic tetragonal crystallographic structures have been identified in Fe-based SCs showing supercon-
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ductivity. They are often referred as the 11, 111, 1111, 122, and 21311 families. They have a common layered structure based on a planar layer of Fe atoms bonded to P or As pnictogen or S, Se, Te chalcogen anions. Depending on the chemical element responsible for building the block layers separating the conducting layers (such as alkali, alkaline earth or rare earth and oxygen/fluorine atoms), Fe-based SCs fall into the different sub-categories. Many experimental and theoretical studies are devoted to the Fe-based SCs. The vast numbers of experimental reports in these systems still require more attention in order to derive a generalized theory of high-temperature superconductivity.

1.2. Aim of the thesis

The main focus of the present thesis is directed to the investigation of the superconducting properties of the Fe-based 122-family by μSR spectroscopy technique. Namely, the system Ba$_{1-x}$Rb$_x$Fe$_2$As$_2$ is studied, one of the basic members of the Fe-based superconductors. Special attention is addressed to the superconducting gap symmetry and its behavior under different circumstances, such as external hydrostatic pressure or changing the doping level. By modifying the doping level, resulting in a change of the lattice parameters, one can compare between hydrostatic and chemical pressures in Ba$_{1-x}$Rb$_x$Fe$_2$As$_2$. A significant part of our investigation is focused on the hole-overdoped case RbFe$_2$As$_2$, where large region of the $B - T - p$ phase diagram is studied. Superconductivity parameters, such as the magnetic penetration depth, gap values and gap-to-$T_c$ ratios are evaluated and tested under hydrostatic pressure.

The second large part of the thesis is dedicated to the investigation of the novel chalcogenide family A$_x$Fe$_{2-y}$Se$_2$ (Cs, K, Rb) with superconducting transition temperatures up to about 32 K. A remarkable observation is that, besides the 100% Meissner state, a strong antiferromagnetic phase with magnetic moments up to 3.3 $\mu_B$ per Fe ion are observed below $T_N = 478$ K, 534 K, and 559 K for A = Cs, Rb, and K, respectively. As the interplay with magnetism is thought to play a major role in understanding the properties of the superconducting state in iron-based systems, main focus has been devoted to this topic. For this purpose, superconducting
and antiferromagnetic phases are investigated by $\mu$SR spectroscopy technique.

The third part of the thesis is devoted to the increase of the upper pressure limit in the hydrostatic pressure cells used for $\mu$SR measurements under pressure. The designs and characteristics of a new double-wall pressure cell is also explained.

1.3. Structure of the thesis

The thesis is organized as follows:

In Chapter 1 a brief review of superconductivity is given emphasizing only the basic characteristics of the phenomenon.

Chapter 2 gives a basic overview of the Iron-based superconductors.

In Chapter 3 a brief description of Muon Spin Rotation Spectroscopy method is given.

In Chapter 4 the design and characteristics of a new double-wall cylindrical shaped hydrostatic pressure cell is presented.

In Chapter 5 a detailed survey of the $\mu$SR experimental investigation of iron pnictides $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ is presented.

In Chapter 6 the experimental results of the $\mu$SR investigation of $\text{A}_x\text{Fe}_{2-y}\text{Se}_2$ ($\text{A} = \text{Cs, Rb, K}$) chalcogenides are presented.

The Chapter 7 concludes the research presented in this thesis.

In Chapter 8 the publications written and the conferences attended by the author are listed.

Appendix A reports the muon sites calculation for the $\text{A}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ systems.
2. Iron based superconductors

Iron-based superconductors represent a new class of high-temperature superconductors (HTSC). In the early 2008, Kamihara et al. discovered a novel fluorine-doped lanthanum oxygen iron arsenide LaO$_{1-x}$F$_x$FeAs [65] system, with $T_c = 26$ K, which generated a new wave of intense investigation of HTSCs. To date, the highest $T_c$ in related superconductors of up to 55 K has been achieved in the samarium compound grown under pressure SmFeAs(O$_{1-x}$F$_x$) [180]. Iron based superconductors have a layer structure with conducting layers made of iron and a pnictide or chalcogenide (As, Se, S or P), which are responsible for the superconductivity. According to the stoichiometry one can split them into several subcategories: The iron chalcogenides Fe$_{1+\delta}$X (X = chalcogenide), called the “11” family [57]; MFeAs (M = alkaline earth), called the “111” family [163]; MFeAsO (M = rare earth elements), called the “1111” family [65]; MFe$_2$As$_2$ (M = alkali metal), called the “122” family [119]; A$_x$Fe$_{2-y}$Se$_2$ (A = Cs, Rb, K, Tl), sometimes called the “122*” family [51]; and the Sr$_2$MO$_3$FePn, (M = Sc, V, Cr), called the “21311” family [107]. The lattice structures of different family of Iron based superconductors are summarized in Fig. 2.1.

The “11”-type family includes the systems FeSe, FeTe$_{1-x}$Se$_x$ and FeTe$_{1-x}$S$_x$, which are the members of the new class of Fe-based HTSCs. This system has the simplest crystallographic PbO-type structure consisting of layers with a Fe square planar sheet tetrahedrally coordinated by the chalcogenide atoms [57]. The starting material is the compound FeSe with $T_c \approx 8$ K at ambient pressure [57]. Upon applying a pressure of 8.9 GPa, the transition temperature rises up to 36.7 K [39, 92] demonstrating that this binary system belongs to the high-temperature superconductors. The superconductivity appears at the proximity to a magnetically ordered state, and is destroyed easily by very small changes in stoichiometry [93]. The
2. Iron based superconductors

system undergoes a structural phase transition at $p = 9$ GPa from a tetragonal to a non-superconducting hexagonal phase [10]. Whereas, FeSe$_{1-x}$ is nonmagnetic at ambient pressure [67], $\mu$SR experiments performed by Bendele et al. showed that the system exhibits an AFM ordering for $p > 0.8$ GPa [11] coexisting with the superconducting state (see Fig. 2.2). This is unexpected since for the other families of iron-based systems, pressure usually destroys magnetism and promote superconductivity.

LiFeAs shows bulk superconductivity at $T_c = 18$ K without additional doping [154]. It crystallizes in the tetragonal PbFCl type crystal structure, with space group $P4/nmm$, and has neither an AFM ordering nor a structural transition. Though a study of $^{75}$As nuclear magnetic resonance showed strong antiferromagnetic fluctuations in the normal state of stoichiometric polycrystalline sample [60].
Figure 2.2.: Phase diagrams of (a) - Fe$_{1.03}$Se$_x$Te$_{1-x}$ and (b) - FeSe$_{1-x}$. The graphs are taken from [70, 10]

The other known superconducting 111 material Na$_{1-x}$FeAs shows a broad transition at $T_c = 23$ K [25], a magnetic transition at $\sim 40$ K [111] and a tetragonal to orthorhombic structural transition at $\sim 50$ K [82]. Despite sharing the same crystallographic type structure Li-111 behaves quite differently from Na-111 when applying a hydrostatic pressure. Pressure suppresses $T_c$ for Li$_x$FeAs [176, 48, 94], while for Na$_{1-x}$FeAs $T_c$ is enhanced to 31 K at 3 GPa [177], reaching the record high $T_c$ in the “111” system. A further increase of the pressure suppresses $T_c$ immensely. Substitution of Fe by Co in NaFe$_{1-x}$Co$_x$As suppress $T_N$ and reduces the size of the ordered moment as revealed by Wright et al. [166]. In this series antiferromagnetism and inhomogeneous magnetism coexist with superconductivity, and the magnetic interaction drives both magnetic long-range order and a structural distortion (see phase diagram 2.3).

MFeAsO$_{1-x}$F$_x$ (M = rare earth) are the most widely investigated members of Fe-based SCs. A first-order-like transition from long-range spin-density-wave (SDW) antiferromagnetic order associated with an orthorhombic distortion to superconductivity in LaFeAsO$_{1-x}$F$_x$ is observed at $x \approx 0.045$ [87]. In this system, the or-
2. Iron based superconductors

Thorhombic distortion and the SDW magnetism have to be suppressed prior that a 100% superconductivity appears. The optimal doping is at \( x \sim 0.15 \) with \( T_c = 47 \) K. Similarly, a progressive suppression of the structural and magnetic-ordering transitions is presented in PrFeAsO\(_{1-x}\)F\(_x\) by doping of fluorine \([124]\). \( T_N \) and the tetragonal-orthorhombic structural transition vanish together in a first-order transition, as the fluorine concentration is approaching the superconductivity phase. An analogous picture is obtained when investigating the F-doped SmFeAsO\(_{1-x}\)F\(_x\) compound \([126]\). Substitution of O by F causes a sharp drop of the magnetic transition temperature, and coexistence of superconductivity and magnetic order is present in a very narrow F-doping range close to a crossover concentration \( x_c = 0.085 \). In general, Sanna et al. \([126]\) suggest a competition between these two order parameters as it is common to many unconventional superconductors. By contrast, in CeFeAsO\(_{1-x}\)F\(_x\), a gradual suppression of \( T_N \) as a function of \( x \) within the orthorhombic phase is observed by neutron scattering \([179]\). As \( x \) increases, the AFM phase disappears more rapidly compared to the structural phase transition. The phase diagrams of MFeAsO\(_{1-x}\)F\(_x\) (M = La, Ce, Pr, and Sm) are shown in Fig. 2.4.

The two-dimensional Fe-based SCs with perovskite-type layers \((\text{Fe}_2\text{As}_2)(\text{Ca}_{n+1}\text{(Sc,Ti)}_n\text{O}_y)\) \((n = 3, 4, 5)\) \([102]\), \((\text{Fe}_2\text{As}_2)(\text{Ca}_{n+1}\text{(Mg,Ti)}_n\text{O}_y)\) \((n = 3, 4)\) \([103, 105]\) and \((\text{Fe}_2\text{As}_2)(\text{Ca}_{n+1}\text{(Al,Ti)}_n\text{O}_y)\) \((n = 2, 3, 4)\) \([104]\) show

![Phase diagram of NaFe\(_{1-x}\)Co\(_x\)As. The graph is taken from [166]](image-url)
Figure 2.4.: Phase diagrams of 1111-family. The graphs in the panel (a) is taken from [87]; (b) - from [179] (c) - from [124]; and (d) - from [126]

bulk superconductivity with transition temperatures of the order of 30-40 K without strong carrier doping. In this family charge carrier doping can be achieved by oxygen doping and by substitution of alkaline earth and transition metal ions in the perovskite layers. It was also found that $T_c$ is maximized when the $a$-axis lengths are close to 3.88 Å [106]. A maximal $T_c \approx 45$ K is obtained in $(\mathrm{Fe}_2\mathrm{As}_2)(\mathrm{Sr}_4\mathrm{Sc}_{2-x}\mathrm{Ti}_x\mathrm{O}_6)$ [26] where superconductivity is induced upon charge doping of the perovskite layers. Also the undoped parent phases such as $(\mathrm{Fe}_2\mathrm{As}_2)(\mathrm{Sr}_4\mathrm{V}_2\mathrm{O}_6)$ [181] and $(\mathrm{Fe}_2\mathrm{P}_2)(\mathrm{Sr}_4\mathrm{Sc}_2\mathrm{O}_6)$ [107] already show superconductivity at 37 K and 17 K, respectively. This new class of layered FeAs-systems have a more complicated crystal structure than that of other members of Fe-based SCs, therefore the electronic structures for this family can be very complex. Indeed the enhanced two-dimensional electronic system increases the
2. Iron based superconductors

![Phase diagram of Sr₄(Mg₀.₅₋ₓTi₀.₅₊ₓ)O₆Fe₂As₂](image)

Figure 2.5.: Phase diagram of Sr₄(Mg₀.₅₋ₓTi₀.₅₊ₓ)O₆Fe₂As₂. The graph is taken from [168]

superconducting transition temperature in these systems and an elucidation of its electronic structure is of interest.

The “122”-family is extensively studied. One has either hole doping with the system (M,K)Fe₂As₂ having \(T_c\) up to 38 K [121, 127] or electron doping with M(Fe,Co)₂As₂ with \(T_c\) up to 23 K [132, 81], where M is an alkaline earth elements. The crystal structure is the tetragonal ThCr₂Si₂ type with space group \(I4/mmm\) [112]. Most members of the “122” family show a tetragonal to orthorhombic transition which is simultaneous with a paramagnetic to antiferromagnetic phase transition at about 140 K (see phase diagrams in the Fig. 2.6).

The most studied system is the hole doped Ba\(_{1-x}\)K\(_x\)Fe₂As₂ with optimal \(T_c\) of 38 K [119]. Several disconnected Fermi-surface sheets and multi-gap superconductivity were observed by ARPES [40], and a perfect agreement with \(\mu\)SR technique is reported [71]. Similarly, the superconductivity is achieved by hole doping in Ba\(_{1-x}\)Rb\(_x\)Fe₂As₂ with a gradual transition from the magnetically ordered ground state [122] to a superconducting state upon substituting Ba with Rb [19, 20, 50]. Again, multi-gap superconductivity in this system was confirmed by our \(\mu\)SR measurements [50]. In RbFe₂As₂, the case of extremely hole-overdoping, is presented multi-gap superconductivity (see chapter 5 and Ref. [136]), and under 1 GPa hydrostatic pressure the smaller gap completely disappears (see chapter 5
In the electron-doped superconductor Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ the magnetic and structural phase transition is observed at 134 K, and both are rapidly suppressed with increasing Co content [29]. The optimal $T_c$ is achieved at $x \sim 0.06$ when the magnetic and structural phase transitions are both totally suppressed. An isovalent doping of phosphorus at the arsenic site in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ leads to gradual transition from spin-density-wave (SDW) to superconductivity [61]. The optimal $T_c = 30$ K coincides to the quantum critical point at $x = 0.32$, where SDW is completely suppressed. There is an overlapping region of SC and SDW on the phase diagram, however, the authors could not confirm the microscopic coexistence of these two phases. In the series of SrFe$_{2-x}$M$_x$As$_2$ (M = transition metals), superconductivity is achieved by substituting Fe atom with Rh, Ir, and Pd elements in the parent compound SrFe$_2$As$_2$ [56]. The optimal $T_c$’s are 21.9, 24.2, and 8.7 K for Rh, Ir, and Pd, respectively. Here, similarly to other members of “122”-family, the AFM order has to be completely suppressed prior to achieve the optimal $T_c$ (see phase diagrams in Fig 2.6).

A very different picture is drawn in the case of the iron-selenide systems...
2. Iron based superconductors

$A_x$Fe$_{2-y}$Se$_2$ ($A = \text{Cs, K, Rb, Tl}$), with $T_c$ up to 32 K [44, 51, 76, 83], where together with the superconducting state, a strong AFM state with magnetic moments up to 3.3 $\mu_B$ per Fe-ion is observed below $T_N = 478$ K, 534 K, and 559 K for $A = \text{Cs, Rb, and K}$, respectively [83, 113, 137, 7]. The average crystal structure of these materials is of the type ThCr$_2$Si$_2$ type (space group $I4/mmm$) [112]. An interesting observation is the electronic and magnetic phase diagram of the $K_x$Fe$_{2-y}$Se$_2$ system as a function of Fe-valence, shown in the Fig. 2.7. The narrow SC state is sandwiched between two AFM insulating phases. These insulating phases are characterized by superstructures built by Fe-vacancy orders [169, 114]. Regions I and III represent long range AFM order. In the region II both phases superconductivity and antiferromagnetism coexist below 30 K. Using a magnetic susceptibility and resistivity measurements Yan et al. cannot confirm a microscopic coexistence of the SC and AFM phases [169]. Studies under external pressure revealed that $T_c$ decreases and superconductivity completely vanishes at a pressure of about 10 GPa. However, when the pressure is increased to 11.5 GPa, superconductivity suddenly reappears and reaches the record for iron selenide temperature of 48.7 K [147]. The study of the interplay between the strong AFM and the SC phase by the $\mu$SR technique is an important topic of the present thesis.

To summarize, each family of iron-based superconductors has its own proper-

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Figure 2.7.: The phase diagram plotted for $T_c$ versus the iron valence. The graph is taken from [169].
ties, but they all share common characteristics. One of the main common properties is that hole and/or electron doping of a non-superconducting parent compound causes superconductivity. Almost all iron-based superconductors have an undoped mother compound which is metallic. SDW or AFM order is present in the phase diagrams of most members of the Fe-based SCs, except LiFeAs and FeSe, which exhibit superconductivity at elevated temperatures without doping or pressure. Due to closely separated electronic bands the Fermi surface of Fe-arsenide SCs is rather complex and consists of various electron and hole pockets. This particular topology of the Fermi surface often leads to a multiband superconducting state. Between some of these bands, nesting conditions are fulfilled. The nesting of the Fermi surface is thought to be responsible for the SDW state, and appears to play an important role for the pairing mechanism of the Cooper pairs. Interband scattering through spin-fluctuations leads in the spin-singlet channel to a gap function changing sign between the distinct bands, i.e. an overall $s\pm$ symmetry. One can note that interband processes enhance $T_c$, and the highest $T_c$ is achieved when static magnetism is destroyed, that is when magnetic fluctuations are maximal. In the chalcogenide systems, the mother compound is a Mott-insulator, and only an electron-like Fermi surface is present below $T_c$. The order parameter is not $s\pm$, but probably with a conventional $s$-symmetry. Moreover, large moment magnetism ($T_N \sim 500$ K) coexist with superconductivity with $T_c \sim 30$ K. Similarly, in many Fe-based SC compounds (for example Ln-1111 and Ba-122), the magnetic phase and the superconducting phase overlap. This led to intense investigations to address the question whether superconductivity and magnetism coexist at the microscopic level, or whether they are phase separated and competitors. As said above, many experiments aimed to determine the pairing symmetry to favor an unconventional pairing mechanism closely related to magnetism. However, the exact nature of the pairing is not yet known. Therefore, each experimental observations have their significance for the overall understanding of the phenomenon of superconductivity in these systems. The present thesis provides an experimental investigation of two families of Fe-based SCs, namely $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ arsenides and $\text{A}_x\text{Fe}_{2-y}\text{Se}_2$ chalcogenides.
3. Muon Spin Rotation Spectroscopy

3.1. Introduction

The particle physics era begun after the discovery of the electron by J.J. Thomson in 1897. In 1937, in the search of the Yukawa’s meson, two independent particle physics groups, Anderson and Neddermeyer on one side and Street and Stevenson on the other, identified the muon ($\mu$) in the cosmic rays [100, 146]. Muons are unstable elementary particles which can also be produced from a pion ($\pi$) decay in particle accelerators. High-intensity muon beams suitable for experiments can be produced in different facilities around the world. 

A first fundamental property which make muons interesting for experiments is the fact that the muons produced are 100% spin polarized. After implanting them into a sample, one can monitor their decay by detecting for positively charged muons a positron which is a product of the muon decay. A second important property of the muon is that the probability distribution of the positron emission has its maximum along the muon-spin direction at the moment of decay. Hence by looking at the positron emission as a function of time and direction, the muons can be used as microscopic local magnetic field probes. The time evolution of the spin polarization of the muon implanted in a sample may be readily monitored giving information on the local fields sensed at the muons sites.

Interestingly, the free muon has the second longest lifetime $\tau_{\mu} = 2.2 \times 10^{-6}$ s after the one of the neutron. Therefore, the typical experimental time window of a $\mu$SR experiment can be up to 10-20 $\mu$s.

The experimental technique which makes use of the muons as a probe has the
3. Muon Spin Rotation Spectroscopy

acronym \( \mu \text{SR} \), denoting Muon Spin Rotation, Relaxation or Resonance. The above described principles on which the \( \mu \text{SR} \) spectroscopy is based were established experimentally by Garwin, Lederman, and Weinrich in 1957 [46]. Two types of muons exist in nature, i.e. positively and negatively charged, which are obtained from the following decays:

\[
\begin{align*}
\pi^+ & \rightarrow \mu^+ + \nu_{\mu} \\
\pi^- & \rightarrow \mu^- + \bar{\nu}_{\mu}
\end{align*}
\]  

Both types of muons are used in \( \mu \text{SR} \) experiments, though \( \mu^- \) behaves as a heavy electron and is easily captured into the atomic orbitals and looses a significant amount of spin polarization. \( \mu^- \) is used only in certain selected areas. On the other hand, the positively charged muon is more popular among the condensed matter experimentalists. \( \mu \text{SR} \) spectroscopy is an important technique in the investigation of condensed matter among other complimentary microscopic methods, such as Mössbauer, NMR, EPR, neutron scattering, etc.

The most intensively studied materials by \( \mu \text{SR} \) technique are superconductors, magnetic materials, metals, semiconductors. One of the advantages of this method is that, unlike Mössbauer and magnetic resonance techniques, the sample does not need special nuclei as one implants polarized muons. Another advantage is the possibility to measure in zero-applied field. Due to its magnetic moment, the muon can sense local magnetic fields as low as \( 10^{-5} \) Tesla. In addition, depending on the resolution of the instrument, internal or external magnetic fields up to 10 Tesla can be detected (see for example the High-Field instrument at the Paul Scherrer Institute). Moreover, adjusting the muon’s energy one can conduct measurements on the surface of a sample, in the bulk, or on very massive targets as cylindrically shaped clamp pressure cells.

Four muon facilities are available around the world. Among them, the most intense one is the Swiss Muon Source (S\( \mu \)S) of the Paul Scherrer Institute (PSI, Villigen, Switzerland) where the measurements presented in this thesis have been performed. The other facilities are i) ISIS pulsed neutron and muon source of the Rutherford Appleton Laboratory (RAL, Didcot, United Kingdom); ii) J-PARC, Proton Accelerator Research Complex (Tokai, Japan); iii) and TRIUMF, Centre
for Molecular and Materials Science (CMMS-TRIUMF, Vancouver, Canada). ISIS and J-PARC are pulsed muon beams, where several thousand of muons are implanted in the sample at the same time. \( S \mu \)-PSI and TRIUMF use continuous muon beams, where an individual muon is implanted in the sample during the specific time period (typically 10 \( \mu \)s). Both types of muons, negative and positive, are available at each muon facility. Throughout the thesis only \( \mu^+ \) were used for all \( \mu \)SR investigations. Therefore, here I shortly review the experimental principles based on \( \mu^+ \).

### 3.1.1. Properties of \( \mu^+ \) muons

In nature, muons are found in the cosmic rays. Cosmic protons, with high energy and infinite lifetime, hit the upper atmospheric nuclei producing pions and neutrinos as decay products. The pion is a short-lived particle and decays in 26 ns still in the atmosphere, and only its decay product, the muon, reaches the surface of the earth. About one muon a minute reaches every square centimeter of the earth’s surface with a mean energy of 2 GeV. Due to their low rate, their high energy and their fully uncontrollable character, the cosmic muons are not suitable for condensed matter experiments. Figure 3.1 represents the pion decay diagram. Note that the pion has a spin \( S = 0 \). The neutrino has only one helicity state, that is only left-handed neutrinos are detected up to now in the nature. Hence, the mirror decay (b) and charge conjugation situation (c), in which the neutrino has a positive helicity, are not allowed. Thus the parity violation in the \( \pi \)-decay allows to generate almost 100% polarized muon beam [129, 170].

As an elementary particle, the muon has the basics properties listed in the Table 3.1. The \( \mu^+ \) itself decays with the following processes with the corresponding

<table>
<thead>
<tr>
<th>( \mu^+ ) properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ( m_\mu )</td>
<td>105.657 MeV/c(^2)</td>
</tr>
<tr>
<td>Charge ( q_\mu )</td>
<td>(+e, -e)</td>
</tr>
<tr>
<td>Spin ( S_\mu )</td>
<td>1/2</td>
</tr>
<tr>
<td>Magnetic moment ( \mu_\mu )</td>
<td>( 4.836 \times 10^{-3} \mu_B )</td>
</tr>
<tr>
<td>Gyromagnetic ratio ( \gamma_\mu )</td>
<td>( 2\pi \times 135.5378 \text{ MHz/T} )</td>
</tr>
<tr>
<td>Lifetime ( \tau_\mu )</td>
<td>( 2.197 \mu\text{s} )</td>
</tr>
</tbody>
</table>

Table 3.1.: List of important muon properties.
3. Muon Spin Rotation Spectroscopy

probabilities:

\[ \mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \quad \text{(event probability } P \approx 100\%) \]

\[ \mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu + \gamma \quad \left( P = 1.4 \pm 0.4 \times 10^{-2}\% \right) \]

\[ \mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu + e^+ + e^- \quad \left( P = 3.4 \pm 0.4 \times 10^{-5}\% \right) \] (3.2)

The angular distribution of the emitted positron following the muon decay is expressed as:

\[ W(E, \varphi) = 1 + A(E) \cos(\varphi) \] (3.3)

where \( \varphi \) is the angle between muon spin and emitted positron path, \( A(E) \) is the energy dependent asymmetry parameter. When all positron energies \( E \) are sampled with equal probability then \( A = 1/3 \). Thus, the positrons are preferentially emitted along the muon spin direction at decay time. This property, together with the availability of 100\% polarized muon beams is at the heart of the \( \mu \)SR spectroscopy. By detecting the spatial positron emission as a function of time, one can readily get the time evolution of the muon spin, reflecting the local magnetic field distribution and time evolution at the muon site.

As an example, consider the simplest experimental schematic diagram of a \( \mu \)SR spectrometer depicted in the Fig. 3.2. In this case an external magnetic field \( B_{\text{ext}} \)
3.1. Introduction

Figure 3.2.: Schematic diagram of a $\mu$SR spectrometer.

is applied perpendicular to the incoming muon spin direction (the generalization of the discussion for a spontaneous internal field is straightforward). A muon with the spin $\vec{S}_\mu$ oriented antiparallel to its momentum $\vec{P}_\mu$ first travels through the thin muon detector, starting the spectrometer clock. It then penetrates into the sample and after some thermalization time comes at rest at a site where the electrostatic potential is minimum. The thermalization time lasts few picoseconds depending on the sample material. An important point is that thermalization processes only involve electrostatic interactions, hence not affecting the muon polarization. Following the muon decay a positron is emitted and then detected by one of the positron detector and the clock is stopped. Then this process is repeated several million times and data are collected for further analysis. Once the muon is implanted into the sample it interacts with the local magnetic field $B$ and it spin rotates around it with the Larmor precession frequency $\omega = \gamma_\mu B$. The identification of the positron momentum direction by the positron detectors allows the experimental determination of the muon spin direction at the moment of decay. Collecting several millions of statistics of muons will then modulate harmonically the decay rate of the ensemble in time, obtained from the positron count rate in a single detector. The time interval between the muon implantation and the positron decay is used to build a time dependent rate histogram, which has the form:

$$N(t) = N_0 e^{-t/\tau_\mu}(1 + A_0 P(t)),$$

(3.4)
3. Muon Spin Rotation Spectroscopy

Figure 3.3.: (a) Single detector, and (b) two-detector combined μSR time spectra.

where $N_t$ is the count rate as a function of time; $N_0$ is the initial count rate at time $t=0$; $\tau_\mu$ is the muon lifetime; $A_0$ is the asymmetry parameter; and $P(t)$ is the polarization function describing the evolution of the muon spin orientation over the time and giving the information on the local magnetic field distribution at the muon site. In the case of two “Forward” and “Backward” detectors (see Fig. 3.2), the polarization function is simply expressed from the known counts recorded by the detectors, i.e.:

$$A_0P(t) = \frac{N_F(t) - N_B(t)}{N_F(t) + N_B(t)}. \quad (3.5)$$

The “Forward” denotes the detector located along the direction to which the muon-spin is pointing at time $t =0$ (“Backward” is for the opposite detector). $N_F(t)$ denotes the number of positrons counted by the Forward detector; correspondingly, $N_B(t)$ by the Backward detector. The single detector and the two-detector combined μSR time spectra are presented in the Fig. 3.3. Depending on the sample characteristics and experimental setup (transverse, longitudinal or zero field configuration) $A_0P(t)$ looks different. The further analysis and fitting of the polarization function depend on the physical properties of the investigated material. In the next section of this chapter I will shortly review some details of the analysis for magnetic and superconducting materials and evaluate corresponding polarization functions for each particular case.
3.2. \( \mu^+ \) muons as a probe

3.2.1. Magnetic materials

The muon \( \mu^+ \) as a magnetic probe is particularly indicated for studies of local magnetic fields and fluctuations in magnetic materials. The \( \mu \)SR technique can measure magnetic fluctuation rates in the range of \( 10^4 \) to \( 10^{12} \) Hz, and internal magnetic fields down to \( \sim 10^{-5} \) Tesla. \( \mu \)SR is often the only method to achieve such a sensitivity. Static magnetic order in the material is easy to identify by \( \mu \)SR experiment as one often observes a spontaneous Larmor precession of the muon spin, i.e. oscillations in the \( \mu \)SR spectra in zero applied magnetic field. By determining the magnitude of the oscillations along the different crystallographic directions information about the directions of the local field may be obtained.

In general, the internal local field of the material sensed by the muon can be complex and composed by a sum of several fields of different origins [170]:

\[
\vec{B}_{\text{loc}} = \vec{B}_{\text{ext}} + \vec{B}_{\text{dem}} + \vec{B}_{\text{Lor}} + \vec{B}_{\text{dip}} + \vec{B}_{\text{hf}}. \tag{3.6}
\]

Here \( \vec{B}_{\text{ext}} \) is the external magnetic field (if applied); \( \vec{B}_{\text{dem}} = -N\mu_0\vec{M} \) is the demagnetization field (\( N \) is the demagnetization tensor and \( \vec{M} \) is the macroscopic magnetization of the sample); \( \vec{B}_{\text{Lor}} = \frac{1}{3}\mu_0\vec{M} \); \( \vec{B}_{\text{dip}} \) is the dipolar contribution of the internal field; and \( \vec{B}_{\text{hf}} \) is the hyperfine field contribution.

The dipole field is obtained by performing the sum:

\[
\vec{B}_{\text{dip}}(\vec{r}) = \frac{\mu_0}{4\pi} \sum_i \frac{3(\vec{\mu}_i \cdot \vec{r}_i) \cdot \vec{r}_i - \vec{\mu}_i \cdot \vec{r}_i^2}{\vec{r}_i^5}, \tag{3.7}
\]

where \( \vec{\mu}_i \) is the dipole moment of the lattice atoms; \( \vec{r}_i \) is the radius-vector from the muon site to the \( i \)-th dipole. The sum is performed inside the Lorentz sphere.

The hyperfine field, sometimes called also the Fermi-contact field, is expressed as:

\[
\vec{B}_{\text{hf}}(\vec{r}_\mu) \simeq -\frac{2\mu_0}{3}\vec{\mu}_B|\varphi(\vec{r}_\mu)|^2\langle \hat{s} \rangle \tag{3.8}
\]

\( \langle \hat{s} \rangle \) is the average spin polarization.
In some $\mu$SR measurement configurations the external field is zero and, therefore, the demagnetization field is also absent $\vec{B}_{\text{ext}} = \vec{B}_{\text{dem}} = 0$. In this case, the local field at the muon site is given by:

\[
\begin{align*}
\vec{B}_{\text{loc,AFM}} & = \vec{B}_{\text{dip}} + \vec{B}_{\text{hf}} & \text{for an antiferromagnet;} \\
\vec{B}_{\text{loc,FM}} & = \vec{B}_{\text{Lor}} + \vec{B}_{\text{dip}} + \vec{B}_{\text{hf}} & \text{for a ferromagnet.} \tag{3.9}
\end{align*}
\]

In the case of a ferromagnet, the Lorentz field is related to the saturation magnetization of a domain.

An enormous variety of magnetic and quasi-magnetic materials can be tested by muons in order to map out microscopic field distributions.

As the polarization function $A_0 P(t)$ monitors the properties of the magnetic field at the muon site, it plays an important role during the analysis of $\mu$SR experimental data. Suppose that all of the muons sense the same static magnetic field, oriented at an angle $\theta$ from the initial muon spin $\vec{S}_\mu$ direction, then the Larmor equation yields:

\[
P(t) = \cos^2 \theta + \sin^2 \theta \cos(\omega_\mu t) \tag{3.10}
\]

where $\omega_\mu = \gamma_\mu B_{\text{loc}}$. This is the situation occurring for a single crystal with only one type of localization site. Note that even if the external field is zero, $B_{\text{loc}}$ can be nonzero in a magnetic state. On the other hand, for a magnet in a polycrystalline form the spatial average of Eq. (3.10) has to be taken into account, and one gets:

\[
P_{ZF}(t) = \frac{1}{3} + \frac{2}{3} \cos(\omega_\mu t) \tag{3.11}
\]

If the material is a disordered magnet, then the polarization function is obtained by performing the integration:

\[
P_{ZF}(t) = \int p(\vec{B}_{\text{loc}}) [\cos^2 \theta + \sin^2 \theta \cos(\omega_\mu t)] d^3 \vec{B}_{\text{loc}}, \tag{3.12}
\]

where $p(\vec{B}_{\text{loc}})$ is the probability distribution of the local magnetic fields. Here $\omega_\mu = \gamma_\mu \langle B_{\text{loc}} \rangle$. A damping of the signal occurs as in a field distribution not all muons are experiencing the same local field. This means that different muons do precess with different frequencies resulting in a dephasing of the muon ensemble.
3.2. $\mu^+$ muons as a probe

detectable by a damping of the $\mu$SR signal. The shape of the damping will be connected to the shape of the field distribution. For a very broad field distribution, the local field at the muon site gets a large number of values and the spontaneous precession might even be suppressed during the dead-time of the spectrometer at early time. As a result, a reduced amplitude of the $\mu$SR signal will be detected. Note that a loss of amplitude may also occur with a narrow field distribution if the local field values are very high resulting in muon spins precessing too quickly relative to the time resolution of the spectrometer.

Assuming a Gaussian field distribution, by applying an external field large enough compared to the width of $\vec{B}_{loc}$, then the polarization function for a polycrystal gets the simple Gaussian expression:

$$P_{TF}(t) = e^{-\frac{\sigma^2}{2} t^2} \cos(\omega_{\mu} t) ,$$

(3.13)

where $\sigma^2 = \gamma_{\mu}^2 M_2$, with $M_2$ representing the second moment of the field distribution along the direction of the external field. Note the external field in this case is applied transverse to the initial muon polarization, i.e. $\theta = \pi/2$ (see Eq. 3.10).

In zero field, or in case of longitudinal field configuration (initial muons spin parallel to external field), when the local field distribution is isotropic and Gaussian, then the polarization function is represented by the well-known Kubo-Toyabe function [78]:

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

(3.14)

Here again, the damping $\Delta^2 / \gamma_{\mu}^2$ represents the second moment of the field distribution along one direction perpendicular to the initial muon polarization. Often the Gaussian approximation describes a paramagnetic system fairly well, with a field distribution arising from the nuclear moments. In this case the fluctuations of the electron moments are too fast to be picked-up within the $\mu$SR time-windows. However, if the dynamical processes becomes visible in the $\mu$SR time-window, the Kubo-Toyabe formula does not hold anymore. For that particular case different analytical and complex models are used. In most common cases the polarization function is represented as a sum of oscillating and non-oscillating parts:

$$P_{ZF}(t) = (1 - \alpha) e^{-\lambda t} + a e^{-\lambda t} \cos(\gamma_{\mu} B_{loc} t + \varphi)$$

(3.15)
where the second oscillating part describes the transverse component with relaxation rate of $\lambda_T$ of the muon spin vector with respect to the internal field; and the first non-oscillating term is the longitudinal component of the muon spin vector, relaxing with the rate of $\lambda_L$. Here $\alpha$ is a weight factor of the oscillating component. The typical example of such a polarization function is depicted in Fig. 3.4. The dashed line represents the exponential relaxation function $e^{-\lambda_T t}$ which reflects the relaxation of the transverse component. In the case of a polycrystalline sample, the oscillating component represents $2/3$ of the full polarization function and non-oscillating one is $1/3$.

In some cases the investigated material exhibits a mixture of regions with different magnetic characteristics. These regions can be magnetic and paramagnetic phases and the $\mu$SR technique is very suitable to determine the respective magnetic and paramagnetic volume fractions. In Fig. 3.5 an example is schematically represented. For this example, one assumes that the bulk magnetization is similar for both samples: If the entire volume of the material is homogeneously ordered then all muons basically experience the same local magnetic field and the precession of the spins are in phase. The amplitude of the resultant polarization function determines the magnetic volume fraction. On the other hand, in the case of an inhomogeneous sample a reduced amplitude of the oscillating component is observed in
3.2. \( \mu^+ \) muons as a probe

Figure 3.5.: Schematic of the magnetic volume fraction determination by \( \mu \)SR.

The \( \mu \)SR spectra. Hence, a direct comparison of the oscillating and non-oscillating parts gives the size of magnetic volume fraction. In both cases the observed frequency determines the size of the magnetic moments. To fulfill our assumption that both sample present a similar bulk magnetization, the magnetic moment in the ordered regions for the inhomogeneous sample will be higher that the one of the homogeneous case. The value of the ordered moment is directly proportional to the value of the field sensed by the muon. Thus \( \mu \)SR can extract independently the magnetic volume and the value of the ordered moment.

All experimental techniques have their limitations. \( \mu \)RS has an upper limit for the detection of local magnetic fields. Due to the time resolution of the \( \mu \)SR apparatus (typically about 0.5 ns), field up to several Tesla can be detected. New \( \mu \)SR detectors developed at PSI allow now a determination of internal fields up to 10 Tesla [145]. Usually, the field range available is suitable for measurements of magnetically ordered and spin-glass systems, frustrated spin systems, low-dimensional systems, heavy-fermion systems, molecular magnets and clusters, quasicrystals, as well as superconductors in the vortex state.
3.2.2. Superconducting materials

Superconductors constitute a very important and highly investigated class of materials in condensed matter physics. Many experimental research techniques have been devoted to superconductivity; among them μSR plays an important role. The μSR technique has been used to study a wide range of phenomena in many different classes of superconductors. The most popular and straightforward experiments are the determination of the field distribution due to the vortex lattice and its dynamic in the type-II superconductors. Such studies provide direct information on the absolute value of the magnetic penetration depth and therefore of the superfluid density. From these studies a determination of the upper critical field is sometimes possible. The penetration depth is determined as a function of temperature and other parameters such as magnetic field strength or pressure giving valuable insights for the understanding of the phenomena of superconductivity.

In order to investigate the superconductivity in the mixed state, field cooled experiments in an external field $B_{c1} \leq B_{\text{ext}} \leq B_{c2}$ are performed. The external magnetic field is applied above $T_c$, then the temperature is gradually lowered (field cooling). Then a regular structured FLL is formed below $T_c$. The field around a vortex can be obtained from the London equations:

$$B_v(r) = \frac{\Phi_0}{2\pi \lambda^2} K_0\left(\frac{r}{\lambda}\right)$$  \hspace{1cm} (3.16)

Here, $K_0$ is the modified Hankel-function of the 0-th order; $\lambda = \left(\frac{m^*}{\mu_0 e^2 n_s}\right)^{1/2}$ is the London magnetic penetration depth ($m^*$ is then effective mass of the superconducting carriers; $n_s$ is the density of the carriers); $\Phi_0 = \frac{h}{2e} = 2 \times 10^{-15}$ T m$^2$ is the flux quantum. The Equation (3.16) can be approximated for different limits:

$$B_v(r) \sim \ln\left(\frac{\lambda}{r}\right) + 0.12; \quad \xi \ll r \ll \lambda$$  \hspace{1cm} (3.17)

$$B_v(r) \sim \sqrt{\frac{\pi \lambda}{2r}} e^{-\frac{r}{\xi}}; \quad r \gg \lambda$$  \hspace{1cm} (3.18)

Assuming the Ginzburg-Landau parameter $k = \lambda/\xi \gg 1$, i.e. we neglect the vortex core. The inner spatial field distribution $B(r)$ is given by the modified London’s


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Equation taking into account the flux source given by the vortices:

\[
\vec{B}(\vec{r}) + \lambda^2 (\text{curl} \ \text{curl} \ \vec{B}(\vec{r})) = \Phi_0 \sum_n \delta(\vec{r} - \vec{r}_n) \hat{z} \\
\vec{B}(\vec{r}) - \lambda^2 \Delta \vec{B}(\vec{r}) = \Phi_0 \sum_n \delta(\vec{r} - \vec{r}_n) \hat{z}
\]

(3.19)

The points \( \vec{r}_n \) represent a periodic two-dimensional lattice structure in an ideal vortex. The solution of Eq. (3.19) can therefore be found by using a Fourier transform:

\[
\vec{B}(\vec{r}) = \sum_{\vec{k}} \vec{b}_k e^{i\vec{k}\vec{r}}
\]

(3.20)

where \( \vec{k}_{m,n} = m\vec{a}^* + n\vec{b}^* \) are the reciprocal vectors (\( |\vec{a}^*| = |\vec{b}^*| = \frac{4\pi}{\sqrt{3}d} \)); \( d \) is the distance between the vortices; and \( \vec{b}_k = \frac{1}{S} \int \vec{B}(\vec{r}) e^{-i\vec{k}\vec{r}} d^2\vec{r} \) are the Fourier components with the surface \( S = d^2 \frac{\sqrt{3}}{2} \). The London equation (fields along the z-direction) gives:

\[
\sum_{\vec{k}} (\vec{b}_k + \lambda^2 k^2 \vec{b}_k) e^{i\vec{k}\vec{r}} = N\Phi_0 \sum_{\vec{k}} e^{i\vec{k}\vec{r}}
\]

(3.21)

here \( N \) is a vortex density. From the Eq. (3.21) one finds:

\[
\vec{b}_k = \frac{\langle B_z \rangle}{1 + k^2 \lambda^2} \hat{z}
\]

(3.22)

where \( \langle B_z \rangle \) is the average internal field, often called also the first moment (\( \langle B_z \rangle = N\Phi_0 = |\vec{b}_0| \)). The values of the fields along the z-direction are:

\[
B_z(\vec{r}) = \sum_{\vec{k}} \frac{\langle B_z \rangle}{1 + k^2 \lambda^2} e^{i\vec{k}\vec{r}}
\]

(3.23)

and the second moment \( \Delta \langle B_z^2 \rangle = \langle B_z^2 \rangle - \langle B_z \rangle^2 \) of the distribution can be written as (with \( \vec{b}_0 = \langle B \rangle \)):

\[
\langle \Delta B_z^2 \rangle = \sum_{k \neq 0} |b_k|^2
\]

(3.24)

In the case of a perfect triangular lattice \( k^2 = k_{m,n}^2 = \frac{16\pi}{3d^2} (m^2 + mn + n^2) \), and when \( k^2 \lambda^2 \gg 1 \) (\( \langle B_z \rangle \gg B_{c1} \)), one gets:

\[
\langle \Delta B_z^2 \rangle = \frac{9\Phi_0^2}{32\pi^4\lambda^4} (1 + \frac{1}{3^2} + \frac{1}{4^2} + \frac{1}{7^2} + ...) \quad \text{i.e.:}
\]

\[
\langle \Delta B_z^2 \rangle = \frac{0.00371\Phi_0^2}{\lambda^4}
\]

(3.25)
Hence, the size of $\langle \Delta B^2 \rangle$ is directly related to the magnetic penetration depth $\lambda$. The measurement of the second moment allows the determination of the London penetration depth. The field width in this case is independent of the external field.

The typical field distribution in the type-II superconductor with perfect flux line lattice is depicted in the Fig. 3.6: $\langle B \rangle$ is the constant mean field; $B_{\text{min}}$ is called the minimal field which is in the center of the triangle of vortices forming the hexagonal FLL: $B_{\text{min}} - \langle B \rangle \propto \lambda^{-2}$; $B_{\text{max}}$ is the maximal field, also called the cutoff field, the field in the vortex core: $B_{\text{max}} - \langle B \rangle \propto \lambda^{-4}$; and $B_{\text{sad}}$ is the saddle point field, located in the middle between neighboring vortices: $B_{\text{sad}} - \langle B \rangle \propto \lambda^{-2}$ [16, 142, 90].

In most cases, the second moment of the field distribution is directly obtained from the $\mu$SR time spectra by fitting the polarization function with a Gaussian relaxation function:

$$P(t) = e^{-\frac{\sigma^2}{2}} \cos(\gamma_\mu Bt + \varphi) \quad (3.26)$$

where $\sigma^2 = \gamma^2_\mu \langle \Delta B^2 \rangle = \gamma^2_\mu (\langle B^2 \rangle - \langle B \rangle^2)$, often called the second moment, is the Gaussian relaxation rate arising from the field distribution from the vortex lattice. In this case, one assumes implicitly that $p(B)$ has a Gaussian shape, which is a good approximation for polycrystalline samples and samples with a high density.
3.2. $\mu^+$ muons as a probe

of pinning centers for the vortices.

Better results are obtained when fitting the polarization function with a sum of $N$ Gaussian relaxation functions [90]. When more than one Gaussians are used the total second moment has to be considered.

It plays an important role, whether one measures polycrystalline samples or single crystal material. In the case of polycrystalline samples, the grain structure has to be taken into account. If the penetration depth below $T_c$ in the high-temperature superconductors is anisotropic, the average value of all possible orientations of single-crystal grains must be considered in a polycrystalline sample. This leads to a more symmetric $p(B)$, and the Fourier transform of $p(B)$ is now more Gaussian shape. In the experiments with oriented single crystals in the external magnetic field: 

$$\langle \Delta B^2(\theta) \rangle = \langle \Delta B^2(0) \rangle \frac{1}{2} [\frac{1}{2} \sin^2 \theta + \cos^2(\theta)]$$

where $\theta$ is an angle between the external field and crystallographic c-axis. Here $\gamma^2 = m_c^* / m_{ab}^* = \lambda_c^2 / \lambda_{ab}^2$. It means that when $\theta = 0$, $B_{ext}$ is parallel to the c-axis, and the shielding current flows in ab-plane.

The temperature dependence of $\lambda(T)$ provides information on the superconducting gap function. Once the temperature dependence of the depolarization rate $\sigma(T) \propto \lambda^{-2} \propto n_s(T) / m^*$ is obtained from the $\mu$SR experiment, the charge carrier concentration $n_s(T)$ is analyzed as it contains information on the superconducting gap $\Delta(T)$. By considering the thermal population of the Cooper pairs the carrier concentration is:

$$n_s(T) = n_s(0) \left( 1 - \frac{1}{\pi k_B T} \int_0^{2\pi} \int_0^\infty f(\epsilon, T) [1 - f(\epsilon, T)] d\phi d\epsilon \right)$$  \hspace{1cm} (3.27)

where the Fermi function is:

$$f(\epsilon, T) = \frac{1}{1 + e^{\frac{\sqrt{\epsilon^2 + \Delta^2(T, \varphi)} - \Delta(0)}{k_B T}}}$$  \hspace{1cm} (3.28)

and $\epsilon$ is the energy measured from the Fermi level. For the isotropic s-wave pairing the superconducting gap $\Delta(\varphi) = \Delta(0)$ is spherically isotropic, and the solution of Eq. (3.27) when $T \ll T_c$ [97] gives:

$$n_s(T) = n_s(0) \left( 1 - \sqrt{\frac{2\pi \Delta(0)}{k_B T}} e^{-\frac{\Delta(0)}{k_B T}} \right)$$  \hspace{1cm} (3.29)
and the penetration depth is:

\[
\lambda(T) = \lambda(0) \left( 1 + \sqrt{\frac{\pi \Delta(0)}{2k_BT} e^{-\frac{\Delta(0)}{4k_BT}}} \right)
\]  

(3.30)

In the case of \(d\)-wave superconductors, the gap function is given as \(\Delta(T, \varphi) = \Delta(T) \cos(2\varphi)\) and the penetration depth will be:

\[
\lambda(T) = \lambda(0) \left( 1 + C \frac{T}{\Delta(0)} \right)
\]

(3.31)

The conventional BCS superconductors have a \(s\)-wave symmetry gap while most high-\(T_c\) superconductors, basically cuprates, have \(d\)-wave symmetry. The superconducting gap symmetries are tested upon fitting the temperature dependence of the inverse square of the penetration depth \(\lambda^{-2}(T)/\lambda^{-2}(0) = n_s(T)/n_s(0)\), obtained from the \(\mu\)SR measurements. The perfect agreement of ARPES data with \(\mu\)SR measurements in the experiments measuring the penetration depth \([71, 40]\), confirms the reliability of the above presented approach (for the comparison see the Fig. 3.7).

Figure 3.7.: Comparison of the experimental techniques ARPES and \(\mu\)SR (The graph is taken from [40]).
Thus the $\mu$SR spectroscopy may be used to investigate magnetic phase diagrams, spin dynamics and the magnetic properties of superconductors and different class of materials. By the extreme sensitivity of the muon’s magnetic moment $\mu$SR is a unique tool to probe magnetism in matter, as the strength of the ordered moments, dynamical processes, or random fields that are static or fluctuating with time. The investigation of the magnetic penetration depth in superconductors gives the possibility to analyze the pairing symmetries in different class of superconductors. The determination of the order parameters in superconductors may provide valuable information in understanding the phenomena of superconductivity, one of the central problem in the condensed matter physics. The high number of publications demonstrates the enormous potential of muons as a probe of magnetism and superconductivity.
4. High pressure cells

4.1. Introduction

High pressure methods represent a powerful tool for experimenters providing them with the opportunity to investigate the change of the properties of a sample during a controllable change of its volume. Applying pressure may cause a structural, electronic or some others phase transition, which in many cases can be seen as reversible processes, and therefore, is a valuable method for the investigation and comparison of the sample properties in the different states. This method has been especially successfully applied to study superconducting properties. Specifically, an important task is to determine the influence of an externally applied pressure to important parameters such as resistivity, superconducting transition temperature $T_c$, superconducting gap $\Delta$, pseudo-gap, carrier concentration, magnetic penetration depth, exchange interaction, superfluid density, etc. For iron-based systems, external pressure was also used to elucidate the importance of interplanar pairing interactions, or the $T_c$ dependence on the anion height [76].

The most prevalent pressure technique is the diamond anvil cell, which can generate above 400 GPa pressure. It allows one to carry out an experiment at low and high temperatures. Also, measurements at high magnetic fields are possible, since the diamond is a dielectric material. However, it has several disadvantages, which prevent it to be used for $\mu$SR spectroscopy measurements. The main disadvantage is the small size of the sample and the big size of the anvil cells. The required sample volume for a $\mu$SR experiment has an upper limit due to the cryogenic equipment and a lower limit due to the muon beam profile. For a successful $\mu$SR experiment using high-energy muons, it is necessary to have a sample size bigger than $10\times5\times5$ mm. In addition, no material is transparent to muons. Therefore the ratio between
sample size and pressure-cell volume has to be maximized. Hence, it is convenient to use a piston-cylinder system for hydrostatic pressure generation. This system mainly consists of a cylindrically shaped body-cell and piston. Using an external force, the piston compresses a pressure transmitter liquid (typically Daphne oil) and generates a high nearly isotropic pressure on the sample. The highest pressure, achieved with this system, depends on the internal channel dimensions of the cell and the material used for the body-cell cylinders. Experiences shows that the pressure limit is about 3-5 GPa, depending on the geometry of the cells.

The implanted muon in the sample is very sensitive to magnetic field, which makes the $\mu$SR spectroscopy a very useful technique for internal field distribution analysis. Therefore, it is mandatory to use non-magnetic material for the design of pressure cells. The most appropriate materials used in production of piston-cylinder cells are CuBe and MP35N alloys. MP35N material is stronger than CuBe, but have more magnetic centers such as Ni and Co, and has a slight temperature dependent background signal, especially below 5 K. On the other hand, CuBe is free from such centers and has a temperature independent background $\mu$SR signal. For example, CuBe, so called Alloy-25, consist of 2% Beryllium, 0.2% Nickel + Cobalt + Iron, and the rest is Copper [1]. MP35N - consist of 35.24% Nickel, 35.11% Cobalt, 19.48% Chromium, 9.61% Molybdenum and 0.015% Carbon [2]. In spite of a lag in strength, CuBe material is preferred, especially when desired pressure is not grater than 2.0 GPa. The pressure limit for a cylindrically shaped single wall pressure cell is 1.8 GPa at room temperature [5]. which additionally reduces by $\sim$0.3 GPa at low temperatures due to shrinking of the pressure transmitter medium. In order to increase the pressure limit one can find an appropriate strong and nonmagnetic material or alloy, which in turn is the task of metallurgy. Alternatively, one can use the available known alloy and improve the design of the cells for pressure increase purpose. For this reason, a CuBe double-wall pressure cell has been designed as a part of this thesis work. Theoretical calculations, which allowed to increase the upper limit of the hydrostatic pressure, are in good agreement with the experimental results. For example, we got a calculated upper limit of pressure of 2.9 GPa, and experimental tests showed 2.45 GPa. An experimental details are shown in the end of this chapter.
4.2. Pressure measurement method

One of the most important aspects of the $\mu$SR experiments under pressure is the pressure determination. There exist several methods for pressure measurements. For example, manganin gauge [158], which needs additional measurement wires connected to the measurement devices. This resistive method needs a relatively large sample volume, which is not convenient in case of limited space. Another method, used for all $\mu$SR experiments, is to use Lead (Pb), Indium (In) or Tin (Sn) small-size probes, located in the pressure medium together with the sample. The size of the used probe is much less compared to the sample to avoid an additional background $\mu$SR signal. These materials have an experimentally very accurately known pressure dependent SC transition temperature [37], which is monitored independently from the $\mu$SR experiments. When performing $\mu$SR measurements in an applied field, in order to avoid a perturbation of the field distribution seen by the muons stopping in the sample due to a possible Meissner effect of the probe, it is sometimes convenient to use Indium which has a relatively low transition temperature $T_c = 3.40$ K at ambient pressure, compared to Pb ($T_c = 7.20$ K) and Sn ($T_c = 3.73$ K). The experimentally defined $T_c(p)$ relation for Indium can be written as [37]

$$T_c(p) = T_c(0) - (0.3812 \pm 0.002)p + (0.0122 \pm 0.0004)p^2,$$  \hspace{1cm} (4.1)

where $T_c(0)$ is the SC transition temperature of Indium at ambient pressure and $p$ the hydrostatic pressure in GPa. Hence, by carefully measuring the SC transition temperature of the probe, one tracks the hydrostatic pressure applied on the sample. The SC temperature of the probe is determined by AC susceptibility measurements, using a lock-in amplifier [47]. The error of the pressure determination is in an interval of 0.1-0.2 GPa.
4. High pressure cells

![Diagram of excitation and pick-up coils alignment]

Figure 4.1: Schematic diagram of the excitation and pick-up coils alignment relative to the sample and pressure probe.

The AC susceptibility measurement coil system consists of one excitation and two oppositely wounded pick-up coils (see Fig. 4.1). In order to reduce the screening effect 72 Hz alternated signal is used, with an amplitude of $A=0.5-1.0 \text{ Volt}$.

Figure 4.1 exhibits the schematic diagram of the AC excitation and pick-up coils alignment relative to the sample and pressure probe. The important point is that the core medium of the coil system have to be symmetric. More specifically, the magnetic permeability of the core medium must be less temperature dependent and symmetric for both, pick-up and excitation coils. If possible, one should keep away the coils from the tungsten-carbide piston, which gives a highly temperature dependent susceptibility signal.

From the generator, the sinusoidal signal with the frequency of 72 Hz and 0.5-1.0 Volt amplitude is applied to the excitation coil, inductively coupled with the pick-up coils. If the above mentioned requirements of the symmetry is fulfilled, the Lock-in amplifier receives a sinusoidal signal with a much less amplitude than was generated. After cooling down to SC transition temperature of the probe, due to the Meissner effect the signal balance of the pick-up coils is violated. Therefore,
the amplifier receives a step-like increased signal which is recorded by a computer as a function of temperature. A typical measurement of pressure determination, at ambient pressure using Pb probe, is depicted in Figure 4.2. A superimposed signal coming from the sample aimed for $\mu$SR investigation which is always included in the cell together with the pressure probe, has no significant influence on the probe transition signal. Typically, a transition signal of a superconducting $\mu$SR sample is much broader compared to that of the probe, and less temperature dependant in the small temperature region. From the Figure 4.2 one can see that the signal before and after Pb transition is almost flat. The overall picture of the pressure determination system is shown on photo 4.3.

### 4.3. Single-wall pressure cell

The main topics to be considered to design a hydrostatic pressure cell appropriate for $\mu$SR experiments are the dimensions and the material used in its design. The size of the cell is limited by the sample environment (in this case a Janis $^4$He Vaporizer Cryostat) which has a sample holder diametrical space of about 25 mm. The
4. High pressure cells

second restriction comes from the physics itself. Therefore nonmagnetic materials such as CuBe and MP35N are preferred.

Under the influence of any external force a solid material undergoes deformation. In engineering and materials science the stress at which a material begins to deform plastically and could not recover the original shape when the applied stress is removed, is called the yield strength, or yield point. In the literature its common abbreviation is $\sigma$ and the unit is Pascal. Once the external pressure passes the yield point, some fraction of the deformation will permanently and non-reversibly
4.3. Single-wall pressure cell

Figure 4.4.: Single-wall pressure cell diagram. $p_a$ denotes the internal pressure, $p_b$ - the outer one. $a$ is the radius of the sample channel, and $b$ is the radius of the cell layer.

remain. Therefore it is necessary to avoid pressures near the yield stress in the material used for high pressure application. Depending on the shape and geometry of the component loaded under pressure, the yield strength distribution varies throughout the volume of the component. In many cases a piston-cylinder pressure cell is designed approximating it to a long cylinder. The cylindrical geometry simplifies the task and the problem is solved analytically with a picture of stress distribution in the cylinders. For more theoretical interest the reader is referred to Ref. [38].

The yield strength distribution for a single-wall pressure cell has been calculated according to the long-cylinder approximation method. Figure 4.4 exhibits the cross section diagram of single-wall pressure cell. $a$ denotes the radius of internal cylinder, where pressure transfer liquid and the sample are located; $b$ - radius of outer cylinder. During the design and calculation of cylindrical shape pressure cells the main important parameters are radial and tangential components of yield strength, which are expressed as:
4. High pressure cells

\[
\sigma_{t,r} = \frac{p_a a^2 - p_b b^2}{b^2 - a^2} \pm \frac{a^2 b^2}{r^2} \frac{p_a - p_b}{b^2 - a^2},
\]  
(4.2)

where a plus sign corresponds to the tangential component (t), and a minus sign to the radial one (r).

In case that the cylinder is loaded with an internal pressure, and \( p_a = p \); \( p_b = 0 \), from eq. (4.2) the tangential and radial components of the yield strength are expressed as:

\[
\sigma_{t,r} = p \frac{a^2}{b^2 - a^2} (1 \pm \frac{b^2}{r^2}),
\]  
(4.3)

For calculation, the complex yield strength is changed by one equivalent stress expressed as \( \sigma_y = \sigma_t - \sigma_r \); and

\[
\sigma_y = p \frac{2b^2}{b^2 - a^2},
\]  
(4.4)

As an example, in case of a single-wall cylinder we calculated the maximal yield strength which corresponds to the maximal pressure. Here, \( a = 2.5 \) mm is the internal and, and \( b = 12 \) mm is the outer radius of the single-wall cell.

The critical yield strength is \( \sigma_{\text{crit}} = 3.78 \) GPa for CuBe material, with \( p_{\text{max}} = 1.8 \) GPa obtained from the experiment.

\[
\sigma_y = \sigma_t - \sigma_r = \frac{1}{b^2 - a^2} \frac{2a^2 b^2}{r^2} (p_a - p_b),
\]  
(4.5)

when \( r = a \); \( p_b = 0 \); for one layer,

\[
\sigma_{\text{crit}}^{\max} = \frac{2b^2}{b^2 - a^2} p_{\text{a max}}^{\max} = 3.78 \text{ GPa}.
\]  
(4.6)

The important point is that the yield strength value is pressure dependent and the above calculated value of \( \sigma_{\text{crit}}^{\max} \) is utilized for further calculations and design of a double-wall pressure cell. Consider a cylinder with some stress in the wall and
4.3. Single-wall pressure cell

Figure 4.5.: The yield strength distribution in the single-wall pressure cell, when the internal pressure is \( p_a = 1.8 \) GPa

loaded additionally with internal pressure. The stress caused by the internal pressure are defined by the Equation (4.3). The radial and tangential components of the yield strength, as well as the equivalent one, are depicted in Fig. 4.5. Note that the radial component describes a compression, and the tangential one corresponds to a stretch of the material. The upper threshold pressure value, 1.8 GPa, for a single-wall cell is often not sufficient for the investigation of superconducting materials, since upon cooling down to low temperatures the internal pressure decreases by 0.3-0.4 GPa, due to shrinking of the pressure transfer medium. Therefore, it is very challenging to perform additional developments to increase the upper limit of the internal pressure. For this purpose a double-wall pressure cell has been designed and described in the next section of this chapter.
4. High pressure cells

4.4. Double-wall pressure cell

4.4.1. Yield strength distribution in the double-wall pressure cell

As evidenced from experiments, a compressive yield strength is 2-3 times greater than a tensile one. This fact is utilized in constructions of compound cylinders, such as double wall pressure cells. In this case the internal cylinder is crowded into the outer one. In the unloaded case the compressive force, due to the contact of the cylinders, produces a compressive strength on the internal cylinder and while applying the internal pressure the compressive yield strength of the internal cylinder gradually undergoes a transition to the tensile strength passing the zero value; see Fig. 4.8 and 4.9. From eq. (4.5), when $p_a = p_c; p_b = 0; r = c$:

$$p_c = \sigma_{yc} \frac{b^2 - c^2}{2b^2}.$$  \hspace{2cm} (4.7)

For the internal cylinder the external pressure is $p_c (p_b = p_c)$, and

$$\sigma_{ya} = \frac{2c^2}{c^2 - a^2} (p_a - p_c),$$  \hspace{2cm} (4.8)

Figure 4.6.: Double-wall pressure cell diagram. $p_a$ denotes internal pressure, $p_b$ the outer one. $p_c$ the share pressure between inner and outer layers. $a$ is the radius of sample channel, $c$ and $b$ are the radii of internal and outer layers, respectively.
4.4. Double-wall pressure cell

Inserting the eq. (4.7) into eq. (4.8) one gets the equivalent yield strength:

\[ \sigma_{ya} = \frac{2c^2}{c^2 - a^2} (p_a - \sigma_{yc} \frac{b^2 - c^2}{2b^2}). \]  \hspace{1cm} (4.9)

Now, considering the maximum possible yield strength for both cylinders \( \sigma_{ya} = \sigma_{yc} = \sigma_{y}^{\text{crit}} \), the internal pressure is given by

\[ p_a = \sigma_{y}^{\text{crit}} \left( 1 - \frac{a^2}{2c^2} - \frac{c^2}{2b^2} \right). \]  \hspace{1cm} (4.10)

In order to find the maximum of the \( p_a = f(c) \) function (eq. (4.10)), when the \( a \) and \( b \) parameters are fixed, one must take the first derivative equal to zero \( \frac{dp}{dc} = 0 \), which gives \( c = \sqrt{ab} \) (see Fig. 4.7). For example, when \( a = 2.6 \) mm; \( b = 12 \) mm; \( c = 5.58 \) mm we get \( p_a^{\text{max}} = 2.9 \) GPa and a share pressure \( p_c = 1.5 \) GPa. The yield strength distribution for a double-wall pressure cell with internal pressure \( p_a = 0 \) and \( p_c = 0.8 \) GPa is shown in Fig. 4.8 and in the loaded case, \( p_a = 2.9 \) and \( p_c = 1.5 \) GPa - in Fig. 4.9. The most important parameter, equivalent yield strength \( \sigma_y \), for both cylinders have nonzero values due to a contact pressure, but still far from the cryptical threshold (Fig. 4.8). In case of loading, the equivalent strength of the outer cylinder \( \sigma_{yc} \) keeps growing to the positive direction, and for

![Figure 4.7: The dependence of the internal pressure on the c parameter for double-wall pressure cell.](image)

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4. High pressure cells

![Diagram](image)

**Figure 4.8.** Yield strength distribution in the unloaded double-wall pressure cell.

![Diagram](image)

**Figure 4.9.** Yield strength distribution in the loaded double-wall pressure cell.

the inner cylinder $\sigma_{ya}$, initially reduces towards to zero and then goes to positive direction; until both reach the critical value (Fig. 4.9). During subsequent loadings, the compressive stress changes to a tensile one, which gives possibility to gain several GPa and increase pressures limit in this system.
4.4.2. Experimental results

The upper limit of the internal pressure, obtained by a calculation during the design of a double-wall pressure cell, is in good agreement with the experimentally observed limit. The experimental upper limit also depends on the so-called autofrettage effect, denoting a repetition process when any micro-disorder or defects reorder in a material. One can see from Fig. 4.10 how the pressure limit improves in a double-wall pressure cell performed after its assembly and first test. When the cell material goes into a plastic region, the piston position changes rapidly, and one has to stop applying external force immediately to avoid damages on the pressure cell. The plastic regions are clearly seen on the graph by an onset of a vertical curve. The third test of the same pressure cell shows that the maximum pressure at the edge of a plastic region is 2.45 GPa. Note that the previously calculated value is 2.9 GPa, which is reasonable close to the experimental one. A part of the applied force is absorbed by the friction between the O-ring and the walls of cell. This friction is unavoidable as it is necessary to seal and maintain the pressure inside the cell.

Figure 4.10.: Piston position versus applied pressure in the double-wall pressure cell. Red stars correspond to a first test, blue stars - to second test, and black circles - to third test.
4. High pressure cells

cell. In Fig. 4.10, the friction effect is seen as a horizontal regions on the graphs. By reducing the applied force - the coordinates of the piston stays at the same position, while the applied pressure decreases. After decreasing the maximum value by 0.3-0.4 GPa the piston starts to move back.

The disassembled photo of the double-wall pressure cell is shown no the Figure 4.11. The internal cylinder (6) is inserted in the outer one (7) by applying a force equivalent of 15 Tons. The target sample is located in the internal 5 mm diameter channel, together with pressure measurement lead or indium probe. Then the rest volume is filled with the pressure transmitter liquid, Daphne oil, and the cylindrical shaped teflon cup (5) is inserted to seal the sample environment. The teflon cup seals and maintains the pressure up to 0.2-0.3 GPa. For high pressures more hard material is necessary for sealing. The so called O-ring (4) is used for high pressures, made by CuBe alloy and hardened by annealing procedure. To apply pressure, the force transmitter cylinder (3) is used, made by very strong tungsten-carbide alloy. The external force is applied by a tungsten-carbide rod, similar to 3, which goes through the screw (1), and the cup (2) is placed between the tungsten-carbide rods, to maintain the rod (3) in the center. After reaching the desired pressure, the screw (1) is tightened, and the external force is removed. Then the loaded pressure cell is ready for the $\mu$SR measurements.

Figure 4.11.: Disassembled double-wall pressure cell.
Figure 4.12.: Schematic diagram of the double-wall pressure cell.

Here, on the Figure 4.12, the detailed schematic diagram is depicted, produced by the Autodesk Inventor 2010 commercial software.
5. Superconductivity in the \( \text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2 \) and \( \text{RbFe}_2\text{As}_2 \) Iron Pnictides

5.1. Introduction

The ternary compound \( \text{BaFe}_2\text{As}_2 \) with a tetragonal \( \text{I}_4/\text{mmm} \) crystal structure (see Fig. 5.1) undergoes a structural and magnetic phase transition at 140 K [119]. Upon hole doping, achieved by partial substitution of the Ba site with K or Rb, the \( \text{Ba}_{1-x}\text{A}_x\text{Fe}_2\text{As}_2 \) \([123, 19, 50]\) system as a function of \( x \) undergoes a gradual transition from the magnetically ordered ground state to a superconducting state.

![Crystal structure of BaFe$_2$As$_2$ from Rotter et al. [119].](image-url)
Superconductivity in the $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ Iron Pnictides

A critical temperature up to $T_c = 38$ K is achieved for $x = 0.4$. Superconductivity emerges also by applying hydrostatic pressure [54, 95, 108, 151, 182]. For the case where $A = \text{K}$, angle-resolved photoemission spectroscopy (ARPES) and $\mu$SR revealed different hole and electron bands crossing the Fermi level in case of the optimal doped system [40, 71, 173] with a large superconducting energy gap $\Delta_2 = 9.1$ meV around the $\Gamma$ and M points of the FS and the small gap $\Delta_1 = 1.1$ meV around the $\Gamma$ point. The superconducting critical temperature $T_c$ decreases monotonically upon increasing the A content $x$ from the optimal doped to the overdoped region. However, in contrast to the overdoped cuprates, $T_c$ remains finite even at the highest doping level $x = 1$ with $T_c = 2.52$ and 3.5 K for $A = \text{Rb}$ and $\text{K}$, respectively.

In the case of the extremely overdoped $\text{KFe}_2\text{As}_2$ system [128], the Fermi surface around the Brillouin-zone center $\Gamma$ is similar to the optimally doped one ($x = 0.4$); while the two electron Fermi surface pockets, $\gamma$ and $\delta$ bands, are completely absent. The interband scattering suppression in the overdoped region due to the absence of the electron pockets around M point is sketched in Fig. 5.3. Upon increasing
the potassium content towards the hole overdoped region, the binding energy
displacement shifts the $\gamma$ ($\delta$) bands above the Fermi level, i.e., towards the unoccupied side. Interband scattering between the hole ($\alpha$) and electron ($\gamma$, $\delta$) bands, as it was happening in the $x = 0.4$ case, is not anymore possible. As a result, no more nesting conditions are satisfied, and a collapse of $T_c$ might occur. Sato et al., for example, suggest that the interband scattering via the antiferromagnetic wave vector (nesting vector) plays the key role for the occurrence of the high-$T_c$ superconductivity. Therefore, an investigation of the superconducting properties of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ as a function of the Rb content $x$, especially in the hole overdoped region, would provide us additional information. Also a comparison with the optimally doped compounds from the same series, might offer valuable insight about the origin of high-$T_c$ superconductivity in the Fe-based materials.

For this purpose, the superconducting properties of the doped $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ ($x = 0.3, 0.35, 0.4$) system are investigated by means of the $\mu$SR technique. Later in this chapter, we will compare the data with the results of $\text{RbFe}_2\text{As}_2$ (i.e. $x = 1$) and discuss the combined results in light of the suppression of interband processes upon hole over-doping.
5. Superconductivity in the $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ Iron Pnictides

5.2. $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$

5.2.1. Sample Synthesis

Polycrystalline samples of $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ were prepared in evacuated quartz ampoules by a solid state reaction method. $\text{Fe}_2\text{As}$, $\text{BaAs}$, and $\text{RbAs}$ were obtained by reacting high purity $\text{As}$, $\text{Fe}$, $\text{Ba}$, and $\text{Rb}$ at 800, 650, and 500 °C, respectively. The terminal compounds $\text{BaFe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ were synthesized at 950 °C and 650 °C, respectively, using the stoichiometric amounts of $\text{BaAs}$ or $\text{RbAs}$ and $\text{Fe}_2\text{As}$. Finally, the samples of $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ with $x = 0.3$, 0.35, 0.4 were prepared from appropriate amounts of single-phase $\text{BaFe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$. The components were mixed, pressed into pellets, placed into alumina crucibles, and annealed for 100 hours at 650 °C with one intermittent grinding. Powder x-ray diffraction analysis revealed that the synthesized samples are single phase materials.

5.2.2. $\mu$SR measurements

The $\mu$SR measurements presented here, were performed on three samples, $x = 0.3$, 0.35 and 0.4. They are located around the optimally-doped region and were chosen to compare their superconducting characteristics to those of the hole-overdoped system, which is presented in the next section. Figure 5.4(a) exhibits the TF $\mu$SR time spectra measured in an applied field of 0.04 T, above and below $T_c = 36.9$ K, for the $x = 0.3$ case. The strong muon-spin depolarization at low temperatures reflects the formation of the flux-line lattice (FLL) in the superconducting state. The long-lived component detectable at low temperatures corresponds to the muon signal stopped outside the sample in the sample holder or cryostat walls. In a polycrystalline sample the magnetic penetration depth $\lambda$ (and consequently the superconducting carrier concentration $n_s \propto \lambda^{-2}$) can be extracted from the Gaussian muon-spin depolarization rate $\sigma_{sc}(T)$, which reflects the second moment ($\sigma_{sc}^2 / \gamma_\mu^2$) of the magnetic field distribution due to the FLL in the mixed state ($B_{c1} \ll B_{\text{ext}} \ll B_{c2}$).
5.2. \( Ba_{1-x}Rb_xFe_2As_2 \)

The TF polarization function has the following form:

\[
A_0P(t) = A_s \exp\left( -\frac{(\sigma_{sc}^2 + \sigma_n^2) t^2}{2} \right) \cos(\gamma \mu \text{B}_\text{int} t + \phi) + A_{bg} \exp\left( -\frac{\sigma_{bg}^2 t^2}{2} \right) \cos(\gamma \mu \text{B}_\text{bg} t + \phi)
\]  

(5.1)

The ZF polarization function is described by a standard Kubo-Toyabe depolarization function [78]:

\[
A_0P(t) = A_z \left[ \frac{1}{3} + \frac{2}{3} (1 - \sigma_{\text{ZF}}^2 t^2) \exp \left( -\frac{\sigma_{\text{ZF}}^2 t^2}{2} \right) \right]
\]  

(5.2)

Figure 5.4.: (a) Transverse-field (TF) \( \mu \)SR time spectra obtained by field cooling in \( B_{\text{ext}} = 0.04 \text{ T} \) above and below \( T_c \); (b) Zero-field (ZF) \( \mu \)SR time spectra above and below \( T_c \). Both for \( Ba_{0.7}Rb_{0.3}Fe_2As_2 \).
Figure 5.5.: (a) Field dependence of the superconducting muon spin depolarization rate $\sigma_{sc}$ at base temperature $T = 1.7$ K; (b) temperature dependence of $\sigma_{sc}$ with an external field $B_{ext} = 0.04$ T in Ba$_{1-x}$Rb$_x$Fe$_2$As$_2$ ($x = 0.3$, 0.35, 0.4).

Similar to TF, $A_z$ denotes the initial asymmetry, and $\sigma_{ZF}$ is the relaxation rate. The first step of the TF $\mu$SR measurements is to determine the optimal external magnetic field $B_{ext}$ (with $B_{ext} > B_{c1}$) for which a maximal muon spin depolarization rate $\sigma_{sc}$ occurs due to the build-up of a FLL in the mixed state of the superconductor [17]. The field dependence of $\sigma_{sc}$ is obtained upon field cooling from above $T_c$ down to 1.7 K for each data point [see Fig. 5.5(a)]. The optimum field is chosen as 0.04 T as described in the next paragraph and a complete temperature scan was performed with this external field. In polycrystalline samples the magnetic penetration depth, $\lambda(T)$, can be calculated from the Gaussian muon spin depolarization rate $\sigma_{sc}(T)$ by the equation [17]:

$$\frac{\sigma_{sc}^2(T)}{\gamma_\mu^2} = 0.00371 \frac{\Phi_0^2}{A^4(T)},$$

(5.3)

where $\Phi_0 = 2.068 \times 10^{-15}$ Wb is the magnetic-flux quantum. This relation is only valid when the separation between the vortices is smaller than $\lambda$. In this case, according to the London model, $\sigma_{sc}$ is field independent [17]. For this purpose $\sigma_{sc}$ is measured as a function of the applied field at 1.7 K. Each data point is ob-
Figure 5.6.: Temperature dependence of $\lambda^{-2}$ for $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$, measured in an external field of $B_{\text{ext}} = 0.04$ T. (a) $x = 0.3$, (b) $x = 0.35$ and (c) $x = 0.4$. The dashed lines correspond to a single gap BCS $s$-wave model; the solid ones to a two-gap ($s+s$)-wave model.

tained by field cooling the sample from above $T_c$ down to 1.7 K. Figure 5.5(a) shows that $\sigma_{\text{sc}}$ strongly increases with increasing magnetic field until reaching a maximum at $B_{\text{ext}} \approx 0.03$ T and above it appears as nearly constant in the investigated field range. Such a behavior is expected within the London model and is typical for polycrystalline High-$T_c$ superconductors (HTSC) [116]. Note that for very high fields (i.e. for $B_{\text{ext}} \rightarrow B_{\text{c2}}$) one expects that the field distribution will decrease again leading to a decrease of $\sigma_{\text{sc}}$. The field dependence of $\sigma_{\text{sc}}$ implies that, for a reliable determination of the penetration depth, the applied field must be larger than 0.03 T. Then, once the optimal external magnetic field is determined, ZF $\mu$SR measurements are performed to check and compare the relaxation rates above and below $T_c$, to exclude any magnetic disorder and instability. As it shown in Fig. 5.4(b), the ZF relaxation rate $\sigma_{\text{ZF}}$ is small and changes very little between 45 and 1.7 K, reflecting solely the field distribution at the muon site created by the nuclear moments. The results are presented in the Fig. 5.6.

Next, the temperature dependence of the London magnetic penetration depth, $\lambda(T)$, is analyzed within the local (London) approximation ($\lambda \gg \xi$) with the fol-
5. Superconductivity in the $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ Iron Pnictides

Figure 5.7: (a) Superconducting gaps to $T_c$ ratios $2\Delta_{1,2}/k_B T_c$; (b) weighting factor $\omega$; both as a function of the Rb content in $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$. The dashed lines are guide to the eyes.

The following expression [155, 150]:

$$\frac{\lambda^{-2}(T, \Delta_i)}{\lambda^{-2}(0, \Delta_i)} = \frac{n_s(T, \Delta_i)}{n_s(0, \Delta_i)}, \quad (5.4)$$

where $\frac{n_s(T, \Delta_i)}{n_s(0, \Delta_i)}$ is the carrier concentration as a function of temperature, calculated as for Eq. (3.27) in the chapter 3.

Several gap symmetries were checked to describe the temperature dependence of the penetration depth, and as evidenced in Fig. 5.6, only a two-gap model is providing reasonable description. This scenario is obtained on the basis of the so-called $\alpha$-model assuming that the superfluid density is a sum of two components [109]:

$$\frac{\lambda^{-2}(T, \Delta_i)}{\lambda^{-2}(0, \Delta_i)} = \omega \frac{\lambda^{-2}(T, \Delta_1)}{\lambda^{-2}(0, \Delta_1)} + (1 - \omega) \frac{\lambda^{-2}(T, \Delta_2)}{\lambda^{-2}(0, \Delta_2)} \quad (5.5)$$

where $\lambda^{-2}(0, \Delta_i)$ is the inverse square of the penetration depth at zero temperature, $\Delta_i$ is the value of the $i$th ($i = 1$ or 2) superconducting gap at $T = 0$ K, and $\omega$ is a weighting factor. The gap values and their weighting factor contribution $\omega$ as a function of the Rb content are presented in Fig. 5.7 (a) and (b), respectively.

Note that the London penetration depth $\lambda$ for the case of $x = 1$ is obtained from $\sigma_{\text{sc}}$ by a different way, which is described in the next section of this chapter. All
Table 5.1.: List of the superconducting order parameters obtained for polycrystalline samples $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ ($x = 0.3, 0.35, 0.4, 1.0$) by means of the $\mu$SR measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$x = 0.3$</th>
<th>$x = 0.35$</th>
<th>$x = 0.4$</th>
<th>$x = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>36.9(2)</td>
<td>35.8(2)</td>
<td>34.0(2)</td>
<td>2.52(1)</td>
</tr>
<tr>
<td>$\Delta_1$ (mev)</td>
<td>3.2(7)</td>
<td>2.9(8)</td>
<td>1.1(8)</td>
<td>0.15(2)</td>
</tr>
<tr>
<td>$2\Delta_1/k_BT_c$</td>
<td>2.0(5)</td>
<td>1.9(5)</td>
<td>0.8(6)</td>
<td>1.4(2)</td>
</tr>
<tr>
<td>$\Delta_2$ (mev)</td>
<td>9.2(3)</td>
<td>8.8(3)</td>
<td>7.5(2)</td>
<td>0.49(4)</td>
</tr>
<tr>
<td>$2\Delta_2/k_BT_c$</td>
<td>5.8(2)</td>
<td>5.7(2)</td>
<td>5.1(2)</td>
<td>4.5(4)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>0.20(5)</td>
<td>0.21(4)</td>
<td>0.15(3)</td>
<td>0.36(3)</td>
</tr>
<tr>
<td>$\lambda$ (nm)</td>
<td>249(15)</td>
<td>250 (17)</td>
<td>255(9)</td>
<td>267(5)</td>
</tr>
</tbody>
</table>

important superconducting parameters extracted from the data analysis are summarized in the Table 5.1. The ratio $2\Delta_1/k_BT_c$ for the small gap is practically independent of Rb content $x$; while the $2\Delta_2/k_BT_c$ ratio decreases, and the weighting factor $\omega$ increases with increasing $x$. A decrease of the interband scattering will lead to a decrease of the pairing amplitude and the ratios $2\Delta/k_BT_c$ in agreement with the result presented in Fig. 5.7. This result supports an influence of interband scattering processes in optimally hole-doped iron-based 122 superconductors. In the next section of this chapter, $x = 1$ case is investigated supporting the discussion presented in the current section.
The alkali metal iron arsenide RbFe$_2$As$_2$ exhibits type-II superconductivity below $T_c = 2.6$ K found, by Bukowski et al. [20]. The estimated value of the upper critical field at zero temperature, $B_{c2} = 2.5$ T, was obtained from magnetization measurements performed at various field down to 1.5 K in the mixed state and by assuming a temperature dependence provided by the Werthamer-Helfand-Hohenberg theory [165]. Compared to the better known compound BaFe$_2$As$_2$, RbFe$_2$As$_2$ possesses a lower Fermi level and is characterized by the absence of a magnetic instability. The electron deficiency in RbFe$_2$As$_2$ leads also to a decrease of the number of bands contributing to the superconducting state, compared for example to optimally doped one Ba$_{1-x}$Rb$_x$Fe$_2$As$_2$ (see Fig. 5.3). Hence, one expects a strong decrease of the contribution of the electron-like bands at the M point of the Fermi surface. Such a decrease has been observed by angle-resolved photoemission spectroscopy [128] in the analog system KFe$_2$As$_2$, which also presents a case of naturally hole-(over)doped system when compared to the alkaline earth 122 iron-based superconductors.

A further microscopic characterization of the RbFe$_2$As$_2$ compound seems highly mandatory as it may, in comparison with the optimally doped compounds from the same series, provide valuable information on the origin of high-$T_c$ superconductivity in Fe-based materials. Therefore, extended studies under hydrostatic pressure are also performed. Due to its comparatively low upper critical field $B_{c2}$ and its reduced $T_c$, the system RbFe$_2$As$_2$ opens also a unique opportunity to fully study the $B-T-p$ phase diagram of an iron-arsenide compound.

The polycrystalline sample of RbFe$_2$As$_2$ was synthesized in the same way as described in the previous section. For pressure measurements, 8 mm diameter pellets were pressed and annealed at 650 °C for several days in evacuated and sealed silica ampoules. Then, these cylindrical shaped synthesized pellets with a total height of 10 mm were loaded into the CuBe pressure cell using Daphne oil as a pressure transfer medium.
5.3.1. Susceptibility under Pressure

Alternating-Current (AC) susceptibility measurements were performed with a conventional lock-in amplifier at 0, 0.27, 0.46, 0.68 and 0.98 GPa pressures in a temperature interval of 1.4-10 K, using the CuBe single-wall cell, and the very same cell was used for μSR experiments. In order to enhance the amount of muons stopping in the sample and to get a clear and reliable signal from the sample, the single wall pressure cell with a internal diameter of 8 mm was chosen. A disadvantage of this pressure cell is that the maximum available pressure is limited to 1.4 GPa at room temperature, which decreases further by 0.25-0.3 GPa at low temperature due to the shrinking of the pressure transfer medium. The susceptibility data for pressures up to 1.0 GPa together with the pressure dependence of $T_c$ is shown in the Fig. 5.8. For comparison purpose, the $T_c(p)$ values obtained from μSR and susceptibility measurements are plotted together on the panel (b). The superconducting transition temperature of RbFe$_2$As$_2$ is $T_c = 2.55(2)$ K at ambient pressure, and strongly decreases as a function of pressure with a rate of $dT_c/dp = -1.32$ K GPa$^{-1}$, i.e. it is reduced by 52% at $p = 1.0$ GPa. A linear extrapolation of the data shown

Figure 5.8.: (a) AC susceptibility measurements up to 0.98 GPa obtained with the same CuBe pressure cell as used for the μSR experiments. (b) Pressure dependence of $T_c$ from μSR and AC. The red solid line corresponds to a linear fit, and the dashed black line is an extrapolation up to 1.92 GPa.
by a dashed line suggests that superconductivity could be completely suppressed by a pressure of 1.92 GPa.

A similar large negative slope was found in another multi-gap superconductor MgB$_2$, where $T_c$ decreases as a function of pressure at a rate of $dT_c/dp \approx -1.11$ K GPa$^{-1}$ [33, 130]. In most superconductors, $T_c$ is found to decrease under pressure; some exceptions are the cuprate oxides or some iron-based systems, which exhibit a remarkable increase [167, 45]. The observed strong reduction of $T_c$ with increasing pressures for RbFe$_2$As$_2$ could be related to a non-monotonic dependence of $T_c$ on pressure with a reappearance of superconductivity at higher pressures as it was recently observed in another Fe-based superconductor [52, 148]. Therefore, we tested this hypothesis by performing further magnetization studies for pressures up to 5.4 GPa on a commercial Quantum Design 7 T Magnetic Property Measurement System XL SQUID Magnetometer using a home-made diamond anvil cell at temperatures between 1.8 K and 10 K. Small lead (Pb) probes were used for pressure determination utilizing the pressure dependence of $T_{c,Pb}$ [37]. No superconducting transition was detected above the lowest available temperature of 1.8 K up to our maximum pressure of 5.4 GPa.

### 5.3.2. $\mu$SR measurements

The $\mu$SR measurements at ambient pressure were performed without pressure cell. The pressed and synthesized pellet with 10 mm diameter and 3 mm hight was investigated on the πM3 beamline of the Paul Scherrer Institute, using the GPS instrument for temperatures down to 1.6 K and field up to 0.6 T; and the LTF instrument for temperatures down to 0.02 K and up to 1.5 T magnetic fields. The $\mu$SR measurements under pressure were performed on the $\mu$E1 beamline using the GPD instrument equipped with an Oxford sorption pumped $^3$He cryostat at temperatures down to 0.27 K. Data were collected at magnetic fields up to 0.25 T and for the three pressures 0.2, 0.6 and 1.0 GPa.

The TF and ZF $\mu$SR time spectra analysis are very similar to the one described in the previous section of this chapter using the Eq. (5.1) and Eq. (5.2). In Fig. 5.9(a) the temperature dependence of $\sigma_{sc}$ extracted from TF-$\mu$SR measurements in four
external magnetic fields is presented. In addition, ZF-µSR measurements have been performed to check the magnetic properties of the system. No sign of magnetism, neither static order nor slow magnetic fluctuations, has been observed up to the highest pressure, as the zero-field depolarization rates $\sigma_{ZF}$ have similar values above and below $T_c$ excluding the occurrence of additional internal magnetic fields.

As evidenced from Fig. 5.9, $\sigma_{sc}$ is zero above $T_c$ in the paramagnetic state for each pressure point and external magnetic field, and starts to increase when the FLL is formed in the superconducting state. Upon lowering the temperature, $\sigma_{sc}$ increases gradually reflecting the decrease of the penetration depth or, alternatively, the increase of the superconducting density. The overall decrease of $\sigma_{sc}$ at very low temperatures observed upon increasing the applied field is a direct consequence of the decrease of the width of the internal field distribution when increasing the field.

Figure 5.9.: Temperature dependence of the depolarization rate due to the FLL in RbFe$_2$As$_2$. (a) $p = 0$ and $B_{ext} = 0.01, 0.1, 0.5, 1.5, T$; (b) $p = 0.2$ GPa and $B_{ext} = 0.01, 0.1, 0.25 T$; (c) $p = 0.6$ GPa and $B_{ext} = 0.01, 0.1, 0.25$; (d) $p = 1.0$ GPa and $B_{ext} = 0.01, 0.1, 0.25 T$. Red lines are guides to the eye.
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Figure 5.10.: Field dependence of $\sigma_{sc}$ obtained at 1.6 K and analyzed using the Eq. 5.6. Red solid line corresponds to an analysis considering $B_{c2}$ and $\lambda^{-2}$ as the free parameters using Eq. (5.6).

Towards $B_{c2}$.

In order to reproduce the London penetration depth from $\sigma_s(T, B_{ext})$, the Eq. (5.3) is not any more valid, since this equation implies a field independent $\sigma_{sc}$, and since the lower upper critical field is $B_{c2} = 2.6$ T in this particular case. Therefore, one has to use the numerical Ginzburg-Landau model, developed by Brandt [17]. This model allows one to calculate the superconducting carrier concentration with good approximation within the local (London) approximation ($\lambda \gg \xi$, $\xi$ is the coherence length). This model predicts the magnetic field dependence of the second moment of the magnetic field distribution or, alternatively, of the $\mu$SR depolarization rate, which can be expressed as:

$$\frac{\sigma_{sc}^2}{\gamma_\mu} = 7.52 \cdot 10^{-4} (1 - \frac{B_{ext}}{B_{c2}})^2 \left[ 1 + 1.21 (1 - \sqrt{\frac{B_{ext}}{B_{c2}}})^{3/2} \frac{\Phi_0^2}{\lambda^4} \right]$$  \hspace{1cm} (5.6)

In the case of low external magnetic field compared to upper critical field, that is when $B_{ext}/B_{c2} \to 0$, then Eq. (5.6) converges to Eq. (5.3).

As exemplified in Fig. 5.10, $\sigma_{sc}$ is field dependent, and in an external magnetic field of $B_{ext} = 0.64$ T its value is strongly reduced from the maximum value at approximately 0.01 T. The field dependence of $\sigma_{sc}$ was obtained upon field cooling from above $T_c$ down to 1.6 K for each data point. The observed behavior is
in sharp contrast to the situation reported in the Fig. 5.5 for the optimum-doped Ba$_{1-x}$Rb$_x$Fe$_2$As$_2$ systems, where the very weak field dependence at high fields was related to the high values of $B_{c2}$ for these systems. For RbFe$_2$As$_2$, an optimal external magnetic field of 0.01 T was chosen, where FLL is optimally build up, for the next temperature scan measurements.

The field dependence of $\sigma_s$ was analyzed with Eq. 5.6 using the values of the upper critical field $B_{c2}$ given based on magnetoresistivity measurements or by leaving the parameters $B_{c2}$ and $\lambda^{-2}$ free. The latter option provides excellent fits for all temperatures and the corresponding fitted values of the superconducting carrier concentration and of the upper critical fields are reported in Fig. 5.11. An additional point provided by this investigation, is that the penetration depth can be assumed to be field independent. This rules out the possibility that RbFe$_2$As$_2$ is a nodal superconductor, since a field should have induced excitations at the gap nodes due to nonlocal and nonlinear effects, thus reducing the superconducting carrier concentration $n_s$ and therefore affecting $\lambda$ (see for example Ref. [4]).
In a second step, the temperature dependence of the superconducting carrier concentration \( \rho_s = n_s(T)/n_s(0) = \lambda^{-2}(T)/\lambda^{-2}(0) \) is calculated from the inverse square of the penetration depth. The calculation and fitting procedure is described in the previous section, using the Eq. (5.4) and Eq. (5.5). The results for all pressures are depicted in Fig. 5.11.

As a function of the hydrostatic pressure, the superfluid density is only slightly decreased. Up to 0.6 GPa pressures \( \lambda^{-2}(T) \) is well described by a \( s+s \) two-gap model, while at 1.0 GPa, one does not need anymore the \( s+s \) model and a single \( s \)-wave gap scenario (i.e. \( \omega \approx 0 \)) is sufficient to describe the data. An additional support for a two-gap superconducting state could be provided by the observed positive curvatures of the \( B_{c2}(T) \) near \( T_c \), in sharp contrast to the usual \( B_{c2} \) BCS temperature dependence. Similar positive curvature of the \( B_{c2}(T) \) near \( T_c \) were observed in MgB\(_2\) [32, 141] and in the borocarbides [140], where it was explained within a two-gap model. However, one should keep in mind that alternative explanations for the observed positive curvature in \( B_{c2}(T) \) are possible and that complementary measurements, as here our \( \lambda^{-2}(T) \) data, are necessary to draw conclusions. It is notable that upon increasing the hydrostatic pressure above 0.6 GPa the positive curvature of \( B_{c2}(T) \) near \( T_c \) gradually disappears and ends up with a usual BCS temperature dependence shape at 1.0 GPa [Fig. 5.11(a)], giving an additional indication of the disappearance of the smaller gap. The superconducting gaps, gaps-to-\( T_c \) ratios, their contributing weighting factor, as well as \( \lambda^{-2} \) and Ginzburg-Landau parameter, \( \kappa = \lambda/\xi \), as a function of pressure are presented in Fig. 5.12. Both \( \Delta_{1,2} \) gaps gradually decrease and at 1.0 GPa the small gap \( \Delta_1 \) completely disappears [Fig. 5.12 (a)]; correspondingly, its weighting factor is falling from a maximum of \( \omega = 0.36 \) value to 0 [Fig. 5.12 (b)]. The BCS ratios \( 2\Delta_1(0)/k_BT_c = 1.5(1) \) and \( 2\Delta_2(0)/k_BT_c = 4.5(1) \) are relatively independent on pressure up to 0.6 GPa followed by a gradual drop for the large gap value in the absence of the smaller gap. Upon increasing the hydrostatic pressure from 0 to 1.0 GPa, \( T_c \) is reduced by \( \sim 52\% \), while the superfluid density \( \rho \propto \lambda^{-2} \) is decreased only by \( \sim 18\% \). In other words, as shown in Fig. 5.12 (d), the superfluid density weakly depends on the hydrostatic pressure in contrast to the strong dependence of \( T_c \). This is untypical for unconventional high-\( T_c \) superconductors where a
5.3. RbFe$_2$As$_2$

Figure 5.12: Pressure dependence of: (a) the zero-temperature gap values $\Delta_1(0)$ and $\Delta_2(0)$, (b) the weight $\omega$ of the small gap, (c) the BCS ratios $2\Delta(0)/k_BT_c$ for both gaps, and (d) the inverse square of the penetration depth $\lambda^{-2}(0)$ and Ginzburg-Landau parameter $k$. The lines are the guides to the eyes.

The proportionality of this two quantities is usually observed (at least in under- and optimally doped compounds). Using the pressure-dependent values of the penetration depths and upper critical field one can determine the characteristic ratio, known as the Ginzburg-Landau parameter, $\kappa = \lambda/\xi$, determined at our base temperature of $0.27$ K [155]. $\xi$ is the superconducting coherent length calculated from the relation $B_{c2} = \Phi_0/2\pi\xi^2$, where $\Phi_0 = 2.0678\times10^{-15}$ Wb is the magnetic flux quantum. A reduction of $\kappa$ by 50% is found at the highest available pressure of this particular experiment, pointing to a clear shift of the superconducting character of RbFe$_2$As$_2$ away from a strong type-II superconductor towards low $\kappa$ classical BCS superconductors. Interestingly, both $T_c$ and $\kappa$ linearly decrease with pressure and therefore we find the experimental correlation $\kappa \propto T_c$ (see Table 5.2).

Another way to visualize and shed light onto the nature of the superconducting state has been presented by Uemura et al. in Refs. [161] and [160]. Accord-
5. Superconductivity in the $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ Iron Pnictides

According to the so-called "Uemura plot" the universal linear relation between $T_c$ and $\sigma_{sc}(T \to 0) \propto \lambda^{-2}$ has been found for high temperature superconductor cuprates. The critical temperature appears to be proportional to the inverse square of the London penetration depth $T_c \propto \rho_s \propto \lambda^{-2}$ for a large number of cuprate superconductors, but the proportionality constant is different for hole- and electron-doped superconductors [135]. A number of Fe-based superconductors appear to follow the Uemura relation (see Fig.5.13). For comparison reason we include the data points of $\text{RbFe}_2\text{As}_2$ to the Uemura plot. As evidenced from Fig. 5.13, various families of unconventional superconductors including high-$T_c$ Fe-based materials are characterized by small $\lambda^{-2}$ values (superfluid density) compared to their $T_c$; i.e. they exhibit a dilute superfluidity. In contrast, conventional phonon mediated superconductors like elemental metals possess a dense superfluid and exhibit low values of $T_c$. $\text{RbFe}_2\text{As}_2$ falls between these two extreme cases. With increased hydrostatic pressure the critical temperature reduces rapidly compared to the superfluid density, and the relation of $T_c$ to $\lambda^{-2}$ moves closer to the one characteristic for conventional superconductors. The pressure dependent superconducting parameters are summarized in the Table 5.2.

Table 5.2.: List of the pressure dependent parameters obtained from the analysis of $\lambda^{-2}(T)$.

<table>
<thead>
<tr>
<th>$p$ (GPa)</th>
<th>$T_c$ (K)</th>
<th>$\Delta_1(0)$ (meV)</th>
<th>$\Delta_2(0)$ (meV)</th>
<th>$\frac{2\Delta_1(0)}{k_B T_c}$</th>
<th>$\frac{2\Delta_2(0)}{k_B T_c}$</th>
<th>$\kappa$</th>
<th>$\lambda(0)$ (nm)</th>
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<tr>
<td>0.00(0)</td>
<td>2.52(2)</td>
<td>0.15(2)</td>
<td>0.49(4)</td>
<td>1.5(2)</td>
<td>4.5(4)</td>
<td>24(1)</td>
<td>267(5)</td>
</tr>
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<td>0.20(1)</td>
<td>2.28(1)</td>
<td>0.11(3)</td>
<td>0.45(7)</td>
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<td>4.6(7)</td>
<td>21(1)</td>
<td>274(5)</td>
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<td>0.08(4)</td>
<td>0.30(2)</td>
<td>1.1(6)</td>
<td>4.1(3)</td>
<td>17(1)</td>
<td>287(6)</td>
</tr>
<tr>
<td>1.00(2)</td>
<td>1.21(1)</td>
<td>0.00(0)</td>
<td>0.15(1)</td>
<td>0.0(0)</td>
<td>2.9(2)</td>
<td>12(1)</td>
<td>295(6)</td>
</tr>
</tbody>
</table>

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Figure 5.13: Logarithmic plot of Uemura relation for some Fe-based high temperature superconductors. The Uemura relation observed for underdoped cuprates is shown as a black dashed line for electron doping and as a solid line for hole doping [135]. The data are taken from the following references: LaFeAsO$_{1-x}$F$_x$ - [86, 87, 152, 23]. NdFeAs$_{1-x}$F$_x$ - [23, 68]. FeSe$_{1-x}$ - [72, 67]. SmFeAs$_{1-x}$F$_x$ - [68, 36]. CeFeAs$_{1-x}$F$_x$ - [23]. LiFeAs - [115]. CaF$_{1-x}$Co$_x$Fe$_2$As$_2$ - [153]. Ba$_{1-x}$K$_x$Fe$_2$As$_2$ - [71]. Fe$_{1-y}$Se$_{1-x}$Te$_x$ - [73, 12]. Pb, Nb and Ta - [149].
5. Superconductivity in the $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ and $\text{RbFe}_2\text{As}_2$ Iron Pnictides

5.4. Summary

In this chapter, the $\mu$SR and magnetization results obtained on the polycrystalline $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ iron-based system and its hole-overdoped analog $\text{RbFe}_2\text{As}_2$ (i.e. $x = 1$) are presented for ambient and hydrostatic pressures (0.2, 0.6 and 1.0 GPa). Transverse-field as well as zero-field $\mu$SR measurements were performed on the $\text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2$ ($x = 0.3, 0.35, 0.4, 1.0$) systems. The temperature dependence of the magnetic penetration depth $\lambda(T)$ is derived from the Gaussian muon spin depolarization rate $\sigma_{sc}(T)$ and analyzed within the local (London) approximation ($\lambda \gg \xi$) using a two-gap model which is based on the so-called $\alpha$ model. Upon increasing the Rb content the BCS ratio $2\Delta_2 / k_B T_c$ for the large gap gradually decreases, while $2\Delta_1 / k_B T_c$ ratio for the small gap is practically unchanged. Consequently, the superconducting transition temperature is dramatically depressed from optimal one $T_c = 36.9$ down to 2.52 K for the hole-overdoped case $x = 1$. Similarly, as it was pointing out by ARPES measurements in the optimally doped 122-system $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, we attribute these gaps to the hole-like $\alpha$ bands around the $\Gamma$ point of the Fermi surface, and to the hole-bands blades around the $M$ point. Assuming that with increasing $x$ the $\gamma$ and $\delta$ electron-like bands around the $M$ point are shifted to the unoccupied side, one would expect an absence of nesting conditions in $\text{RbFe}_2\text{As}_2$ system. The consequence would be an absence of magnetic order, as it is confirmed by our ZF $\mu$SR data, and a strong decrease of the interband processes between the $\alpha$ and $\gamma(\delta)$ bands. In this respect, it is remarkable to see that the ratio between the gaps values is decreased by a factor more than 2 compared to optimally doped 122-systems. Similarly, the BCS ratio $2\Delta_1 / k_B T_c$ for the small gap that we assign to the $\beta$ band is almost identical to the values observed for optimally doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, i.e. $2\Delta_1 / k_B T_c \approx 1.4$. On the other hand, for the large gap of the $\alpha$ band, this ratio is strongly reduced [71, 42], confirming therefore the possible role played by interband processes which might be related to the collapse of $T_c$ in optimally hole-doped iron-based 122-superconductors. Furthermore, it was found that the superfluid density for the end compound of the series, $x = 1$, is much larger than in other Fe-based and unconventional superconductors. This might indicate a more conventional nature of the superconducting ground state of
5.4. Summary

RbFe$_2$As$_2$. To check this idea, a $\mu$SR investigation on RbFe$_2$As$_2$ was extended by performing measurements under hydrostatic pressure. Also, due to its comparatively low upper critical field $B_{c2} = 2.6(1)$ T and its reduced $T_c = 2.52(2)$ K, this system allowed to study a large section of the $B - T - p$ phase diagram.

As revealed by AC susceptibility measurements, a negative pressure effect is observed on the critical temperature with a rate of $dT_c/dp = -1.32$ K GPa$^{-1}$ in contrast to a positive effect expected for an equivalence of chemical and hydrostatic pressures. The zero temperature values of the London penetration depth $\lambda(0)$, superconducting gaps $\Delta(0)$, upper critical field $B_{c2}$, and Ginzburg-Landau parameter $\kappa = \lambda/\xi$ have been evaluated from the experimental data. The superfluid density was found to be weakly pressure dependent, while $\kappa$ and $T_c$ are linearly reduced by 50% by the application of pressures up to 1.0 GPa. Upon increasing the hydrostatic pressure, the system undergoes a transition from a $s+s$-wave multi-gap superconducting state to a single $s$-wave gap state. Interestingly, the different effects of hydrostatic pressure and reduction of the lattice parameters (sometimes referred as chemical pressure) by substitution with smaller ions on the RbFe$_2$As$_2$ system are observed. As mentioned above, the related compound KFe$_2$As$_2$ is also superconducting with an increased $T_c = 3.8$ K compared to $T_c = 2.6$ K in RbFe$_2$As$_2$. Due to the smaller ionic radius of K$^+$ compared to Rb$^+$ both the $a$- and $c$-axis parameters of KFe$_2$As$_2$ are reduced [127, 19, 120, 122, 121]. In other words, in the up-to-now hypothetical series Rb$_{1-y}$K$_y$Fe$_2$As$_2$ the shrinkage of lattice with increasing $y$ should finally lead to the experimentally observed increased $T_c$. In sharp contrast, the hydrostatic pressure experiments on RbFe$_2$As$_2$ show a strong reduction of $T_c$ with increasing pressure. A possible way out of the apparent discrepancy could be a non-monotonic dependence of $T_c$ on pressure with a reappearance of superconductivity at higher pressures as it was recently observed in another Fe-based superconductor [52, 148]. Therefore, we tested this hypothesis by performing further magnetization studies under high pressure using a diamond anvil cell. No superconducting transition was detected above 1.8 K up to our maximum pressure of 5.4 GPa. Based on these experimental facts, one has to conclude that external pressure is not simply equivalent to a chemical pressure in this particular compound. This is probably related to the different effects of the two forms of pressure.
on the local atomic structure within the FeAs tetrahedra which is known to be one of the governing parameters determining $T_c$ in Fe-based superconductors [96]. Hence, one can highlight three main points in favor of a tendency towards a conventional superconductor BCS behavior:

(i) Upon increasing the hydrostatic pressure the RbFe$_2$As$_2$ compound exhibits a gradual transition from two gap to single gap state ending up with the BCS ratio of $2\Delta/k_B T_c = 2.9(2)$.

(ii) A strong reduction of $\kappa$ from 24 down to 12 is observed, getting closer to the conventional BCS superconductors, and in the limit of high pressures it extrapolates to a value typical for the type I superconductors.

(iii) The Uemura classification scheme shows that with increased hydrostatic pressure the critical temperature reduces more rapidly than the superfluid density, and the relation of $T_c$ to $\lambda^{-2}$ moves closer to the region where low critical temperature and high superfluid density are characteristics for conventional superconductors.

Moreover, $\rho_s$ is only diminished by 18% at $p = 1.0$ GPa indicating that the proportionality of $\rho_s$ and $T_c$ found for several families of under and optimally doped unconventional superconductors does not hold for RbFe$_2$As$_2$ either. On the other hand, these observations are rather typical for classical low temperature BCS superconductors [66]. In addition, the temperature dependence of $\rho_s$ is best described by a two gap s-wave model with both superconducting gaps being decreased by hydrostatic pressure until the smaller gap completely disappears at 1 GPa. Hence, the hydrostatic pressure appears to shift the nature of the ground state of the hole-overdoped RbFe$_2$As$_2$ system to an even more classical superconducting state. The superconducting ground state of the hole-overdoped RbFe$_2$As$_2$ system appears to be rather conventional. Since no superconducting transition was detected above 1.8 K up to 5.4 GPa pressure, one may conclude that external pressure is not equivalent to reduction of lattice parameters in this particular compound. The experimental and theoretical comparisons of the electronic properties of RbFe$_2$As$_2$ under pressure with optimally doped members of the same family should therefore provide new insight into the origin of the high-$T_c$ phenomena in Fe-based superconductors.
6. μSR studies of chalcogenide $A_xFe_{2-y}Se_2$ (A = Cs, Rb, K) superconductors

6.1. Introduction

The chalcogenides are the chemical compounds consisting of one or more chalcogen ions. Together with iron atoms chalcogenides may exhibit superconducting properties. One of the most up-to-now known iron-based selenide superconductor with a simple crystal structure is FeSe$_{1-x}$ with a critical transition temperature of 8 K [57, 65] exhibiting a structural phase transition from tetragonal to orthorhombic below 70 K at ambient pressure [91]. An unusual behavior has been reported in this family under pressure, where one observes that both the magnetic and superconducting phase coexist [11, 92], and their corresponding transition temperatures increase with increasing pressure above 0.8 GPa. Subsequently, the superconducting transition temperature increased up to about 32 K by intercalating alkali atoms between the Fe$_2$Se$_2$ layers, getting $A_xFe_{2-y}Se_2$ and (Tl, A)$_x$Fe$_{2-y}Se_2$ (where A = K, Rb, Cs) structure. The average crystal structure of these materials is of the ThCr$_2$Si$_2$ type (space group $I4/mmm$) [51, 76, 162, 53, 44] (see Fig. 6.1). The lattice parameters of the crystals studied in this work are summarized in Table 6.1. The stoichiometry of the parent compound appears to be near to $A_{0.8}Fe_{1.6}Se_2$, therefore the denomination “245” is often used. Beside the superconducting state, a strong antiferromagnetic state is observed with magnetic moments up to 3.3 $\mu_B$ per Fe ion below $T_N = 478$ K, 534 K and 559 K for A = Cs, Rb and K, respectively [139, 83, 7, 113]. Fe vacancy order has been found to occur below a struc-
6. $\mu$SR studies of chalcogenide $A_xFe_{2-y}Se_2$ ($A = Cs, Rb, K$) superconductors

![Crystal structure of $A_xFe_{2-y}Se_2$.](image)

Figure 6.1.: Crystal structure of $A_xFe_{2-y}Se_2$.

...tural phase transition $T_S$ taking place well above $T_N$ [7, 113, 114].

One of the most fundamental issues in high temperature superconductors is the interplay between antiferromagnetism and superconductivity. Superconductivity in high temperature cuprate superconductors emerges by suppressing an antiferromagnetic (AFM) Mott insulator phase [80]. In iron-pnictide family, superconducting and AFM semimetal phases can coexist [65, 27, 36, 62, 39, 84, 99]. The $A_xFe_{2-y}Se_2$ ($A = K, Rb,$ and Cs) family has a similar crystal structure as the iron-pnictide 122-system, and superconductivity coexist with AFM insulating phases. This latter phase is characterized by a Fe vacancy order superstructure [7, 43, 169].

<table>
<thead>
<tr>
<th>Formula</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$K, Cs, Rb(2a)$</th>
<th>Fe($4d$)</th>
<th>Se($4e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{0.8}(FeSe_{0.98})_2$</td>
<td>3.9038(1)</td>
<td>14.1148(6)</td>
<td>(0, 0, 0)</td>
<td>(0, 0.5, 0.25)</td>
<td>(0, 0, 0.3560(3))</td>
</tr>
<tr>
<td>$Cs_{0.8}(FeSe_{0.98})_2$</td>
<td>3.9601(2)</td>
<td>15.2846(11)</td>
<td>(0, 0, 0)</td>
<td>(0, 0.5, 0.25)</td>
<td>(0, 0, 0.3439(3))</td>
</tr>
<tr>
<td>$Rb_{0.88}(FeSe_{0.91})_2$</td>
<td>3.925</td>
<td>14.5655</td>
<td>(0, 0, 0)</td>
<td>(0, 0.5, 0.25)</td>
<td>(0, 0, 0.34(1))</td>
</tr>
</tbody>
</table>

Table 6.1.: Crystallographic data of $A_xFe_{2-y}Se_2$
6.1. Introduction

There are many experimental evidence for both, coexistence and phase separation of superconductivity and magnetism, but the exact relation between these different phases is still under debate. In the 245 system, first superconductivity disappears and then re-emerges as a second phase by applying the hydrostatic pressure above 11.5 GPa with $T_c = 48$ K [147, 53]. The magnetic phase diagram of $K_xFe_{2-y}Se_2$ investigated by Y. J. Yan et al. [169] shows a $T_c$ dependence on the Fe valence (see Fig. 2.7 in the chapter 2). In the region $1.935 < V_{Fe} < 2.00$, a superconducting phase coexists with a long range AFM order, and outside of this region an insulating state is observed, again, together with long range AFM order.

The angle resolved photoemission (ARPES) experiments on $K_xFe_2Se_2$ (A = K, Cs) revealed an isotropic, nodeless SC gap of value 10.3 meV [178]. Large electron-like pockets are detected at the FS around the zone corners, without the hole pockets around the $\Gamma$ point. The observed Fermi surface topology indicates a different pearing mechanism as it is believed in the case of the optimally doped Iron-based pnictides family, where an interaction between the electron and hole like pockets takes place, and therefore, nesting conditions are necessary ingredient for the superconductivity. Obviously, more work is needed to clarify the symmetry and pairing mechanism of the SC state.

Hence, as a new iron-based chalcogenide superconductors family, the $A_xFe_{2-y}Se_2$ systems have attracted many studies focused on the understanding of the nature of the interplay between the strong magnetic state occurring at high temperature and the superconductivity in the same samples. $\mu$SR [139], transport and magnetization [83], specific heat, magneto-optical imaging [58] and Mössbauer [125] spectroscopy suggest a microscopic coexistence and the bulk character of both strong antiferromagnetism and superconductivity. Some studies claim that superconductivity only occurs in the compositions when the Fe content is compatible with a vacancy order pattern, the ground state of the material becomes metallic and superconductivity sets in [7]. Alternatively, others suggest that superconductivity is achieved when the Fe-vacancies are disordered, and that superconductivity and magnetism occur in the same samples, but microscopically separated [55].

In this work the superconducting and magnetic properties are investigated by $\mu$SR spectroscopy technique.
6. µSR studies of chalcogenide $A_x Fe_{2-y}Se_2$ ($A = Cs, Rb, K$) superconductors

6.2. Magnetic properties

6.2.1. $T_N$ and magnetic volume fractions

By µSR spectroscopy one can detect and investigate the magnetic state and its volume fraction in the sample. For this purpose, weak-transverse-field (WTF) µSR measurements have been performed up to 500 K. µSR measurements in the WTF configuration are used to determine the volume fractions of the sample with and without static magnetic order. A persistent oscillation amplitude in WTF µSR spectra reflects the fraction of the muons ensemble (i.e. fraction of the sample volume) with a nonmagnetic environment. The WTF µSR measurements were performed with static and dynamical helium flow cryostats between 2 and 315 K and with a Janis closed-cycle refrigerator between 300 and 600 K.

Figure 6.2 shows the paramagnetic volume fraction as a function of temperature, obtained from WTF µSR measurements, normalized to its value obtained in the paramagnetic state. Below magnetic ordering temperatures $T_N=478$, 536 K and 557 K ($A = Cs, Rb$ and $K$, respectively), the µSR amplitudes are very low, indicating that the $A_x Fe_{2-y}Se_2$ systems are in a magnetic state. The paramagnetic volume fractions are 5%, 11% and 12% of the total volume of the samples for $A =$
6.2. Magnetic properties

Cs, K and Rb, respectively. Upon increasing the temperature, a step-like increase of the WTF $\mu$SR amplitudes are observed indicating the transition to a paramagnetic state at higher temperatures. The ordering temperature $T_N$ is determined by fitting a Fermi-type function [69]:

$$f(T) = \sum_{i=1}^{2} \left( \frac{(A^i - A^{pm})}{1 + \exp[(T - T^i_N)/\Delta T^i_N]} + A^{pm} \right)$$  \hspace{1cm} (6.1)

Here $\Delta T^i_N$ are the widths, and $T^i_N$ - the corresponding values of the magnetic transitions. $A^i$ and $A^{pm}$ are the normalized WTF amplitudes of the paramagnetic signal, below and above $T^i_N$, respectively.

6.2.2. Muon precession frequencies

As evidenced from WTF $\mu$SR experiment, about 90% of the sample volumes are antiferromagnetically ordered. In the usual experimental setup, using 2-5 million statistics and 900 picosecond resolution, this majority fraction is observed as a very fast damped signal in the muon spin polarization time spectra. In order to investigate this strong internal field and observe a high frequency muon precession signal, increased time window resolution, 600 picosecond, and more than 100 millions of statistics of implanted muons in the sample were used.

Below the magnetic transitions $T_N$ of $A_xFe_{2-y}Se_2$ system, the large internal magnetic fields $B_{int}$ are present due to the magnetic ordering of the moments of iron atoms. The low temperature magnetic structure is very well ordered as evidenced by the oscillations observed in the $\mu$SR spectra shown in Fig. 6.3. Very high $\mu$SR oscillations, $f = 398(2)$ MHz, are observed when the implanted muon spin is aligned perpendicular to the c-axis, for all $A = Cs$, Rb and K samples, but when the muon spin is parallel to the c-axis, only $A = K$ shows a comparatively small amplitude of oscillation with 135 MHz. These observations are consistent with a long range ordered block spin antiferromagnetic state observed for the Fe vacancy ordered structure. From these experimental observations one can conclude that the corresponding internal fields at the muon site due to ordering of Fe moments are along the crystallographic c-axis. For $A = K$ the additional frequency may be caused by a disordered state of Fe moments. At 2 K the internal field
6. $\mu$SR studies of chalcogenide $A_xFe_{2-y}Se_2$ ($A = Cs, Rb, K$) superconductors

![Graphs showing $\mu$SR time spectra and their corresponding Fourier powers for different samples.]

Figure 6.3: $\mu$SR time spectra and their corresponding Fourier powers of $A_xFe_{2-y}Se_2$ ($A = Cs, Rb, K$) series recorded below $T_c$. LR denotes the left-right, FB - forward-backward detectors.

$B_{int}(2K) = 2.929(7)$ T at the muon site is also well defined in the direction of the crystallographic c-axis. As it is depicted in Fig.6.3, high frequencies of muon spin rotations are observed for the left-right detector configuration. The investigated crystals were oriented such that the crystallographic c-axes were aligned parallel to the muon beam. The initial spins of 100% polarized muons were perpendicular to the beam (spin rotated mode). This means that the internal magnetic field, sensed by the implanted muons, is oriented along the c-axis. This conclusion is supported by the fact that no significant oscillations are observed on the forward-backward detectors configuration. Only a minor peak in the fourier transform of forward-backward $\mu$SR time spectra shows a 135 MHz oscillation (see Fig. 6.3(k,l)). Such a different frequency may be a result of a different muon stopping sites within the crystallographic lattice and/or maybe caused by a coexistence of different magnetic phase. To answer this question a more detailed investigation of the 245 system is
6.2. Magnetic properties

6.2.3. Zero Field $\mu$SR investigation

A more detailed investigation of the internal field has been done by measuring the temperature dependence of the high frequency precession of the muon spins in zero-field (ZF) $\mu$SR experiments. For this purpose, about 80 millions of positron events were collected for each temperature points. Again, rotated-spin beam setup and enhanced resolution (600 picosecond) of $\mu$SR time window were used to detect the internal field orientation and its value. As shown in Fig. 6.3 (e, f), Rb$_{0.85}$Fe$_2$Se$_2$ exhibits a very clear and clean oscillation compared to other A = Cs and K samples. Therefore, it has been chosen for the detailed ZF investigation. ZF measurements were carried out for four temperatures and are depicted in Fig. 6.4. The Fourier powers of the low temperature time spectra show relatively sharp and high peaks. As the temperature increases, above 40 K the peak height gradually decreases, and the muons precession frequencies reduces from 397 MHz at 2 K down to 350 MHz at 290 K. The temperature dependence of the observed muon precision frequency

![Figure 6.4: Internal field in Rb$_{0.85}$Fe$_2$Se$_2$.](image)


was fitted with the phenomenological formula [30]:

\[ f(T) = f_0 \cdot [1 - \left( \frac{T}{T_N} \right)^\alpha]^\beta \]  

(6.2)

where \( f_0 = 398(1) \text{ MHz} \), \( \alpha = 2.0(3) \) and \( \beta = 0.4(1) \) are free parameters, and \( T_N \) is fixed at 536 K taken from previous WTF \( \mu \text{SR} \) experiment. The very small difference in the observed frequencies between 2 K and 40 K, that is above and below SC transition temperature \( T_c = 32.6 \text{ K} \), [see Fig. 6.4(b)] might be an indication of the phase separation of superconductivity and magnetism. The difference is 1 MHz, which is in the region of the measurements uncertainty, and prevents to draw any significant conclusion. In the case of coexistence of these phases, one expects more pronounced change of the muon precision frequency above and below \( T_c \).

6.3. Superconducting properties

As evidenced from the WTF \( \mu \text{SR} \) experiment, discussed in the previous sections of this chapter, about 5\%, 11\% and 12\% of the volumes of of the \( \text{A}_x\text{Fe}_{2-y}\text{Se}_2 \) crystals are in the paramagnetic state. These regions, free from the strong antiferromagnetic ordering, allows us to check the superconducting properties of the paramagnetic fractions by \( \mu \text{SR} \) spectroscopy.

As a first step in the investigation of the superconducting properties of the \( \text{A}_x\text{Fe}_{2-y}\text{Se}_2 \) compounds, I performed in-plane zero-field cooling (ZFC) magnetization measurements shown in Fig. 6.5. The samples exhibit sharp superconducting transitions at \( T_c = 27.4(2) \text{ K}, 31.0(2) \text{ K}, \) and \( 32.6(2) \text{ K} \) for \( A = \text{Cs}, \text{K} \) and \( \text{Rb} \), respectively, and a nearly 100% Meissner screening is observed. The values of the respective \( T_c \) are compatible from the ones extracted from resistivity measurements. However, as will be discussed below, the magnetization study alone is not sufficient to claim a 100% superconducting volume fraction [134], even though it is very often used that way. The first step of the \( \mu \text{SR} \) investigation is to check the magnetic properties of the paramagnetic fraction by the ZF and WTF technique. As discussed above, a large fraction of the \( \mu \text{SR} \) signal is wiped out at very early time (i.e. \( t \ll 0.1 \mu\text{s} \)) in the WTF as well as in the ZF measurements, due to a large internal field and/or a broad field distribution in the antiferromagnetic phase of the
6.3. Superconducting properties

sample. Due to the very high damping signal occurring in the antiferromagnetic phase of the sample [139], it is not possible to check any superconducting properties of this fraction. However, as will be discussed below, this does not exclude that such a phase presents also a superconducting state.

From the WTF measurements is derived that about 88% and 89% and 95% of the sample volume for \( A = \text{Rb}, \text{K} \) and \( \text{Cs} \), respectively, represent a strong antiferromagnetic phase. The rest of the signal represents a fraction of the sample volume remaining in a paramagnetic state below \( T_N \). This sample volume fraction is characterized by a weak muon depolarization which is found to be constant between 40 K and 2 K. This temperature independence of the ZF relaxation indicates that 12% (11%) of the Rb (K) sample volume is free of any magnetic transition at least down to 2 K. This remaining paramagnetic fraction of the sample below \( T_N \) opens the possibility to study the superconducting state by \( \mu\text{SR} \), using the TF configuration [143]. The \( A = \text{Cs} \) sample has only 5%, and \( A = \text{Rb} \) and \( \text{K} \) have 10-11% paramagnetic fraction below \( T_N \). Therefore it is more reliable to investigate and check the superconducting properties of these last two samples due to the relatively large paramagnetic volume fractions, compared to \( A = \text{Cs} \).

The typical \( \mu\text{SR} \) spectra, as well as the corresponding Fourier transforms, are

![Figure 6.5: Temperature dependence of the dc magnetic susceptibility obtained in a zero-field cooling (ZFC) procedure. The data were obtained with an external magnetic field of \( \mu_0 H_{\text{ext}} = 30 \mu\text{T} \) applied along the c-axis.](image)

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6. μSR studies of chalcogenide \( A_xFe_{2-y}Se_2 \) (\( A = Cs, Rb, K \)) superconductors

depicted on the panels (a) and (b) of Fig. 6.6 for \( A = Rb \). The TF-μSR time spectra is analyzed using a two-Gaussian depolarization function:

\[
A_0 P(t) = A_{sc} \exp \left( -\frac{(\sigma_{sc}^2 + \sigma_n^2) t^2}{2} \right) \cos(\gamma \mu B_{int} t + \varphi) + A_{bg} \exp \left( -\frac{\sigma_{bg}^2 t^2}{2} \right) \cos(\gamma \mu B_{bg} t + \varphi),
\]

(6.3)

where \( A_{sc} \) is an initial asymmetry, \( B_{int} \) represents the internal magnetic field at the muon site, and \( \sigma_{sc} \) is the Gaussian relaxation rate reflecting the second moment of the magnetic field distribution due to the FLL in the mixed state. \( \sigma_n \), representing the depolarization due to the nuclear magnetic moments, is taken from the fits above \( T_c \) and considered as temperature independent down to 2 K. The second term of Eq. 6.3 represents a background signal (bg) corresponding to muons stopping in the cryostat walls; \( A_{bg} \), \( \sigma_{bg} \) and \( B_{bg} \) denote the initial asymmetry (about 18% of \( A_0 \)), the relaxation rate and magnetic field (which has essentially the value of the external field) sensed by muons stopped in the background.

The next step of the TF μSR measurements is to determine the optimal external magnetic field \( H_{ext} \) (with \( H_{ext} > H_{c1} \)) for which a maximal muon spin depolarization rate \( \sigma_{sc} \) occurs due to the build-up of a Flux Line Lattice (FLL) in the mixed state of the superconductor [17]. The field dependence of \( \sigma_{sc} \) is obtained upon field cooling from above \( T_c \) down to 2 K for each data point (see Fig. 6.7-c). For both Rb- and K-systems, the optimum field is above 0.07 T and a complete temperature scan is performed with this external field applied along the crystallographic c-axis. Figure 6.7-a exhibits for both systems the temperature dependence of the muon depolarization rate \( \sigma_{sc} \) reflecting the field distribution created by the FLL. The temperature dependence of the average value of the internal field \( B_{int} \) sensed by the muon ensemble is reported in Fig. 6.7-b. A clear diamagnetic response of the samples is observed below \( T_c \). Considering an extreme type II superconductor, one can evaluate the London magnetic penetration depth \( \lambda \) and superfluid density \( n_s \) from the second moment of the magnetic field distribution inside the sample in the mixed SC state, or alternatively, from the Gaussian muon spin depolarization
6.3. Superconducting properties

Figure 6.6.: a) Transverse field (TF) $\mu$SR time spectra recorded above and below $T_c$. The TF data have been obtained with an external field of 0.07 T and in a field-cooling procedure. b) Fourier transform of the TF $\mu$SR spectra shown in panel a.

Figure 6.7.: a) Field dependence of the muon depolarization rate above (40 K - open symbols) and below (2 K - closed symbols) $T_c$. The external field was applied along the crystallographic c-axis. b) Temperature dependence of the internal field $B_{\text{int}}$ sensed by the muons. c) Temperature dependence of $\sigma_{\text{sc}} \sim \lambda_{\text{ab}}^{-2}$ and therefore of the superfluid density $n_s(T)$ measured in an applied field of $\mu_0H_{\text{ext}} = 0.07$ T.
6. **μSR studies of chalcogenide** $A_xFe_{2-y}Se_2$ $(A = Cs, Rb, K)$ **superconductors**

Table 6.2.: List of the parameters obtained from the analysis of the $n_s(T)$

<table>
<thead>
<tr>
<th></th>
<th>$Rb_{0.77}Fe_{1.61}Se_2$</th>
<th>$K_{0.74}Fe_{1.66}Se_2$</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>32.6(2)</td>
<td>31.0(2)</td>
<td>K</td>
</tr>
<tr>
<td>$\lambda_{ab}(0)$</td>
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<td>225(2)</td>
<td>nm</td>
</tr>
<tr>
<td>$\Delta(0)$</td>
<td>7.7(2)</td>
<td>6.3(2)</td>
<td>meV</td>
</tr>
<tr>
<td>$2\Delta(0)/k_BT_c$</td>
<td>5.5(2)</td>
<td>4.7(2)</td>
<td></td>
</tr>
</tbody>
</table>

rate $\sigma_{sc}$ [17]:

$$\frac{\sigma_{sc}^2(T)}{\gamma_\mu^2} = 0.00371 \frac{\Phi_0^2}{\lambda_{ab}^4(T)}, \quad (6.4)$$

where $\Phi_0 = 2.068 \times 10^{-15}$ Wb is the magnetic flux quantum, and $\gamma_\mu = 2\pi \times 135.5$ MHz T$^{-1}$ is the muon gyromagnetic ratio. As the external field is applied along the $c$-axis, we are probing the penetration depth $\lambda_{ab}$ in the basal plane. In turn, from the temperature dependence of $\lambda_{ab}$, one obtains the temperature evolution of the superfluid density $n_s$ as $n_s(T)/n_s(0) = \lambda_{ab}^{-2}(T)/\lambda_{ab}^{-2}(0)$. The described analysis neglects any additional contribution to the $\mu$SR relaxation rate due to possible FLL disorder or induced magnetism [144]. Therefore the extracted value of the penetration depth represents a lower limit. The temperature dependence of $n_s$ is analyzed within the framework of a BCS single $s$-wave symmetry superconducting gap $\Delta$ [155, 150]. The results of the analysis for $A_xFe_{2-y}Se_2$ $(A = K, Rb)$ are reported in Fig. 6.7. The solid line represents the fit of simple $s$-wave model to the data. Due to the flattening of $\sigma_{sc}(T)$ below $T_c/2$ a clean $d$-wave model is incompatible with the data. Note that a two gaps $(s+s)$ as well as anisotropic $s$-wave scenarios provide also a satisfactory $\chi^2$ fitting criteria. The parameters extracted from the fitting procedure using the simplest $s$-wave model are summarized in the Table 6.2. The observed values of $2\Delta(0)/k_BT_c$ indicate that the $A_xFe_{2-y}Se_2$ systems are in the strong coupling limit.

The penetration depths obtained from the data analysis correspond to the para-
magnetic fractions representing about 11-12% of a total sample volumes. We note that NMR measurements [156] gave $\lambda = 290$ nm, which is also almost certainly representative for the paramagnetic fraction only since the NMR signal from the strong antiferromagnetic regions of the sample is probably wiped out. On the other hand, macroscopic magnetisation [157] and torque [15] measurements give a considerably longer $\lambda = 580$ and 1800 nm, respectively, since they probably reflect a kind of average over the whole sample. Our analysis provides also a slightly lower value of the superconducting gap than the one measured by ARPES technique [178] (isotropic superconducting gap of 10.3 meV). Figure 6.7-a shows the field dependence at 2 K of the muon depolarization rate obtained upon field cooling from above $T_c$ down to base temperature. Above $\mu_0H_{\text{ext}} = 0.07$ T $\sigma_{\text{sc}}$ decreases only very slightly indicating a high value of the critical field $H_{c2}$. Previous measurements reported values of the order $\mu_0H_{c2}(0) = 60$ T for Rb$_{0.88}$Fe$_{1.76}$Se$_2$ [162] and for K$_{0.8}$Fe$_{1.81}$Se$_2$ [98]. The solid lines in Fig. 6.7-c correspond to fit based on the numerical Ginzburg-Landau model (NGL) with the local (London) approximation ($\lambda \gg \xi$, $\xi$ is the coherence length) [17] for both systems. This model describes the magnetic field dependence of the second moment of the field distribution created by the FLL and therefore the field dependence of the $\mu$SR depolarization rate. Fixing the value of $\mu_0H_{c2}(2K) = 55$ T, found in the literature [162, 98] and considering $\lambda_{ab}$ as a free parameter, we get $\lambda_{ab}(2K) = 246(1)$ and 221(3) nm for A = Rb and K, respectively. These values are in good agreement with the values obtained by studying the temperature dependence of the muon depolarization rate (see Table 6.2).

6.4. Coexistence or phase separation of magnetism and superconductivity

Since the first observation of strong magnetism ($m_{Fe} > 2 \mu_B$ and $T_N = 478$ K) [137] in one of the members of the newly discovered $A_xFe_{2-y}Se_2$ superconductors the most intriguing question to answer by theory as well as by experimental observation is whether or not superconductivity and magnetism may
coexist microscopically or if they are phase separated. Unfortunately experimental techniques that can measure strong magnetism and superconductivity simultaneously on a local scale are lacking. Therefore, conclusions have to be drawn from a combination of observations obtained from two or more experimental methods. There are good arguments for both scenarios. First we will summarize a few arguments in favor of bulk superconductivity. In the majority of the reports on the superconducting properties of the new compounds a 100% Meissner screening is observed by magnetization measurements, for a great variety of compounds (see e.g. Ref. [83]). Even a decent diamagnetic screening is sometimes observed in field cooled magnetization experiments [171]. Also a sizeable peak is observed in specific heat measurements [58, 174, 159] at the superconducting $T_c$. A superconducting volume fraction of 92-98% is estimated from the specific heat data by comparing the zero temperature residual and the normal state Sommerfeld coefficients [159]. These two different macroscopic observations in favor of bulk superconductivity can anyhow be questioned. In samples showing a 100% Meissner response, anomalies in the magnetic hysteresis loop were found that can be understood in the picture that superconductivity in the sample is percolative with weakly coupled superconducting islands [134]. The interpretation of specific heat data in view of the superconducting volume fraction is dangerous since it relies on the determination of the electronic Sommerfeld coefficient which is assumed to be the same for the whole sample. This assumption might not be valid for a potential phase separation into metallic and insulating volumes. A strong evidence for bulk superconductivity comes from magneto-optical imaging [58] of a uniform flux distribution after the sample was cooled in a field which was switched off at low temperatures. This is consistent with the bulk superconducting nature of the sample and shows that it is not filamentary or phase separated [58]. Further on, different magnetization measurements yield a rather large $\mu_0 H_{c1} = 13$ mT and corresponding magnetic penetration depth of $\lambda = 580$ nm [157] which is hard to understand for filamentary superconductivity. On the other hand, in the samples showing indications of bulk superconductivity, i.e. 100% Meissner screening, neutron scattering experiments observe a block spin antiferromagnetic ordering without traces of a secondary phase, suggesting a microscopic coexistence of mag-
netism and superconductivity \cite{7, 114, 113}. Recent inelastic neutron scattering study \cite{110} observed a magnetic resonant mode below $T_c$ in the Rb$_2$Fe$_4$Se$_5$ system. Such observation also suggests that bulk SC coexists with $\sqrt{5} \times \sqrt{5}$ magnetic superstructure.

There are several experiments revealing different kinds of phase separation in different A$_x$Fe$_{2-y}$Se$_2$ compounds. Dependent on the experimental technique they are able to directly detect a structural, non-superconducting/superconducting or a magnetic/non-magnetic phase separation. The determination of a magnetic/superconducting phase separation by these techniques is anyhow only possible on the basis of plausible arguments. Transmission electron microscopy (TEM) revealed a rich variety of microstructures related to Fe vacancy order \cite{164}. The superconducting samples clearly appear to be phase separated suggesting that the superconducting phase could have a Fe-vacancy disordered state. Similarly, scanning nano-focus single crystal X-ray diffraction \cite{118} reveals a structural phase separation in domains with a compressed and an expanded lattice structure where the later might be associated with a magnetic phase adopting an Fe vacancy ordered structure. On the contrary, scanning tunneling microscopy (STM) able to detect local structural and electronic properties indicates a microscopic coexistence of superconductivity and a $\sqrt{2} \times \sqrt{2}$ charge modulation likely caused by blockspin antiferromagnetic ordering \cite{21}. However, it should be noted that the STM measurements did not observe the usually observed Fe vacancy ordering pattern (which according to neutron measurements exhibits a block-spin antiferromagnetic state) but rather a vacancy-free FeSe layer and therefore there might be as well two different magnetic structures. Optical spectroscopy observes a Josephson-coupling plasmon of the superconducting condensate \cite{172}. This together with a TEM analysis suggests a nanoscale stripe-type phase separation between superconductivity and insulating phases. In addition, optical conductivity measurements in the THz region observe a very low charge carrier density in favor of a phase separated picture with a minor metallic and a dominant semiconducting phase \cite{24}. Local probe techniques like $\mu$SR (our present and earlier study \cite{137}) and Mössbauer \cite{77, 125, 101} show a phase separation into a 85-95% major magnetic and 15-5% minor non-magnetic volume fraction. Another argument for a nanoscopic phase separation comes from
two-magnon Raman-scattering [175]. The intensity of the two-magnon peak which reflects directly magnetic order undergoes a clear, step-like reduction on entering the superconducting phase which suggests a competition between antiferromagnetic order and superconductivity. The paramagnetic fraction studied by $\mu$SR gives a typical response of superconducting character. Based on the experimental results one can suppose that: i) only the antiferromagnetic, ii) only the paramagnetic, or iii) both regions are superconducting. The experimental evidence, reported in the present article, strongly excludes the first case. On the other hand, the second scenario is challenged by many experimental results mentioned above. Unfortunately, the $\mu$SR technique alone is unable to exclude any of the second and third scenarios due to a very high damped muon polarization signal coming from the large antiferromagnetic fraction. Since both scenarios have their own experimental support the question remains open and should trigger further studies of these systems.

6.5. Summary

In the present chapter, the superconducting and magnetic properties of the single crystalline $A_xFe_{2-y}Se_2$ ($A = Cs, Rb, K$) system are presented. All investigated samples exhibit a paramagnetic volume fractions of about 5%, 11% and 12% below the magnetic transition temperatures of $T_N = 478$ K, 534 K and 559 K for $A = Cs, Rb$ and $K$, respectively. The rest, about 90% of the volume is antiferromagnetically ordered with the magnetic moments up to 3.3$\mu_B$ per Fe atom. Very high $\mu$SR oscillations with the frequencies of about $f = 398(2)$ MHz are observed in all investigated samples. The analysis show that the strong internal field at the muon site is aligned parallel to the crystallographic c-axis. Only the $A = K$ sample shows an additional internal field in the ab-plane. The temperature dependency of the internal magnetic field follows a conventional sublattice magnetization curve. Besides, muon site and potential map analysis using the modified Thomas Fermi approach are presented in the appendix of this thesis. According to this calculations, muon stopped in the Fe-Se layer should precess with the Larmor frequency of 195 MHz. The experimentally observed value is about 400 MHz, two times more, than predicted. Presumably, some non-localized part of Fe magnetic moments contribute
and enhance the magnetic field at the muon sites; i.e. for dipole-dipole field calculation, one should use not only the local moment approximation, but also the exact spin density distribution.

The paramagnetic volume fractions of the samples clearly show a superconducting response. The $\mu$SR signal of these fractions exhibit a rather weak ZF muon-spin depolarization indicating that the paramagnetic islands are rather large, probably $>100$ nm. The superconducting responses obtained by TF $\mu$SR are typical for a FLL of type-II superconductors, again indicating paramagnetic grains larger than the distance of the flux lines. The temperature dependence of the superfluid density was described by a single $s$-wave gap model with zero-temperature values of the in-plane magnetic penetration depth $\lambda_{ab}(0) = 258(2)$ and $225(2)$ nm and superconducting gaps $\Delta(0) = 7.7(2)$ and $6.3(2)$ meV for A = Rb and K, respectively.

Whether the magnetic and SC states are competing or cooperating, phase separated or sharing the same volume elements in $A_xFe_{2-y}Se_2$ system, are the main puzzling and open questions. In the current chapter, we show that about 11% of the total sample volume is in the paramagnetic state, clearly showing a superconducting response and being free from any magnetic ordering. The rest majority fraction is antiferromagnetically ordered, and the question, whether it is also superconducting, stays unanswered.
7. Summary

In the present thesis, an experimental investigation of the iron-based \( \text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2 \) arsenides and \( \text{A}_x\text{Fe}_{2-y}\text{Se}_2 \) (\( \text{A} = \text{Cs, Rb, K} \)) chalcogenides by the Muon Spin Rotation Spectroscopy technique is presented. The magnetic and superconducting order parameters are evaluated from transverse and zero field \( \mu \text{SR} \) measurements. Their temperature, pressure and doping dependence have been investigated. The temperature, magnetic field and pressure dependence of the magnetic penetration depth \( \lambda \) is obtained from \( \mu \text{SR} \) experiments and analyzed to probe the superconducting gap-symmetries for each sample. The zero-temperature values of \( \lambda(0) \) in \( \text{Ba}_{1-x}\text{Rb}_x\text{Fe}_2\text{As}_2 \) (\( x = 0.3, 0.35, 0.4, 1 \)) arsenides for each Rb content are reproduced from the zero-temperature relaxation rates \( \sigma_{sc}(0) \propto \lambda^{-2}(0) \) obtained from transverse-field \( \mu \text{SR} \) measurements. The analysis of the temperature dependence of the superfluid density \( n_s \propto \lambda^{-2}(T) \) favors the \( s+s \)-wave scenario with a small gap \( \Delta_1 \approx 1-3 \) meV and a large gap \( \Delta_2 \approx 7-9 \) meV. The BCS ratio for the small gap \( 2\Delta_1/k_B T_c \) was found to stay unchanged, and ratio for the large one \( 2\Delta_2/k_B T_c \) slightly decreases upon increasing Rb content. The results are discussed in light of the suppression of interband processes upon hole doping. As revealed from the combined results of ARPES and \( \mu \text{SR} \) [40, 35, 173], in the optimally doped \( \text{Ba}_{0.6}\text{Rb}_{0.4}\text{Fe}_2\text{As}_2 \) compound several bands cross the Fermi surface (FS), an inner (\( \alpha \)) and outer (\( \beta \)) hole-like bands, both centered at the zone center \( \Gamma \), and an electron-like band (\( \gamma \)) centered at the \( M \) point. The superconducting gap opened on the \( \beta \) band was found to be smaller than those on the \( \alpha \) and \( \gamma \) bands. It was proposed that the enhanced interband scattering between the \( \alpha \) and \( \beta \) bands might promote the kinetic process of pair scattering between these two FSs, leading to an increase of the pairing amplitude [128]. Hole doping causes a shift of the band bottom of the electron pockets above the Fermi level. As a result, the
interband scattering between $\alpha$ and $\gamma$ bands diminishes since the $\gamma$ band becomes unoccupied and concomitantly the size of the $\alpha$ band is increased. A decrease of interband scattering will lead to a decrease of the pairing amplitude and the ratio $2\Delta/k_B T_c$, which also might cause the reduction of $T_c$ for the hole overdoped case RbFe$_2$As$_2$. Furthermore, it was found that the superfluid density for the end compound of the series, RbFe$_2$As$_2$, is much larger than in other Fe-based and unconventional superconductors [19]. This indicates a more conventional nature of its superconducting ground state. Therefore, a further investigation of this end compound and a comparison with the optimally doped ones was done. The pressure dependence of $T_c$ was obtained by susceptibility measurements at $p = 0, 0.27, 0.46, 0.68$ and $0.98$ GPa pressures. These measurements revealed a strong, linear decrease of the $T$ with the rate of $dT_c/dp = -1.32$ K GPa$^{-1}$. A linear extrapolation of the $T_c(p)$ curve showed a complete disappearance of SC state at 1.92 GPa. Further magnetization experiments were performed on a SQUID Magnetometer using a home-made diamond anvil cell. No superconducting transition was detected above lowest available temperature 1.8 K up to our maximum pressure of 5.4 GPa.

The zero temperature values of the London penetration depth $\lambda(0)$, superconducting gaps $\Delta(0)$, upper critical field $B_{c2}$, and Ginzburg-Landau parameter $\kappa = \lambda/\xi$ have been evaluated from the $\mu$SR experimental data. The superfluid density $\rho_s$ was found to be weakly pressure dependent, while $\kappa$ and $T_c$ are linearly reduced by 50% by the application of pressures up to 1.0 GPa. Upon increasing the hydrostatic pressure, the system undergoes a transition from a $s+s$-wave multi-gap superconducting state to a single $s$-wave gap state. By observing the different effects of hydrostatic pressure and reduction of the lattice parameters by substitution with smaller ions on the RbFeFe$_2$As$_2$ system, and considering the experimental fact that no superconducting transition was detected above 1.8 K up to 5.4 GPa pressure, one can conclude that external pressure is not simply equivalent to a chemical pressure in this particular compound. This is probably related to the different effects of the two forms of pressure on the local atomic structure within the FeAs tetrahedra which is known to be one of the governing parameters determining $T_c$ in Fe-based superconductors [96]. Based on these experimental facts, one notice a tendency towards a conventional superconductor BCS behavior for
RbFe$_2$As$_2$, highlighting three main points:

(i) Upon increasing the hydrostatic pressure the RbFe$_2$As$_2$ compound exhibits a gradual transition from a two gap to a single gap state ending up with the BCS ratio of $2\Delta / k_B T_c = 2.9(2)$.

(ii) A Strong reduction of $\kappa$ from 24 down to 12 is observed, getting closer to the conventional BCS superconductors, and in the limit of high pressures it extrapolates to value typical for type I superconductors.

(iii) The Uemura classification scheme shows that with increased hydrostatic pressure the critical temperature reduces more rapidly than the superfluid density, and the relation of $T_c$ to $\lambda^{-2}$ moves closer to the region where low critical temperature and high superfluid density are characteristics for conventional superconductors.

Moreover, $\rho_s$ is only diminished by 18% at $p = 1.0$ GPa indicating that the proportionality of $\rho_s$ and $T_c$, which is found for several families of under and optimally doped unconventional superconductors, does not hold for RbFe$_2$As$_2$ either. On the other hand, these observations are rather typical for classical low temperature BCS superconductors [66]. Hence, the hydrostatic pressure appears to shift the nature of the ground state of the hole-overdoped RbFe$_2$As$_2$ system to an even more classical superconducting state. The superconducting ground state of the hole-overdoped RbFe$_2$As$_2$ system appears to be rather conventional. A further microscopic characterization of compounds from similar series such as KFe$_2$As$_2$ and CsFe$_2$As$_2$, and a study of the hydrostatic pressure effect on their order parameters seems highly mandatory since they may, in comparison with the corresponding optimally doped compounds from the same series, provide valuable information on the origin of high-$T_c$ superconductivity in Fe-based materials.

A relatively large part of the thesis is devoted to studies of the iron-based selenides. The superconducting and magnetic properties of single crystals of the A$_x$Fe$_{2-y}$Se$_2$ ($A = \text{Cs, Rb, K}$) systems are presented. By performing magnetization measurements sharp superconducting transitions and nearly 100% Meissner screenings are observed at $T_c = 27.4(2)$, 31.0(2) K and 32.6(2) K for $A = \text{Cs, K and Rb}$, respectively. $\mu$SR experiments revealed that all investigated samples exhibit paramagnetic volume fractions of about 5%, 11% and 12% below the mag-
nentic transition temperatures of $T_N = 478\,\text{K}$, 534\,K and 559\,K for $A = \text{Cs}$, Rb and K, respectively. The rest, about 90\% of the volumes are antiferromagnetically ordered. $\mu$SR oscillations with very high frequencies of about $f = 398(2)\,\text{MHz}$ are observed in all investigated samples. The analysis show that the strong internal field, at the muon site is aligned to the crystallographic $c$-axis. Only the $A = \text{K}$ sample shows an additional internal field in the $ab$-plane. Besides, muon site and potential map analysis using the modified Thomas Fermi approach are presented in the Appendix. According to these calculations, muons stopped in the Fe-Se layer should precess with the Larmor frequency of 195\,MHz. The experimentally observed value is about 400\,MHz, two times more, than predicted. Presumably, some non-localized part of Fe magnetic moments contribute and enhance the magnetic field at the muon sites; i.e. for dipole-dipole field calculation, one should use not only the local moment approximation, but also the exact spin density distribution. The paramagnetic volume fractions of the samples clearly show a superconducting response. The $\mu$SR signal of these fractions exhibit a rather weak ZF muon-spin depolarization indicating that the paramagnetic islands are rather large, probably $>100$\,nm. The superconducting responses obtained by TF $\mu$SR are typical for a FLL of type-II superconductors, again indicating paramagnetic grains larger than the distance of the flux lines. The temperature dependence of the superfluid density was described by a single $s$-wave gap model with zero-temperature values of the in-plane magnetic penetration depth $\lambda_{ab}(0) = 258(2)\,$ and $225(2)\,$nm and superconducting gaps $\Delta(0) = 7.7(2)\,$ and $6.3(2)\,$meV for $A = \text{Rb}$ and K, respectively. Whether the magnetic and SC states are competing or cooperating, phase separated, or sharing the same volume in the $A_x\text{Fe}_{2-y}\text{Se}_2$ systems, are the main open questions. The measurements show that about 11\% of the total sample volume is in a paramagnetic state, clearly showing a superconducting response and free from any magnetic ordering. The remaining majority fraction is in the antiferromagnetic phase, and the question, whether it is also superconducting, stays unanswered. The magnetization and $\mu$SR data are not sufficient to claim or exclude a 100\% superconducting volume fraction, and further investigations by other microscopic techniques are inevitable to shed light on the exact nature of the interplay between superconductivity and magnetism in the iron-based chalcogenide superconductors.
As part of my Ph.D. project, I developed and produced a new design of a double-wall pressure cell satisfying the demands of \( \mu \)SR experiments. The limited space of the cryogenic equipment and a large size of the muon beam spot are the main reasons which prevent other pressure equipments such as diamond anvil cell to be used in \( \mu \)SR experiments. Moreover, due to very high sensitivity of the muons to a magnetic field, using a nonmagnetic material for the pressure cell body is unavoidable. For this reason, cylindrically shaped body-cells made by nonmagnetic materials such as CuBe and MP35N were used. The internal cylinder was crowded into the outer one, producing the compressive force in the unloaded case. While applying the internal pressure a compressive yield strength of the internal cylinder gradually undergoes a transition to the tensile strength passing the zero value and reaching the maximum, permissible strength for both cylinders. This procedure allowed to increase the pressure limit compared to single-wall pressure cell by a factor of about 1.3. The calculated upper limit of the internal pressure is in good agreement with an experimentally observed limit. Using the new double-wall pressure cell the upper limit of hydrostatic pressures at room temperatures was raised from 1.8 to 2.4 GPa, and from 2.8 to 3.8 GPa for CuBe and MP35N, respectively.
8. Publication and Conferences

Publications


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A. Amato. Coexistence of Magnetism and Superconductivity in the Iron-Based Compound Cs$_{0.8}$(FeSe$_{0.98}$)$_2$. Phys. Rev. Lett. 106, 117602 (2011).


8. Publication and Conferences

Conferences

1. **Z. Shermadini.** Iron based pnictides and chalcogenides studied using muon spin spectroscopy (invited talk). Graduate school "Itinerant magnetism and superconductivity in intermetallic compounds". 12 November 2012, Institut für Festkörperphysik, TU Dresden, Germany.


3. Z. Guguchia, **Z. Shermadini,** A. Amato, A. Maisuradze, A. Shengelaya, Z. Bukowski, H. Luetkens, R. Khasanov, J. Karpinski, and H.Keller. Muon-spin rotation measurements of the magnetic penetration depth in the Fe-based Superconductors Ba$_{1-x}$RbxFe$_2$As$_2$ (x= 0.3, 0.35, 0.4) (poster). Swiss physical society. Joint Annual Meeting 2011. June 15-17, 2011 at EPF Lausanne, Switzerland.


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Appendices
A. Muon site calculation for the $A_{0.8}Fe_{1.6}Se_2$ system

In order to extract more quantitative information about the magnetic order from our data, the knowledge of the muon site is mandatory. Possible muon stopping sites have been computed by using a symmetry analysis considering all possible magnetic structures in the systems $A_xFe_{2-y}Se_2$ ($A = \text{Cs, Rb, K}$). The internal magnetic field at possible muon sites has been calculated and analyzed for some representative magnetic modes. In this present appendix we show that the type of magnetic order can be defined from $\mu$SR experiments due to the high symmetry of the muon stopping sites. The special location of the muon sites, almost in the iron layers, leads to a very high $\mu$SR frequency for some types of magnetic order.

A well defined (integer) valence state of each ion occurs in the ideal stoichiometry $A_{0.8}Fe_{1.6}Se_2$. Due to the presence of alkali ions, every fifth Fe-ion should be removed from a Fe-Se layer creating vacancies. Under special growth conditions \[76\], one can obtain a perfect ordering of the iron vacancies so that $A_{0.8}Fe_{1.6}Se_2$ possesses a translation symmetry and a rotational tetragonal symmetry corresponding to the $I4/m$ space group, and two formula units per primitive cell. The Fe ions occupy the sites $8i$ (Wyckoff notation), the Se ions are distributed between the $i$ and $2e$ sites and the Rb ions adopt to $4h$ sites \[162, 137, 7\]. The possible magnetic structures can be described in terms of Fe-square units (see Fig. A.1), where each unit includes four Fe ions. Such a description is possible as the Fe-Se-Fe bond lengths and angles between Fe-ions located in a given Fe-square are very different than those observed between Fe-ions located in adjacent squares. From symmetry reason, the exchange integrals $K_{\alpha\beta}$ between nearest neighbors $\alpha$ and $\beta$ located in a same square are equal to each other, i.e. $K_{14} = K_{13} = K_{24} =$
K_{23} (see Fig. A.1). Similarly the “external” integrals between neighbors located on adjacent squares are also equal to each other, i.e. $K_{15} = K_{48} = K_{26} = K_{37}$. Thus, one may apply the nearest-neighbors approximation model which includes just two exchange interactions: 1) $J_{i}$ - the internal exchange between the Fe in a square; 2) $J_{e}$ - the external exchange between two neighboring Fe-squares in the $ab$-plane. Interlayer exchange along the crystallographic $c$-axis is not needed as it is effectively accounted for by $J_{e}$. According to neutron diffraction studies, there is no consensus about the exact type of magnetic order in $A_{0.8}Fe_{1.6}Se_{2}$. Particularly, for $Cs_{0.8}Fe_{1.6}Se_{2}$, the solution space is highly degenerated [114], and one cannot make a choice between different types of magnetic order parameters. For $K_{0.8}Fe_{1.6}Se_{2}$, a magnetic structure with a magnetic order parameter belonging to the irreducible representation (IR) $\tau_{2}$, with the magnetic moments directed along the $c$-axis was suggested by Bao et. al. [7]. A problem arises due to the expected strong Dzyaloshinskii-Moriya interaction and the low site-symmetry of the Fe ions. Therefore, each IR includes three magnetic modes (three types of magnetic order parameters with the same rotation symmetry) so that the realization of a certain type of magnetic symmetry should create a canted magnetic structure. A more
A. Muon site calculation for the A$_{0.8}$Fe$_{1.6}$Se$_2$ system

Figure A.2.: Potential map of Rb$_{0.85}$Fe$_2$Se$_2$. The $ab$-plane drawn through the Fe layer. The cross denotes the muon site with the ($\frac{1}{2}$, $\frac{1}{2}$, 0.252) coordinates and the electrostatic potential magnitude of 0.574 a.u.

conclusive determination of the magnetic order type in A$_{0.8}$Fe$_{1.6}$Se$_2$ compounds can be derived from $\mu$SR experiments. For this purpose, we performed an analysis of the electrostatic potential distribution in the primitive cell of the A$_{0.8}$Fe$_{1.6}$Se$_2$ systems with a symmetry analysis of iron and muon sites. The internal field was obtained using magnetic dipole-dipole field calculations. To calculate the muon sites a modified Thomas-Fermi approach [117] was used. This method has been successfully probed for the description of $\mu$SR data in different compounds [86, 89]. Using available structural data [76, 162, 137, 7, 114] this method allows to directly determine the self-consistent distribution of the valence electron density, and hence to restore the electrostatic potential. Local interstitial minima of this potential are identified as possible stopping sites for muons. The deepest potential observed in A$_x$Fe$_{2-y}$Se$_2$ is located almost in the center of the Fe-squares, having a very high 2e-site symmetry with coordinates ($\frac{1}{2}$, $\frac{1}{2}$, $z$). For Rb$_{0.8}$Fe$_{1.6}$Se$_2$, $z = 0.252$, and the respective potential map is shown in Fig. A.2.
In the Table A.1 we present the results of the symmetry analysis of possible iron magnetic order parameters, using the Bertout [14], and Izyumov and Naish [59] approach, and supposing that the paramagnetic phase has $I4/m$ symmetry. Following the experimental results [7, 114], there is no multiplication of the crystal primitive cells in these compounds, thus one can consider only the $K = 0$ magnetic propagation vector for the Fe-order. Besides, we consider the symmetry and direction of staggered magnetic fields at the muon sites, induced by the given symmetry of the magnetic order. We suppose that the overall distribution of a magnetic field in the magnetic cell has the same symmetry as the magnetic order parameter. In order to determine the orientation of a magnetic field at the muon site, one should ascribe to this site some hypothetical magnetic moment - the magnetic degree of freedom. The set of magnetic degrees of freedom for some points (Wyckoff positions) forms the magnetic representation. The standard decompositions of that magnetic representations, the symmetry of magnetic order parameters and the respective staggered magnetic fields at the muon sites in $A_{0.8}Fe_{1.6}Se_2$, for the $K = 0$ magnetic propagation vectors, are summarized in Table A.1. Here, the enumeration of IR is given in accordance with the Kovalev notation [75]. For convenience, we also list the spectroscopic notations.

Magnetic order parameters consists of Fourier components $S_\alpha^q(K)$ of the magnetic propagation vector of $K = 0$ of $\alpha = 1$ to 8 sub-lattice magnetic moments. $S_\alpha$ are the irreducible representations of the space group. One can analyze the possible symmetry of the magnetic moment (i.e. the staggered magnetic field) distributions at the muon sites which are compatible with a given space group. This symmetry must belong to the same IR as the magnetic order parameter.

For the calculated 2$e$ muon sites, which include only two points, we introduce the respective staggered magnetic fields in the forms: $M_i = \frac{1}{2}(B_i^{(1)} + B_i^{(2)})$; $L_i = \frac{1}{2}(B_i^{(1)} - B_i^{(2)})$. Here $B_i^{(\alpha)}$ are the $i$-cartesian components of a magnetic fields at $\alpha$-muon sites ($\alpha = 1, 2$). For a given type of magnetic symmetry the respective entity $M_i$ or $L_i$ will be nonzero if $B_i^{(1)} = B_i^{(2)}$ or $B_i^{(1)} = -B_i^{(2)}$.

The Table A.1 demonstrates a few remarkable features.

- Due to the high local symmetry of the muon sites, some possible types of iron magnetic structure cannot create magnetic fields at the muon sites, i.e.
A. Muon site calculation for the A$_{0.8}$Fe$_{1.6}$Se$_2$ system

Table A.1.: List of the possible iron magnetic modes.

<table>
<thead>
<tr>
<th>IR of the I4/m group</th>
<th>Iron magnetic modes (magnetic basis functions)</th>
<th>Symmetry of the staggered fields</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>$\Psi_x^1 = 1/8(-S_{1x} + S_{2x} - S_{3x} + S_{4x} - S_{5x} + S_{6x} - S_{7x} + S_{8x});$</td>
<td>$M_z$</td>
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<td>$\Psi_y = 1/8(S_{1y} - S_{2y} + S_{3y} + S_{4y} + S_{5y} - S_{6y} - S_{7y} + S_{8y});$</td>
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<td>$\Psi_z^1 = 1/8(S_{1z} + S_{2z} + S_{3z} + S_{4z} + S_{5z} + S_{6z} + S_{7z} + S_{8z});$</td>
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<tr>
<td>$\tau_3 + \tau_7$</td>
<td>$\Psi_x^{3+7} = 1/4(S_{1x} + S_{2x} + S_{3x} + S_{6x});$</td>
<td>$M_x$</td>
</tr>
<tr>
<td>$(E_g^{(1)} + E_g^{(2)})$</td>
<td>$\Psi_y^{3+7} = 1/4(S_{1y} + S_{2y} + S_{3y} + S_{6y});$</td>
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<tr>
<td></td>
<td>$\Psi_z^{3+7} = 1/4(S_{1z} - S_{2z} + S_{3z} - S_{6z});$</td>
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<tr>
<td>$\tau_3 - \tau_7$</td>
<td>$\Psi_x^{3-7} = 1/4(S_{3x} + S_{4x} + S_{5x} + S_{6x})$</td>
<td>$M_y$</td>
</tr>
<tr>
<td>$(E_g^{(1)} - E_g^{(2)})$</td>
<td>$\Psi_y^{3-7} = 1/4(-S_{3y} - S_{4y} - S_{5y} - S_{6y})$</td>
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<tr>
<td></td>
<td>$\Psi_z^{3-7} = 1/4(S_{3z} - S_{4z} + S_{5z} - S_{6z});$</td>
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<tr>
<td>$\tau_2(A_u)$</td>
<td>$\Psi_x^2 = 1/8(S_{1x} - S_{2x} + S_{3x} - S_{4x} - S_{5x} + S_{6x} - S_{7x} + S_{8x});$</td>
<td>$L_z$</td>
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<td>$\Psi_y^2 = 1/8(S_{1y} - S_{2y} - S_{3y} + S_{4y} + S_{5y} - S_{6y} + S_{7y} - S_{8y});$</td>
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<td></td>
<td>$\Psi_z^2 = 1/8(S_{1z} + S_{2z} - S_{3z} + S_{4z} - S_{5z} - S_{6z} - S_{7z} - S_{8z});$</td>
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<tr>
<td>$\tau_4 + \tau_8$</td>
<td>$\Psi_x^{4+8} = 1/4(S_{1x} + S_{2x} - S_{3x} - S_{6x});$</td>
<td>$L_x$</td>
</tr>
<tr>
<td>$(E_u^{(1)} + E_u^{(2)})$</td>
<td>$\Psi_y^{4+8} = 1/4(S_{1y} + S_{2y} - S_{3y} - S_{6y});$</td>
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<td></td>
<td>$\Psi_z^{4+8} = 1/4(S_{1z} - S_{2z} - S_{3z} + S_{6z});$</td>
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<tr>
<td>$\tau_4 - \tau_8$</td>
<td>$\Psi_x^{4-8} = 1/4(S_{3y} + S_{4y} - S_{5y} - S_{8y});$</td>
<td>$L_y$</td>
</tr>
<tr>
<td>$(E_u^{(1)} - E_u^{(2)})$</td>
<td>$\Psi_y^{4-8} = 1/4(-S_{3x} - S_{4x} + S_{5x} + S_{8x});$</td>
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<tr>
<td></td>
<td>$\Psi_z^{4-8} = 1/4(S_{3z} - S_{4z} + S_{5z} + S_{8z});$</td>
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<tr>
<td>$\tau_5(B_g)$</td>
<td>$\Psi_x^5 = 1/8(S_{1x} - S_{2x} - S_{3x} + S_{4x} + S_{5x} - S_{6x} - S_{7x} + S_{8x});$</td>
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<td>$\Psi_y^5 = 1/8(S_{1y} - S_{2y} + S_{3y} - S_{4y} + S_{5y} - S_{6y} - S_{7y} - S_{8y});$</td>
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<td></td>
<td>$\Psi_z^5 = 1/8(S_{1z} + S_{2z} - S_{3z} + S_{4z} - S_{5z} + S_{6z} + S_{7z} - S_{8z});$</td>
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<tr>
<td>$\tau_6(B_u)$</td>
<td>$\Psi_x^2 = 1/8(S_{1x} - S_{3x} + S_{4x} - S_{5x} + S_{6x} + S_{7x} - S_{8x});$</td>
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<td>$\Psi_y^2 = 1/8(S_{1y} + S_{2y} - S_{3y} - S_{4y} + S_{5y} - S_{6y} - S_{7y} + S_{8x});$</td>
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<td></td>
<td>$\Psi_z^2 = 1/8(S_{1z} + S_{2z} - S_{3z} - S_{4z} - S_{5z} - S_{6z} + S_{7z} + S_{8x});$</td>
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no $\mu$SR response can be detected. Therefore, one can exclude at least two possible types of magnetic order with the $\tau_5$ and/or $\tau_6$ magnetic symmetries.

- Despite the presence of three types of iron magnetic modes in a given IR, all of them create dipole-dipole magnetic fields which have a unique direction.

- Three IR (i.e. $\tau_1$, $\tau_3$ and $\tau_7$) describe ferromagnetic phases and should therefore be excluded as the experiments clearly indicate an antiferromagnetic ground state.

Regarding the remaining three IR, the iron magnetic order $\tau_2$ induces a dipole-dipole magnetic field at muon sites along the crystallographic $c$-axis. This field orientation has been detected by $\mu$SR experiments in single crystals of $A_{0.8}Fe_{1.6}Se_2$. Thus, from this observation one can conclude that the $\tau_2$ magnetic symmetry occurs in the system. The possible magnetic structure of type $\tau_2$ is shown in Fig. A.3.

![Figure A.3: Magnetic structure of type of $\tau_2$ for $Cs_{0.8}Fe_{1.6}Se_2$. Left-hand side: $\Psi_z^{(2)}$ magnetic order. Right-hand side: an admixture of the orders $\Psi_x^{(2)}$ and $\Psi_y^{(2)}$ caused by the Dzyaloshinskii-Moriya interaction.](image-url)
A. Muon site calculation for the A$_{0.8}$Fe$_{1.6}$Se$_2$ system

A.0.1. Dipole magnetic field at the muon site

Suppose that the orientation of the magnetic moment at the first iron site is as follows:

$$S_1 = S_0 (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta).$$  \hspace{1cm} (A.1)

Here, $S_0$ is the magnitude of iron magnetic moment. For a direct comparison with the experimental data, the magnetic fields are given in MHz (i.e. already taking into account the gyromagnetic ratio of the muon), and basis functions $\Psi$ with the Bohr magneton ($\mu_B$) unit. The magnetic structure of $\tau_2$-type is described by the three magnetic modes:

$$\Psi_{x}^{(2)} = S_0 \sin \theta \cos \phi$$
$$\Psi_{y}^{(2)} = S_0 \sin \theta \sin \phi$$
$$\Psi_{z}^{(2)} = S_0 \cos \theta.$$  \hspace{1cm} (A.2)

Here the magnitude of the angle $\theta$ is determined by the ratio $D/J_i$, where $D$ is the value of Dzyaloshinskii-Moriya interaction. One can suppose that the value of $\theta$ is small, so that the $\Psi_{z}^{(2)}$ order parameter is dominant. In the case of $S_0 = 1 \mu_B$, the calculations of the dipole field (in MHz) gives:

$$L_z = B_z(\tau_2)$$
$$= 8.246 \cdot \Psi_{x}^{(2)} - 3.545 \cdot \Psi_{y}^{(2)} - 59.033 \cdot \Psi_{z}^{(2)}$$
$$= 8.246 \sin \theta \cos \phi - 3.545 \sin \theta \sin \phi - 59.033 \cos \theta.$$  \hspace{1cm} (A.3)

Hence, from equation (A.3) one sees that the $\Psi_{z}^{(2)}$ order parameter provides the strongest contribution for the internal magnetic field. This is the case of an easy axis anisotropy when the “internal” exchange constant $J_i$ is ferromagnetic, whereas the “external” one, $J_e$, is antiferromagnetic. It is shown on the left-hand side of Fig. A.3. This kind of structure has been observed in K$_{0.8}$Fe$_{1.6}$Se$_2$ [7] and, as having the lowest ground state energy, was predicted by Cao et. al. [22]. Equation (A.3) allows one to estimate the value of the magnetic moment. For instance, for an Fe magnetic moment of $3.31 \mu_B$, as in the case of K$_{0.8}$Fe$_{1.6}$Se$_2$ [7], we obtain a theoretical $\mu$SR response of roughly 195 MHz. As seen, the experimentally
observed $\mu$SR frequency is 400 MHz, i.e. about two times larger than the calculated one. Presumably, a non-localized part of the Fe spin density contributes and enhances the magnetic field at the muon sites; i.e. for the dipole-dipole field calculation, one should not only use the local moment approximation, but also the exact spin density distribution. Another possibility would be a non-negligible contact hyperfine contribution.

In the case of the IR combination $\tau_4 + \tau_8$, the iron sites 3, 4, 7 and 8 do not participate to the formation of the magnetic modes. While for the combination $\tau_4 - \tau_8$, the sites numbers 1, 2, 5 and 6 do not. However, as both of those sets originate from $\tau_4$ or $\tau_8$, they can be written in a similar form. Making the choice for the magnetic moment orientation at the first iron site in the form expressed by Eq. (A.1), we get the expressions for the magnetic modes $\tau_4 + \tau_8$ and $\tau_4 - \tau_8$ similar to Eq. (A.2), i.e.:

$$
\Psi_x^{(4+8)} = S_0 \sin \theta \cos \phi \\
\Psi_y^{(4+8)} = S_0 \sin \theta \sin \phi \\
\Psi_z^{(4+8)} = S_0 \cos \theta
$$

$$
\Psi_x^{(4-8)} = S_0 \sin \theta \cos \phi \\
\Psi_y^{(4-8)} = S_0 \sin \theta \sin \phi \\
\Psi_z^{(4-8)} = S_0 \cos \theta .
$$

(A.4)

Here again, the magnitude of the angle $\theta$ is determined by the ratio $D/J_i$, where $D$ is the value of the Dzyaloshinskii-Moriya interaction.

The phase between the two different sets of basis functions of the two-dimensional IR is not fixed in the tetragonal symmetry. In other words, one can make an arbitrary choice for directions of $x$ and $y$ axes for two basis functions of the two-dimensional IR. Therefore, for the 16$i$ position, the direction of the dipole fields created by the exact realization of the three sets of magnetic modes, like shown in Eq. (A.4), does not coincide with the crystallographic $x$ and $y$ axes. The only request is that these fields for the $\tau_4 + \tau_8$ and $\tau_4 - \tau_8$ modes must be perpendicular to each other.
A. Muon site calculation for the $A_{0.8}Fe_{1.6}Se_2$ system

The magnetic modes, expressed by Eq. (A.4), create the following two components for dipole field at the muon sites:

\[
\begin{align*}
B_x(\tau_4 + \tau_8) &= 49.18 \cdot \Psi_x^{(4+8)} - 34.03 \cdot \Psi_y^{(4+8)} + 4.12 \cdot \Psi_z^{(4+8)} \\
B_y(\tau_4 + \tau_8) &= -34.03 \cdot \Psi_x^{(4+8)} - 19.66 \cdot \Psi_y^{(4+8)} - 1.77 \cdot \Psi_z^{(4+8)} \\
B_x(\tau_4 - \tau_8) &= 34.03 \cdot \Psi_x^{(4-8)} + 19.66 \cdot \Psi_y^{(4-8)} + 1.77 \cdot \Psi_z^{(4-8)} \\
B_y(\tau_4 - \tau_8) &= 49.18 \cdot \Psi_x^{(4-8)} - 34.03 \cdot \Psi_y^{(4-8)} + 4.12 \cdot \Psi_z^{(4-8)}.
\end{align*}
\] (A.5)

These fields, corresponding to the $\tau_4 + \tau_8$ and $\tau_4 - \tau_8$ modes, are mutually perpendicular in the $ab$-plane.

From Eq. (A.5), for the easy axis anisotropy (along the $z$-axis) both magnetic order types $\tau_4$ and $\tau_8$, like $\Psi_x^4 = \frac{1}{8}(S_1 - S_2 + S_3 - S_4 + S_5 - S_6 - S_7 + S_8)$, create very small magnetic fields at the muon site. For these symmetries, very high frequency muon signals can be achieved in the case of an easy plane anisotropy, i.e. for magnetic moments lying in $ab$-plane, when $J_i$ is antiferromagnetic and $J_e$ is either ferro- or antiferromagnetic.

The calculations of the potential map and of the magnitude of the dipole magnetic fields at the muon sites in $A_xFe_{2-y}Se_2$ system were preformed by Professor Y. G. Pashkevich (Donetsk Institute for Physics and Engineering, National Academy of Science, Ukraine). I kindly acknowledge his support and help, and I am thankful that he gave me the permission to include his calculations in my thesis.
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