Field-induced antiferromagnetic quantum critical behavior in Ce(Ru,Fe)$_2$Ge$_2$.

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UNIVERSITEIT VAN AMSTERDAM
To dear Uttam and lovely Maitreyi
Abstract

In the classical picture, matter freezes at absolute zero temperature whereas in the quantum world, the quantum fluctuations persist down to zero temperature. A quantum system can be tuned through a quantum critical point by changing a non-thermal control parameter such as pressure, chemical doping or applied magnetic field. Heavy-fermion materials, notably Ce and Yb, rare-earth or U-based intermetallic compounds, are good candidates to observe quantum critical behavior. In heavy-fermion compounds there is a competition between long range (anti)ferromagnetic order and the screened local moments at low temperature. This competition is described by the Doniach model. The study of the ground state of such systems can help to understand new phenomena like unconventional superconductivity or non-Fermi liquid behavior. In this thesis we report an antiferromagnetic quantum critical point in Ce(Ru\(_{0.24}\)Fe\(_{0.76}\))\(_2\)Ge\(_2\) which is induced by applying magnetic field. We performed resistivity, thermal expansion and specific heat measurements in applied magnetic fields up to 6 T. By applying a range magnetic field the system can be tuned in order to probe the magnetic phase, the quantum critical point and the Fermi liquid phase. The resistivity data in field show non-Fermi liquid behavior as the critical field (\(B_{cr} = 0.75\) T) was approached. Thermal expansion and specific heat data were used to calculate the effective Grüneisen ratio and to study its divergence at the critical point. In addition we studied the newly discovered high temperature superconductor Re(O,F)FeAs. Superconductivity emerges in Re(O,F)FeAs compounds by replacing O by F, while magnetic order is suppressed. In this thesis we report thermal expansion measurements carried out on LaOFeAs, LaO\(_{0.90}\)F\(_{0.10}\)FeAs and GdOFeAs. The data are compared to the specific heat data in order to calculate the pressure dependence of the transition temperature using the Ehrenfest relation.
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Chapter 1.

Introduction and survey

Nature is flourishing with phase transitions. Classical phase transitions like the boiling and freezing of water are driven by temperature. In the twentieth century there was extensive attention from condensed matter and theoretical physicists to second order transition like the Curie point of a ferromagnet and the critical end-point of carbon dioxide. Phase transitions that happen at the absolute zero of temperature are dominated by quantum rather than thermal fluctuations. These fluctuations can lead to new ground states of correlated metals, the so called non Fermi-liquid state, unconventional superconductivity, superfluidity and perhaps more unusual states of matter. Even more surprisingly the effect of the quantum critical point extends up to surprisingly high temperatures. Many believe that the strange properties of the high temperature superconductors may be related to unknown properties of a quantum critical point in these materials [1]. Heavy-fermion systems with strongly correlated f-electrons like Ce-, Yb- and U- compounds have recently been used as prototype materials to study quantum criticality [2-4]. Most of these are intermetallic compounds of lanthanides and actinides in which the quantum critical phenomena are usually generated by an antiferromagnetic (AF) instability.

An increasing number of f-electron systems have been found, mainly Ce-based heavy fermion (HF) metals, which show pronounced deviations from the properties of a conventional Landau Fermi liquid (FL) when they are tuned through an antiferromagnetic (AF) quantum critical point.

We here report on a new system Ce(Ru\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{2}Ge\textsubscript{2}, where the ground state goes from ferromagnetic to antiferromagnetic and then paramagnetic. Ce(Ru\textsubscript{0.24}Fe\textsubscript{0.76})\textsubscript{2}Ge\textsubscript{2} shows an AF QCP by doping [7,8] or by applying pressure [9]. In the system a substantial doping of Fe is necessary to suppress AF ordering leading to a QCP where NFL characteristic temperature dependencies such as power laws ($\rho \propto T^n$ with $n < 2$) over a substantial temperature range can be observed. In this work we report on Ce(Ru\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{2}Ge\textsubscript{2} with a nominal concentration
of $x = 0.76$ which can be tuned to an $AF\, QCP$ by applying a magnetic field $B_{cr} = 0.75$ T. Near the $QCP$, this compound is strongly influenced by magnetic disorder [10] due to which the $AF\, QCP$ cannot be explained by the spin density wave model (SDW) [11] or a locally critical phase transition [12]. The main aim of this thesis is to describe the field induced $AF\, QCP$ in the $Ce(Ru_{1-x}Fe_x)_2Ge_2$ with nominal concentration of $x = 0.76$. The critical applied magnetic field is $B_{cr} = 0.75$ T. Near the $QCP$ we study the thermal and transport properties of the system and analyze the NFL characteristic temperature dependence of the resistivity.

In chapter 2 “Theoretical aspects” a basic introduction to heavy fermion system and the Doniach model is given. Aspects of a diverging Grüneisen ratio near a $QCP$ are summarized. The experimental methods and techniques used for our work are described in chapter 3 “Experimental techniques”. The various experiments on the $Ce(Ru_{1-x}Fe_x)_2Ge_2$ sample with $x \approx 0.76$, carried out in magnetic field up to 4 T are reported in chapter 4 together with the analysis. In chapter 5 the newly discovered rare-earth ($RE$) iron-based oxide systems $REO_{1-x}F_xFeAs$ with $RE = La, Gd$ are discussed. We report on the spin density wave (SDW) transition at high temperature and superconductivity. Thermal expansion data are reported and analyzed with the help of the Ehrenfest relation in chapter 5.
References:

CHAPTER 2.

Theoretical background

In this chapter we present the basic concepts of the theories applicable to the work described in this thesis. First the Fermi liquid and non-Fermi liquid behavior is described followed by the quantum critical point. The Grüneisen parameter is described as function of the entropy and the divergence of the Grüneisen parameter is explained.

2.1 Fermi liquid and non-Fermi liquid behavior

2.1.1 Fermi liquid behavior

Intermetallic compounds known as heavy-fermion compounds have a partially filled f-electron shell. The extensively studied heavy-fermion (HF) systems contain mainly rare-earth or actinide atoms like Ce, Yb and U. In these compounds at high temperature, the conduction electrons are decoupled from the f-electron resulting in localized f-moments. At low temperatures the f-electron couples to the conduction electron and delocalizes with an enhanced effective mass \( m^* \). This effective mass \( m^* \) is 100-1000 times larger than the free-electron mass, \( m_e \), which is attributed to strong electron-electron interactions.

In the Landau Fermi-liquid theory [1] an independent quasiparticle approximation is considered to explain these interacting systems or Fermi liquids (FL). At low temperatures \( T < T_{FL} \) these system behave similar to a non interacting Fermi gas. The interacting Fermi liquid shows similar thermodynamic properties, like a linear \( T \) dependence of the specific heat and a constant Pauli paramagnetic susceptibility \( \chi_0 \). The electronic part of the specific heat is given by:

\[
c_{el} = \gamma T \equiv (m^* / m_0) \gamma_0 T \quad \text{(Eq. 2.1)}
\]
where \( \gamma_0 = \frac{1}{3} \pi^2 N(E_F) k_B^2 \) is the Sommerfeld constant of the free-electron gas and \( N(E_F) \) is the density of state at the Fermi energy. This shows that the specific heat coefficient at low temperature gives direct information on the effective mass \( m^* \). The electrical resistivity \( \rho(T) \) shows a quadratic temperature dependence due to electron-electron interactions:

\[
\rho(T) = \rho_0 + AT^2 \quad \text{(Eq. 2.2)}
\]

where \( \rho_0 \) is the residual resistivity. In heavy fermion systems there is a universal relation between the coefficient \( A \) and the coefficient of the electronic specific heat, \( \gamma \), as presented by the empirical Kadowaki-Woods ratio \( A/\gamma^2 \approx 10 \mu \Omega \text{cmK}^2 \text{mol}^2 \text{J}^{-2} \) [2].

The most successful model to explain \( f \)-electron HF systems is the phase diagram suggested by S. Doniach. (see Chapter 4, page 33) It involves the competition between two types of interactions. In the Kondo coupling [3] the conduction electrons screen the local \( f \)-moments, and for the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling [4] the magnetic interaction between neighboring \( f \)-moments is mediated by the polarized electron cloud surrounding them. The Hamiltonian of a one-dimensional Kondo lattice is given by:

\[
H = H_K + H_{RKKY} \quad \text{(Eq. 2.3)}
\]

where \( H_K \) is the Kondo Hamiltonian and \( H_{RKKY} \) is due to the RKKY interaction.

The Kondo Hamiltonian describes the interaction between a local magnetic impurity with spin \( \vec{S} \) and the conduction electron with spin \( \vec{s} \).

\[
H_K = -2 J \vec{s} \cdot \vec{S} \quad \text{(Eq. 2.4)}
\]

The exchange constant \( J \) is negative and thus the coupling is of antiferromagnetic nature. It was reported that the transition from a magnetic state \( (T >> T_K) \) to a non-magnetic state \( (T << T_K) \) of the Kondo impurity is related to a narrow peak in the density of states close to the Fermi-level [5]. This is also known as the Kondo-resonance. The density of states and Kondo temperature at the Fermi level are related by:
\[ k_B T_K = \frac{1}{N(E_F)} \exp\left(\frac{-1}{JN(E_F)}\right) \]  \hspace{1cm} (Eq. 2.5)

where \( T_K \) is Kondo temperature. \( T_K \) is of the order of \( 10 - 100 \) K.

The Hamiltonian due to RKKY interactions is given by:

\[ H_{RKKY} = \sum I_{ij} \vec{s}_i \cdot \vec{s}_j \]  \hspace{1cm} (Eq. 2.6)

Where \( I_{ij} = N(E_F)J_{ij}^2 F(x) \) with \( F(x) \) as the oscillating term. The binding energy due to the RKKY interaction is given as:

\[ k_B T_{RKKY} = N(E_F) C J^2 \]  \hspace{1cm} (Eq. 2.7)

\( C \) is a constant which depends on the band structure.

### 2.1.2 Non-Fermi liquid behavior

Many intermetallic compounds, where the interactions are weak, can be described as a gas of Fermi particles. These particles obey Pauli’s exclusion principle and the FL theory is successful to describe these intermetallic compounds. But at low temperature, \( T \to 0 \), some HF systems [6,7] show deviations from the physical properties predicted by the FL theory. In these systems thermodynamic and transport properties show a power law or logarithmic temperature dependence at low temperature. These systems are known as non-Fermi liquid (NFL) systems. The electrical resistivity shows a non-quadratic temperature dependence \( \rho(T) \approx T^n \) with \( n < 2 \) and the specific heat, \( c(T)/T \), for instance diverges logarithmically. This unusual NFL behavior is observed mainly in doped HF compounds but there is still not a universal theoretical model to explain NFL systems. Several theoretical models have been proposed to explain the physical properties of NFL systems by comparing the measured temperature dependencies of \( c/T \), \( \chi \) and \( \rho \) [8-12].
2.2 Quantum critical point

Classical or thermal phase transitions occur at finite temperature. These phase transitions driven by thermal fluctuations are characterized by the thermal energy scale \( k_B T \). At absolute zero temperature, a continuous phase transition may occur due to quantum fluctuations, which characterize the quantum energy scale \( \hbar \omega_c \) [13]. Such a phase transition is called a quantum phase transition (QPT). The QPT in Fermi liquids was first investigated by J.A. Hertz [13]. A.J. Millis [12] extended this work for several magnetic phase transitions. QPT can be obtained at absolute zero temperature by controlling a non-thermal parameter, like pressure, chemical doping, magnetic field or electron density. Fermi liquid theory in the itinerant electron system fails near the QPT.

The Landau theory for phase transitions is used to explain the continuous phase transitions with diverging correlation length and time. Near the critical point or transition point the correlation length diverges, like a power law,

\[
\xi \propto t^{-\nu} \quad \text{(Eq. 2.8)}
\]

where \( \nu \) is the correlation length critical exponent and \( t \) is the dimensionless distance from the critical point. For the classical phase transition the \( t \) is defined as \( t = |T - T_c| / T_c \) and for the QPT the \( t \) is defined as \( t = |r - r_c| / r_c \) where \( T \) is temperature and \( r \) is control parameter.

The correlation time \( \xi_T \) for the system near a critical point is given by:

\[
\xi_T \propto \xi^z \propto t^{-\nu z} \quad \text{(Eq.2.9)}
\]

where \( z \) is the dynamical critical exponent.

For the classical phase transition at the critical temperature \( T_c \) the energy scale is:

\[
k_B T > \hbar \omega_c \quad \text{(Eq. 2.10)}
\]

For the QPT at \( T = 0 \) the energy scale is:

\[
\hbar \omega_c > k_B T \quad \text{(Eq. 2.11)}
\]
The generic phase diagram in the vicinity of a continuous $QPT$ is shown in Fig. 1. It shows the ordering temperature as a function of the non-thermal control parameter $r$ which can be pressure, chemical doping or magnetic field [14]. A classical phase transition can be observed at small $r$ by changing the temperature $T$. At $T = 0$ and $r = r_c$ a quantum critical point ($QCP$) is obtained. For $r > r_c$ at low $T$, the system with a quantum disordered state can be observed. In the high temperature regime above the $QCP$ both thermal and quantum fluctuations are important. The boundaries are determined by:

$$k_B T > \hbar \omega_c \propto |r - r_c|^{\nu}$$

(Eq. 2.12)

In this regime the unusual finite temperature properties such as unconventional power laws and non-Fermi liquid behavior are observed.

Fig. 1 Schematic phase diagram in the vicinity of a quantum critical point. Temperature as a function of control parameter $t$. The dashed lines indicate the boundaries of the quantum critical region. The lower crossover lines are given by $T \propto |t|^{\nu}$. (Picture is taken from Ref. 14)
2.3 Grüneisen parameter

As follows from Fig. 1 the QCP can be approached in two ways: at $T = 0$, $r \to 0$ or at $r = 0$, $T \to 0$. Both cases can be related to power-law behavior of physical observables. The Grüneisen parameter gives the volume dependence of the characteristic temperature $T^*$. The Grüneisen ratio can be defined as:

$$\Gamma \propto \alpha / c$$  \hspace{1cm} (Eq. 2.13)

where the thermal expansion is

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_{p,N} = -\frac{1}{V} \left. \frac{\partial S}{\partial p} \right|_{T,N}$$  \hspace{1cm} (Eq. 2.14)

and the specific heat is

$$c_p = \frac{T}{N} \left. \frac{\partial S}{\partial T} \right|_p$$  \hspace{1cm} (Eq. 2.15)

The Grüneisen ratio in terms of the entropy $S$ is given as:

$$\Gamma = -\frac{1}{V_m T} \frac{\partial S / \partial p}{\partial S / \partial T}$$  \hspace{1cm} (Eq. 2.16)

where $V_m$ is the molar volume. At the QCP the entropy $S(T, r)$ goes to zero, but its derivatives are singular [14, 15]. In the low temperature limit, the singular terms in $S$ and $T$ in Eq. 2.16 cancel each other and $\Gamma$ depends on the pressure dependent singularities. As pressure is the control parameter to tune the system to the quantum critical transition, $\Gamma$ diverges at any QCP [16]. The temperature dependence of Grüneisen ratio is given as:

$$\Gamma \propto \frac{1}{T^{1/vz}}$$  \hspace{1cm} (Eq. 2.17)

where $v$ is the correlation length exponent and $z$ is the dynamic exponent of time. So the temperature exponent of the Grüneisen ratio provides a direct means to measure $vz$ and characterize a QCP. The experimentally derived Grüneisen ratio is called effective Grüneisen ratio, $\Gamma_{\text{eff}}(T)$. At high temperatures the phonon contribution is the largest factor in the volume dependence and $\Gamma_{\text{eff}}(T) \approx 2$. At low temperature in heavy fermion systems the electronic contribution is larger.
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<th>AFM, $z = 2$</th>
<th>FM, $z = 3$</th>
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<td>$\alpha_{cr}$</td>
<td>$\log \log(1/T)$</td>
<td>$T^{1/2}$</td>
</tr>
<tr>
<td>$c_{cr}$</td>
<td>$T \log(1/T)$</td>
<td>$-T^{3/2}$</td>
</tr>
<tr>
<td>$\Gamma_{cr}$</td>
<td>$\frac{\log \log(1/T)}{T \log(1/T)}$</td>
<td>$-T^{-1}$</td>
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*Table 1 Results for SDW-QCPs in the quantum critical regime. The $z$ is the dynamic exponent of time and $d$ is dimension of the system. (Table is taken from Ref. 16)*

The renormalization group scheme [12] and spin density wave transition (SDW) model [16] have been used to calculate the temperature dependence of the thermal expansion, and Grüneisen ratio for an antiferromagnet ($z = 2$) and a ferromagnet ($z = 3$) at the QCP. The results are summarized in Table 1 for two ($d = 2$) and three ($d = 3$) dimensional systems.
References:

CHAPTER 3.

Experimental techniques

In this chapter we present the experimental setups and techniques such as thermal expansion cell and cryogenic systems (bath cryostat and \(^3\)He refrigerator) which we used to measure the thermal, transport and magnetic properties of our samples.

3.1 Cryogenic systems

3.1.1 Bath cryostat

A bath cryostat was used to measure the thermal expansion in the temperature range 1.2 - 200 K, it consists of two dewars made of glass. The outer dewar contains liquid nitrogen at 77 K and the inner dewar contains liquid helium at 4.2 K. By pumping on the liquid helium, temperatures down to 1.5 K can be achieved. A thermal expansion insert can be fitted into the glass dewar system. The insert consists of a sample chamber which consists of a copper can and contains the thermal expansion cell. The sample chamber is surrounded by an exchange chamber made of stainless steel. A manganin wire is bifilarly wound around the copper can and serves as a heater. The heater current is provided by a power supply of Delta Electronics. The pressure in the sample chamber is about 0.1 mbar to ensure a homogeneous temperature. The pressure in the exchange chamber is somewhat lower (~ \(10^{-3}\) mbar). The temperature of the thermal expansion cell is measured using a carbon glass thermometer coupled to an AVS 45 resistance bridge \((R_{T=4.2\,K} = 849 \,\Omega)\). Fig. 1 shows a picture of the “glass dewar system” used [1].
3.1.2 $^3\text{He}$ refrigerator

The $^3\text{He}$ refrigerator used for our measurement is the Heliox VL from Oxford Instruments. This system operates in the temperature range from 0.24 K to 20 K. The Heliox can also be used in combination with a magnetic field up to 14 T, as it is integrated with a superconducting magnet. The schematic diagram with the working principle of the Heliox is shown in Fig. 2 [2]. A temperature of 1.5 K can be achieved by condensation of $^4\text{He}$ in the 1 K pot as shown in the left figure. This will condense the $^3\text{He}$ in the $^3\text{He}$ pot. To achieve base temperature, the vapour pressure above the liquid $^3\text{He}$ is reduced by using the sorb pump as shown in the right figure. At the bottom of the $^3\text{He}$ pot, a multipurpose sample

Fig. 1 Glass dewar system for the thermal expansion measurements.
platform is made with the sample holder (for transport properties or thermal expansion), the heater and the thermometer. The thermometer is a RuO₂ chip resistor. Its resistance is controlled by the resistance bridge ORPX. The heater consists of a coil made of bifilarly wound manganin wire.

![Schematic diagram of the working principle of the HelioxVL](Picture taken from Ref. 2)

3.2 Thermal expansion capacitance cell

To measure the thermal expansion we make use of a three terminal capacitance method [3], with a parallel plate capacitance dilatometer [4]. The dilatometer is made of OFHC (Oxygen Free High conductivity) copper to guarantee a good thermal conductivity. A cross section of the dilatometer is shown in Fig. 3 [4]. Typical sample dimensions are 5× 5× 5 mm³. The upper capacitance plate (1) is fixed while the lower capacitance plate (2) is in contact with sample (3). The sample is clamped between the capacitance plate (2) and the bottom of the cell with help of three rods (only one shown) that pass through the bottom of the cell and are connected to a disk. A small pressure is exerted by a screw on a spring like plate. The distance between the upper and lower plate (∼ 100 μm at room temp.) is maintained by three copper foils between the guard rings to reach the optimal capacitance of
about 10 pF. The electrical insulation of the plates from the guard rings is obtained by a thin sheet of kapton (25 μm).

For temperatures ranging from 2 K to 200 K, measurements are carried out in the glass dewar system. The capacitance is measured with a three terminal capacitance bridge Andeen Hagerling (2700A) working at a frequency of 1 kHz. The applied voltage is 15 Volt. For temperatures ranging from 0.25 K to 10 K, the measurements are carried out in the Heliox system.

Fig. 3 Cross-section of the dilatometer used for thermal expansion measurements. {Picture taken from Ref. 3}
3.3 **Thermal expansion measurement**

The capacitance of a parallel plate capacitor is given by:

\[
C = \frac{\varepsilon A}{d}
\]

(Eq. 3.1)

where \(\varepsilon = \varepsilon_r \varepsilon_o\) is the dielectric constant of the medium between the plates, \(A\) is the area of the plates and \(d\) is the distance between the plates. The value of \(\varepsilon A\) has been experimentally determined and amounts to \(\varepsilon A = 9.45 \times 10^{16} \text{ Fm}\) for the cell used in the glass dewar system and \(9.73 \times 10^{16} \text{ Fm}\) for the cell in the Heliox [5]. The length change of the sample as a function of temperature is proportional to the capacitance change. The effect of a small amount of helium gas present in the cell can be neglected. From Eq. 3.1 for a temperature step \(\Delta T\), we calculate \((\Delta d/\Delta T) = -\left(\varepsilon A/C^2\right) \times (\Delta C/\Delta T)\). The change \(\Delta d\) of the distance between the plates can be calculated from the following equation.

\[
\Delta d = d_1 - d_2 = -\varepsilon A\left(\frac{1}{C_1} - \frac{1}{C_2}\right) = -\varepsilon A\left(\frac{C_1 - C_2}{C^2}\right)
\]

(Eq. 3.2)

where \(C \approx \left(\frac{C_1 + C_2}{2}\right)\)

The capacitance resolution is \(\Delta C = 5 \times 10^{-7} \text{ pF}\) and \(C = 10 \text{ pF}\). In equation 3.2 the maximum sensitivity for a sample with length 5 mm which can be achieved in both cryogenic systems is \(\Delta d = 0.05 \text{ Å}\). The coefficient of linear thermal expansion is defined as:

\[
\alpha (T) = \frac{1}{L} \left(\frac{\Delta L}{\Delta T}\right)
\]

(Eq.3.3)

where \(L\) is the length of the sample. The thermal expansion is measured by a stepwise or a continuous heating method. The measured \(\alpha\) of the sample is obtained by:
\[
\alpha(T) = -\frac{1}{L} \left( \frac{\Delta d}{\Delta T} \right)_{\text{cell+sample}} + \frac{1}{L} \left( \frac{\Delta d}{\Delta T} \right)_{\text{cell+Cu}} + \alpha_{\text{Cu}} \quad \text{Eq.3.4}
\]

The first term is the measured change in the gap-distance with a temperature change, when the sample is mounted. The second term is the cell effect. It was measured in a separate run for a copper sample with length 5 mm. The cell effect reproduces well and is small (< 1% of the \( \alpha(T) \) measured for our samples) in the investigated temperature range. Fig 4 shows the plot of \( \Delta d/\Delta T \) as a function of T which is used as correction for the cell effect. The third term is the correction for the thermal expansion coefficient of the copper. We use the data by Kroeger and Swenson [6]. At low temperature the thermal coefficient of copper is very small.

![Graph](image)

*Fig. 4* \( \Delta d/\Delta T \) as a function of T used to calculate the cell effect.
3.4 Transport properties measurement

The transport and magnetic properties of the samples such as electrical resistance ($R$) and ac-susceptibility ($\chi_{ac}$) were measured in the Heliox using a Linear Research Resistance Bridge (LR700). For resistance a current in the range of 30 $\mu$A and 100 $\mu$A and a fixed frequency of 16 Hz is used.

For resistivity measurements samples with dimensions $1 \times 1 \times 4$ mm$^3$ are used. Cu wire is attached to the sample by silver paint to make four point contacts as shown in Fig. 5. From the outer pins the current ($I$) passes through the sample and the voltage drop ($V$) across the sample is measured at the inner pins. The resistivity of the sample is measured as function of temperature or magnetic field.

![Fig. 5 The schematic diagram for the four-point probe contact method.](image)

The measurements are done for different ranges of temperature and magnetic field. The variation of the temperature or magnetic field is controlled by an Oxford LabVIEW program. The resistivity is calculated using the following formula:

$$\rho = R \frac{A}{L}$$

(Eq 3.5)
where A is area of the cross-section and L the distance between the voltage probes.

The ac-susceptibility ($\chi_{ac}$) of the sample is measured by the mutual inductance transformer method [7], where a fixed frequency $f = 16$ Hz was used.

### 3.5 Specific heat measurements

Specific heat measurements were carried out in a home-built $^3$He cryostat which is equipped with a 17 T superconducting magnet [8,9] in the temperature range 0.5-50 K. We used a semi-adiabatic method where electrical heat pulses of 15-30 seconds duration are applied to a sample holder. The temperatures change before and after the heat pulse is monitored by a combination thermometer. This thermometer exhibits very small field dependence.

A pico-watt AVS-47 resistance bridge was used for measuring the temperature. By measuring the heater voltage and current and the time interval, the amount of dissipated heat $Q$ can be determined accurately [10]. The heat capacitance for the sample can be calculated by:

$$C = \frac{Q}{\Delta T}$$  \hspace{1cm} (Eq 3.6)

where $Q$ is the heat added and $\Delta T$ the change in temperature. For our measurement the samples used have a typical mass of 3 g. The sample is placed in a gold-plated cold-rolled silver sample holder. The average accuracy, depend on the sample mass and temperature region, is of the order of 1%. We also performed measurements applying magnetic fields up to 6 T. The sample holder contribution is taken into account and subtracted from the raw data prior to a further analysis.
References:

Chapter 4.

Field-induced antiferromagnetic quantum critical behavior in Ce(Ru,Fe)$_2$Ge$_2$.

$\text{Ce(Ru}_{1-x}\text{Fe}_x\text{)}^2\text{Ge}_2$ was prepared to be at quantum critical point with nominal concentration of $x = 0.76$. The experimental result however showed antiferromagnetic ordering at a Néel temperature $T_N = 2$ K. From the phase diagram we estimate the prepared sample is in the regime of quantum critical point. In this chapter we present the results of the field-induced antiferromagnetic (AF) quantum critical behavior in Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$. The thermal, magnetic and transport properties of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ were studied in zero and applied magnetic field. At a critical field $B_{cr} \approx 0.80$ T the cross-over of non-Fermi liquid (NFL) to Fermi liquid (FL) characteristic near $T = 2$ K is observed. The Grüneisen ratio of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ at low temperature for the magnetic field above and below the critical field is studied and reported.

4.1 Introduction

Heavy fermion (HF) metallic systems show a strong departure from the conventional Landau Fermi liquid (FL) behavior when tuned to an antiferromagnetic (AF) quantum critical point (QCP). The tuning can be done by chemical pressure, hydrostatic pressure or magnetic field [1-5]. In HF metallic systems near a quantum critical point (QCP), the magnetic interactions, dimensionality and the type of quantum criticality can result in various types of NFL behavior [6-7]. For CeCu$_{6-x}$R$_x$ (R = Au, Ag), the Landau FL behavior at $x = 0$ is driven to a magnetically ordered state via chemical doping [8], whereas in AF ordered HF compounds, such as CeIn$_3$ [9] or CePd$_2$Si$_2$ [9,10], the magnetic moments of the Ce 4f-electrons are suppressed by applying hydrostatic pressure. The physics of the Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$ system near the QCP can be described by a competition between the Kondo coupling, where the local 4f electron moments are screened by the conduction electrons and the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling, where the interaction between the neighboring 4f moments is mediated by the polarized electron clouds surrounding them.
The energies of this coupling depend on the exchange coupling constant $J$ between the local spins and the spins of the conduction electrons. $N(E_F)$ is the density of state at the Fermi energy. (For details see page 14)

$$E_{RKKY} \propto N(E_F)J^2$$

$$E_K \propto \exp\left(-\frac{1}{N(E_F)J}\right)$$  \hspace{1cm} (Eq. 4.1)

For $E_{RKKY} > E_K$, there is long range magnetic ordering in the system, but for $E_{RKKY} < E_K$, the 4$f$-moments are screened and the system remains magnetically disordered down to the lowest temperature. The most successful attempt to rationalize this heavy fermion phase diagram was proposed by S. Doniach as shown in Fig. 1 [11]. By controlling $T_K/T_{RKKY}$ ratio we can tune the $Ce(Ru_{1-x}Fe_x)_{2}Ge_2$ system between the antiferromagnet (AF), non Fermi liquid (NFL) and the Fermi liquid (FL). In this chapter we report the field induced AF quantum critical point (QCP) for $Ce(Ru_{1-x}Fe_x)_{2}Ge_2$ with the nominal value of $x = 0.76$ which was reported as critical concentration by Montfrooij and co-workers [12,13].
**Doniach model**

**Fig.1 Upper panel:** The characteristic energies connected to the Kondo-effect and the RKKY-interaction as function of the coupling constant $J$. Lower panel: The “phase diagram” in the Doniach model, i.e. ordering temperature or Fermi liquid temperature as a function of coupling constant $J$ for heavy fermion systems. {Picture taken from Ref. 11}

### 4.1.1 Crystallographic structure of Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$

We used a Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$ single crystal that was prepared in the Van der Waals Zeeman Institute (UvA) by Y.K. Huang. The single crystal was grown by the Czochralski method with the nominal concentration $x = 0.76$. Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$ crystallizes in the ThCr$_2$Si$_2$ structure [13] as shown in Fig. 2, with the magnetic Ce atoms forming a body centered tetragonal lattice with lattice parameters $a = 4.1$ Å and $c = 10.4$ Å. There are 2 formula units
per unit cell. Magnetization measurements, in the temperature range 2 - 300 K, show the tetragonal axis is the easy axis. [14]. At low temperature the cerium moments (0.15 $\mu_B$/Ce-ion) are on the verge of forming a spin density wave (SDW) with the propagation wave vector $2k_F = (0,0,0.45)$ where $k_F$ is the Fermi wave vector. The moments are directed along the c-axis.

![Crystallographic structure of the parent compound CeRu$_2$Ge$_2$ with the body centered tetragonal lattice.](Picture taken from Ref. 13)

**Fig 2** Crystallographic structure of the parent compound CeRu$_2$Ge$_2$ with the body centered tetragonal lattice. {Picture taken from Ref. 13}

### 4.1.2 Phase diagram of the $\text{Ce}(\text{Ru}_{1-x}\text{Fe}_x)_{2}\text{Ge}_2$ series

The $\text{Ce}(\text{Ru}_{1-x}\text{Fe}_x)_{2}\text{Ge}_2$ phase diagram obtained by applied mechanical pressure and by Fe doping is shown in Fig. 3. The parent compound, $\text{CeRu}_2\text{Ge}_2$, is a ferromagnet (FM) below 8 K [13,15]. By applying pressure, as shown on the upper x-axis, FM is suppressed and evolves into two AF phases. These AF phases then vanish at $p_{cr} = 67$ kbar. A further increase of the pressure brings the system to the FL regime. The pressure dependence of the Kondo temperature is shown by the filled circles. As presented in Fig. 3, the chemical doping (lower axis) shows a similar phase diagram [15,16]. When we tune the system from the ferromagnetic (FM) to the AF state, the FM transition temperature $T_C$ decreases with the increase of Fe concentration, followed by a decrease of the Néel temperature $T_N$. The AF QCP is observed for the critical Fe concentration $x = 0.76 \pm 0.05$ [12]. Ac and dc susceptibility measurements show good agreement with the pressure results. The resistivity curve shows a $T^2$ dependence in the FL part denoted by the shaded area in Fig.3.
Fig. 3 The magnetic phase diagram of Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$ as a function of doping (lower axis) and pressure (upper axis). The dot-dashed lines show the pressure data [16]. The ◇ show the FM boundary by Fe doping [13]. The * show the AF phase boundary [12]. The pressure dependence of the Kondo temperature is shown by the filled circles. The FL regime observed in the resistivity is shown with the shaded area. [Picture taken from Ref. 12]

4.2 Experimental results and discussion

4.2.1 Thermal expansion of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ in zero field.

The thermal expansion of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ was measured on a cubic single crystal with dimensions 5 × 5 × 5 mm$^3$. The coefficient of linear thermal expansion ($\alpha$) was measured in the bath cryostat and in the Heliox system. At low temperature the thermal expansion was measured by step-wise heating, while at high temperatures the continuous heating method was used. (See Chapter 3)

The sample was mounted in the capacitance dilatometer. The $\alpha(T)$ data along the three crystallographic axes are presented in Fig. 4. Thermal expansion in the temperature range of 0.3 - 12 K was measured in the Heliox system. For 2 K < T < 150 K $\alpha(T)$ was measured in the bath cryostat.
Fig. 4 Coefficient of linear thermal expansion, $\alpha$, along the $a, b, c$ axes of the Ce(Ru$_{0.24}$Fe$_{0.74}$)$_2$Ge$_2$ sample as a function of temperature in zero field. The green curve gives the average of the three directions.

The data show a large anisotropy between the $c$-axis and the tetragonal plane. The average of the three curves is presented in Fig. 4. The volumetric thermal expansion, $\beta$, is calculated from the average thermal expansion as:

$$\beta = 3 \times \alpha_{\text{avg}}$$  \hspace{1cm} (Eq. 4.2)
Fig. 5 Low temperature coefficient of linear thermal expansion, $\alpha$, along a,b,c axes of Ce(Ru$_{0.24}$Fe$_{0.74}$)$_2$Ge$_2$ sample as a function of temperature in zero field. The green curve gives the average of the three directions.

The thermal expansion along the c-axis (easy axes for the magnetization) is bigger than the thermal expansion for the other two axes. The thermal expansion in the basal plane axis is not completely isotropic, which can be due to the contribution from the c-axis thermal expansion. The thermal expansion data show the presence of three main contributions: (i) the phononic contribution which is dominant for $T > 50$ K, (ii) a heavy fermion contribution which is dominant for $T < 50$ K, and (iii) antiferromagnetic ordering of the 4f moments below $T_N = 2$ K.

Fig. 5 shows the low temperature data along the three principal axis and the average thermal expansion. For temperature $T < 2$ K, the negative thermal expansion is mainly due to antiferromagnetic ordering of 4f moments. The maximum value of the thermal expansion is observed at $T = 6$ K.
4.2.2 Specific heat of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ in zero field.

Specific-heat measurements on the Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ sample with a mass of 3 g were carried out in the home built $^3$He system. The data obtained using a semi-adiabatic method down to 0.5 K (see Chapter 3) are presented in Fig. 6. The inset shows the temperature dependence of the specific heat of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ measured in the temperature range 0.5 K to 40 K in zero field. At high temperature the linear electronic contribution in the specific heat is very small compared to the lattice contribution but at low temperature the linear electronic contribution is comparable to the lattice term and the specific heat is described by:

\[ c = c_{\text{electron}} + c_{\text{lattice}} = \gamma T + \beta T^3 \]  

(Eq.4.3)

where $\gamma$ is the Sommerfeld coefficient of the linear electronic specific heat and the second term corresponds to the lattice contribution.

*Fig.6 Temperature dependence of the specific heat of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ in zero field. The inset shows the high temperature data.*
Fig. 7 Specific heat, plotted as \( c/T \) vs \( T^2 \), of \( \text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2 \) in zero field. The solid line is a linear fit to the data.

To calculate Debye temperature we fit the \( c/T \) data in the temperature range 32 – 36 K as shown in Fig. 7. The roughly estimated the values are \( \gamma = 132 \text{ mJ/molK}^2 \) and \( \beta = 0.347 \text{ mJ/molK}^4 \). The Debye temperature \( \theta_D = 302 \text{ K} \) is calculated with help of the relation:

\[
\theta_D^3 = N \frac{12\pi^4 R}{5\beta} \quad \text{(Eq. 4.4)}
\]

where \( R = 8.314 \text{ J/K mol} \) is the gas constant and \( N = 5 \) is the number of atoms per formula unit for \( \text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2 \).
Fig. 8 Specific heat $c/T$ as a function of $T$ for single crystalline $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ in zero field. The empty circles are our data, the red circles represent data by Montfrooij and co-workers in zero field and solid line gives the lattice contribution represented by $\text{LaFe}_2\text{Ge}_2$.

The low temperature magnetic state of $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ can be investigated by examining the magnetic contribution to the specific heat below 50 K. $c_{\text{mag}}$ is obtained by subtracting the lattice contribution, which is represented by the non-$f$-electron system $\text{LaFe}_2\text{Ge}_2$, from the specific heat of $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ in 0 T. Data of Montfrooij and co-workers on a different $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ single crystal is shown in Fig. 8 for comparison.

The $\text{Ce}$-atoms in $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ are in a doublet crystal-field ground state, the $2J+1=6$ $\text{Ce}$ levels being split into three doublets. Transitions between the crystal-field split $f$-levels give a large contribution to the electronic specific heat, the Schottky effect, which can be expressed as:
\[
c_{Sch} = R \left( \frac{\Delta}{k_B T} \right)^2 \frac{g_o}{g_1} \frac{\exp(\Delta/k_B T)}{\left[ 1 + \left( \frac{g_0}{g_1} \right) \exp(\Delta/k_B T) \right]^2}
\]

\[
c_{Sch} = R \left( \frac{\Delta}{k_B T} \right)^2 \frac{g_o}{g_1} \exp \left( \frac{-\Delta}{k_B T} \right) \quad \text{for } T << \frac{\Delta}{k_B} \quad \text{(Eq.4.5)}
\]

\[
= \frac{R g_o g_1}{(g_o + g_1)^2} \left( \frac{\Delta}{k_B T} \right)^2 \quad \text{for } T >> \frac{\Delta}{k_B}
\]

Here $\Delta$ is the energy separation between two electron levels and $g_0$ and $g_1$ are the degeneracies. At the temperature comparable to $\Delta/k_B$, the transition from one level to another takes place.

In Fig.9 we show $c/T$ as a function of temperature for our sample and the data by Montfrooij. A difference is observed below 4 K. The maximum in $c/T$ observed for our sample shows the presence of magnetic order near 2 K.

*Fig. 9 f-electron specific heat of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ plotted as $c_{mag}/T$ versus $T$. The empty circles are our data and the red circles represent data by Montfrooij and co-workers [12] in zero applied field. The inset shows the data sets for the low temperature regime.*
4.2.3 The effective Grüneisen parameter in zero field

The effective Grüneisen parameter, $\Gamma_{\text{eff}}(T)$, gives the relation between the volumetric thermal expansion, $\beta$, and the specific heat, $c$. When $\beta$ and $c$ have the same temperature dependence, the effective Grüneisen parameter is quasi-constant. $\Gamma_{\text{eff}}(T)$ is calculated from the measured temperature dependent volumetric thermal expansion $\beta(T)$ and the specific heat $c(T)$ by the following formula:

$$
\Gamma_{\text{eff}}(T) = \frac{V_m}{\kappa} \frac{\alpha_v(T)}{c(T)}
$$  \hspace{1cm} (Eq. 4.6)

where $\kappa = 10^{-11}$ Pa$^{-1}$ is the isothermal compressibility. The volumetric thermal expansion, the specific heat and the Grüneisen ratio as a function of temperature of Ce($\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ are presented in Fig. 10. We can observe the antiferromagnetic ordering of the $4f$ moments at $T_N = 2$ K in all three data sets. The high temperature Grüneisen ratio shows the overall constant value $\Gamma_{\text{ph}} = 2$ for the phononic contribution. Below 20 K the Grüneisen ratio increases and reaches the maximum value of 70 at $T = 6$ K. The negative value of the Grüneisen ratio below 2 K is due to antiferromagnetic ordering of the $4f$ moments.

![Graph](image.png)

*Fig.10 Coefficient of volumetric thermal expansion, $\beta$, specific heat and the Grüneisen ratio of Ce($\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ as a function of temperature in zero field.*
The ac-susceptibility of $\text{Ce}(\text{Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ at low temperature was measured on a sample with size $1 \times 1 \times 4.5$ mm$^3$ at a frequency 16 Hz and with a driving field of $10^{-5}$ T. The data obtained by the mutual induction method are presented in Fig.11. The small peak below 2 K shows the sample orders magnetically. We also observe the $AF$ ordering as a weak maximum in the specific heat ($c/T$) and as a drop in the coefficient of thermal expansion data ($\beta/T$).

In previous studies it was reported that the $\text{Ce}(\text{Ru}_{1-x}\text{Fe}_x)_2\text{Ge}_2$ system has an $AF$ QCP for $x = 0.76$ [12]. For such a QCP the critical behavior of the thermal expansion and the specific heat as the function of temperature is expected [19] to vary with temperature as:
\[ \alpha_{cr} \propto T^{1/2} \]
\[ c_{cr} \propto T^{3/2} \]  

(Eq. 4.7)

Our data do not show this critical behavior in \( Ce(Ru_{1-x}Fe_x)2Ge2 \) with the nominal Fe concentration \( x = 0.76 \) of our sample. The presence of ordering in our sample indicates the real concentration is lower than the nominal concentration. From the phase diagram Fig. 3 we estimate the \( x \)-value of our sample is 0.74.

As reported for the heavy fermion metal \( YbRh_2(Si_{1-x}Ge_x)2 \) [18] the antiferromagnetic ordering temperature can be driven to zero Kelvin by applying magnetic field. As our \( Ce(Ru_{0.24}Fe_{0.76})2Ge2 \) compound is near the quantum critical regime \( (x \sim 0.74 \pm 0.005) \) a field-induced AF QCP may be achieved at a critical field \( B_{cr} \). For \( B > B_{cr} \) we expect the system to recover the Landau Fermi liquid \((FL)\) behavior which in the resistivity is characterized by:

\[ \rho = \rho_0 + AT^2 \]  

(Eq. 4.8)

Here \( \rho_0 \) is the residual resistivity due to impurities and defects and \( A \) is the \( FL \) coefficient. For heavy fermion system, there is an empirical relation between the coefficient \( A \) and the coefficient of the electronic specific heat, \( \gamma \), namely the empirical Kadowaki-Woods ratio [18].

Magnetoresistance measurements were carried out on bar shaped samples \((size \ 1 \times 1 \times 4.5 \ mm^3)\) using the four-probe contact method in order to investigate the presence of the critical field. In Fig.12 we show the magnetoresistance data at \( T = 0.24 \) K of \( Ce(Ru_{0.24}Fe_{0.76})2Ge2 \) for a current applied along the \( a \)-axis and the \( c \)-axis. The magnetic field was applied along the \( c \)-axis (easy axis) for both orientations. The derivative of the magnetoresistance as the function of temperature \((dp/dB)\) gives an inflexion point at \( B_{cr}^R = 0.70 \) T.
Fig. 12 Resistance of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ as a function of magnetic field at $T = 0.24$ K for field along the c-axis and current along the c-axis (green curve) and along the a-axis (red curve).

The magnetostriction of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ has been measured up to 4 T at the base temperature (0.24 K) of the Heliox system to further examine the suppression of the AF state. The field was applied along the easy axis for magnetization (c-axis) and the length change was measured along the field ($\lambda_\parallel$) and perpendicular to the field ($\lambda_\perp$). The linear magnetostriction is strongly anisotropic like the magnetoresistance: $\lambda_\parallel > \lambda_\perp$. The volume magnetostriction is calculated by using the relation: $\lambda_v = \lambda_\parallel + 2\lambda_\perp$. The data of $\lambda_\perp$, $\lambda_\parallel$ and $\lambda_v/3$ are shown in Fig.13 (left panel).
Fig. 13 Left panel: Relative length change as a function of the magnetic field at $T= 0.24 \, K$ for single crystalline Ce(Ru,Fe)$_2$Ge$_2$. For $B || c$-axis $\Delta L/L$ was measured along the $a$ and $c$ axes. Right panel: $d\lambda/|dB$ as a function of the magnetic field.

In the right panel of Fig. 13 the coefficient of linear magnetostriction $\tau = d\lambda/|dB$ is presented as a function of magnetic field. The derivative of $\lambda(T)$ has an inflection point at $B_{cr}^c = 0.75 \, T$. This value is comparable to the $B_{cr}^R = 0.70 \, T$ derived from the magnetoresistance. Notice the measurements of magnetoresistance and magnetostriction were performed on different samples prepared from the same batch.

To study the transport properties near and at the critical magnetic field, we measured the electrical resistance of the sample in magnetic fields of 0, 0.5, 0.75, 1 and 1.5 $T$. The measurements were carried out on two different samples with the current along the $a$ and $c$ axis. The magnetic field was always applied along the $c$- axis. The residual resistance ratio (RRR) for the bar along the $a$-axis is 1.4 and for the bar along the $c$-axis is 2.3. (see Chapter 3)
Fig. 14 shows the electrical resistivity as a function of temperature for a current along the $a$-axis and a current along the $c$-axis with the magnetic field applied along the $c$-axis. The effect of the magnetic field is much more pronounced on the resistivity along the $c$-axis than along the $a$-axis. For low applied fields (0, 0.25 and 0.5 T) the electrical resistivity shows an upturn below 2 K which is due to the magnetic ordering. At $B = 0.75$ T the upturn due to magnetic ordering completely vanishes. By increasing the field to 1 T and 1.5 T, the resistivity recovers the $T^2$ dependence at low temperatures. The data for $B = 1.5$ T show a $T^2$ temperature dependence in the range of $0.25 \text{ K} < T < 2 \text{ K}$. Fig. 15 shows the electrical resistivity as a function of $T^2$ for magnetic field $B = 1.5$ T.

Fig. 14 The electrical resistivity versus temperature in a magnetic field applied along the $c$-axis and current parallel and perpendicular to the applied field.
Fig. 15 The electrical resistivity versus $T^2$ in applied magnetic field of 1.5 T. The solid line gives $\rho \propto T^2$ dependence at 1.5 T.

At the critical field $B_{cr} = 0.75$ T, the electrical resistivity is characterized by non-Fermi liquid behavior:

$$\rho = \rho_0 + AT^n$$

(Eq. 4.10)

where $n < 2$. We have extracted the value of $n$ by fitting the data for $I \parallel c$-axis. We find $n = 1.5$ in the range $0.25 \text{ K} < T < 2.5 \text{ K}$. The exponent is lower above 2.5 K as shown in Fig. 16. The electrical resistivity for $I \parallel c$-axis and $B \parallel c$-axis is plotted as a function of $T^{d.5}$ in Fig.16.
4.2.5 Thermal expansion and specific heat in applied field

We studied the magnetic-field tuned quantum critical point (QCP) at $B_{cr} = 0.75$ T in a single crystalline sample with composition $\text{Ce(Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$. The very weak AF state below $T_N = 2$ K, with ordered moments as small as 0.15 $\mu_B$ [14], is continuously suppressed by the applied magnetic field and quantum critical behavior arises.

To study the effect of an applied field on the thermal expansion we applied the magnetic field along the $c$-axis and measure the thermal expansion along the $a$-axis and the $c$-axis. The thermal expansion coefficient along the $c$-axis as a function of temperature is reported in Fig. 17. The data were taken in magnetic fields of 0, 0.5, 0.6, 0.75, 0.85, 1, 1.5, 2, 4 and 6 T applied along the $c$-axis. For $B < B_{cr}$, we observe ordering of the AF moments below $T_N = 2$ K. For $B_{cr} = 0.75$ T, the AF order is suppressed and the thermal expansion
coefficient shows a linear temperature dependence. For $B > 0.85$ T, the thermal expansion coefficient gradually decreases.

![Graph showing thermal expansion coefficient along the c-axis in magnetic fields](image)

**Fig. 17** Thermal expansion coefficient along the c-axis in magnetic fields (0, 0.5, 0.6, 0.75, 0.85, 1, 1.5, 2, 4 and 6 T) applied along the c-axis. The solid (0 T) and dashed line (0.75 T) are data points and serve to guide the eye.

Fig. 18 shows the coefficient of thermal expansion, measured along the $a$-axis for the magnetic field applied along the c-axis. The magnetic fields applied are 0, 0.5, 0.75, 0.85 and 1 T. The effect of the applied magnetic field in the basal plane is smaller than along the tetragonal axis.
Fig. 18 Coefficient of thermal expansion along the a-axis in magnetic fields of 0, 0.5, 0.75, 0.85 and 1 T applied along the c-axis.

The calculated volumetric thermal expansion, $\beta$, is presented in Fig 19. The curve for $B = 0.8$ T is obtained by averaging the curves of 0.75 T and 0.85 T. As the data for $B_{cr} = 0.75$ T and $B = 0.85$ T are almost equal at low temperature the $B_{cr} \approx 0.80$ T is used for further analysis.
The specific heat over temperature, $c/T$, as a function of the temperature measured in applied field of $0, 0.6, 0.8, 1, 1.5$ and $4$ T along the $c$-axis is presented in Fig. 20. At $0$ T we can see shoulder in the graph below $T = 2$K which shifts to lower temperature as the magnetic field increases. At $B = 0.80$ T, $c/T$ is linear as function of temperature and for higher applied magnetic fields the specific heat shows the NFL behavior in the low temperature regime. This crossover from NFL to FL observed at $B = 0.80$ T is in good agreement with the thermal expansion and electrical resistivity data.
**Fig. 20** Specific heat, $c/T$ as a function of the temperature in magnetic field of 0, 0.6, 0.8 and 1 T.

### 4.2.6 Grüneisen ratio and entropy analysis in applied fields

Thermal expansion and the specific heat data are used to calculate the effective Grüneisen ratio of $\text{Ce(Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ in applied magnetic fields. Fig. 21 presents the effective Grüneisen ratio at magnetic fields of 0, 0.60, 0.80 and 1 T. $\Gamma_{\text{eff}}$ shows that the AF ordering of the moments below $T_N = 2$ K for 0 T and 0.60 T is suppressed by applying the magnetic field. The maximum value of $\Gamma_{\text{eff}}$ at the lowest temperature reaches 35 for $B = 0.80$ T. At 4 K $\Gamma_{\text{eff}} \sim 80$, which is a large value and suggests that at $B = 0.80$ T, $\text{Ce(Ru}_{0.24}\text{Fe}_{0.76})_2\text{Ge}_2$ is near a critical point. Above $B = 0.80$ T, $\Gamma_{\text{eff}}$ decreases at low temperature and loses the critical behavior. The AF critical behavior of the Gruneisen ratio as a function of temperature is characterized by: [19]
\[ \Gamma_{cr} \propto T^{-1/\nu} \]  
(Eq. 4.11)

where \( z \) is the dynamical critical exponent and \( \nu \) is the correlation-length exponent. The critical behavior of the effective Gruneisen ratio as a function of temperature is theoretically expected [19] to diverge for a disorder compound in zero field. Notice the compound we used is doped and quantum critical behavior is induced by applying a magnetic field, due to which we do not observe divergence at \( B = 0.80 \) T.

![Graph showing the effective Grünisen ratio for the applied fields of 0, 0.5, 0.6, and 0.8 T.](image)

*Fig. 20 The effective Grünisen ratio for the applied fields of 0, 0.5, 0.6, and 0.8 T.*

At low temperature, the entropy due to the crystal electric field effect in zero field is studied and compared with the data from Montfrooij and co-worker at the critical concentration compound [14]. The magnetic entropy below 2 K indicates that there is a lowest level doublet influencing the specific heat, \( c(T) \) [20]. The \( f \)-electron contribution to the entropy, \( S_{mag} \), for the single crystal, \( Ce(Ru_{0.24}Fe_{0.76})_2Ge_2 \), is obtained by integrating \( c_{mag}/T \) versus \( T \). The data is presented in Fig. 21 for the applied magnetic field of 0, 0.50,
0.80 and 1 T. The entropy associated with the doublet of ground state equals $R \ln 2$. At $T \sim 40$ K the entropy, $S_{\text{mag}}$, reaches this value, for Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ in zero field.

![Graph](image)

Fig. 21 The 4 f-electron entropy for Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ in the applied magnetic field of 0, 0.50, 0.80 and 1 T. The data of Montfrooij and co-worker (Michigan data) is shown for comparison.

### 4.3 Summary

The thermal, magnetic and transport properties of a Ce(Ru$_{1-x}$Fe$_x$)$_2$Ge$_2$ single crystal grown with nominal concentration of $x = 0.76$ were studied and reported in this chapter. The thermal expansion measurements in zero applied magnetic field show an AF ordering of the Ce-moments at $T_N = 2$ K. The specific heat measurements showed a good agreement with the thermal expansion data. The Debye function with $\theta_D = 210$ K is calculated from the $c/T$ versus $T^2$ curve. At high temperatures the effective Grüneisen ratio, $\Gamma_{\text{ph}} = 2$ due to the phononic contribution. The AF ordering of the f-electron moments below 2 K results in a negative value of the Gruneisen ratio.
We applied a magnetic field to suppress the $AF$ ordering and reach the quantum critical point. Magnetoresistance and magnetostriction measurements were performed to estimate the critical magnetic field. The effect of the applied magnetic field was bigger on the resistivity along the tetragonal axis than along the basal plane axes. At the critical applied magnetic field, $B_{cr} = 0.75$ T, the electrical resistivity, $\rho_{cr}$, shows the temperature dependence, $T^{d.5}$, in the range $0.25$ – $2.5$ K. For $B > B_{cr}$, $FL$ behavior is observed at low temperatures.

The thermal expansion and the specific heat data for $Ce(Ru_{0.24}Fe_{0.76})_2Ge_2$ in applied magnetic field are studied and reported in this chapter. Near the critical magnetic field, $B = 0.80$ T, the NFL to FL cross-over is observed near $2$ K. The $4f$-electron entropy, $S_{mag}$ for the applied magnetic field $B = 0.80$ T show good agreement with the $Ce(Ru_{0.24}Fe_{0.76})_2Ge_2$ critical concentration data obtained from the work of Montrooij and co-workers. At the applied zero magnetic field, the $4f$-electron entropy was equal to $Rln2$ at $T \sim 40$ K which is due to the ground state doublet of the $Ce 4f^1$ electron.
References:

CHAPTER 5.

Magnetic ordering and superconductivity in rare-earth oxypnictide

In this chapter we present results of thermal expansion experiments carried out on the newly discovered FeAs-based superconductor La(O$_{1-x}$F$_x$)FeAs and magnetically ordered GdOFeAs. In the La(O$_{1-x}$F$_x$)FeAs compound the Spin Density Wave (SDW) and crystallographic transitions at high temperature were observed. In the thermal expansion of GdOFeAs we observed the ordering of Gd magnetic moments at low temperature.

5.1 Introduction

The discovery of superconductivity in the LaO$_{1-x}$F$_x$FeAs series ($T_{SC}$= 26 K, for x=0.10) [1] has stimulated great interest in the family of layered rare-earth metal oxypnictides, notably because superconducting transition temperatures ($T_{SC}$) have been observed to exceed 50 K. The highest $T_{SC}$ of 43 K, 52 K, 52 K and 41 K have been reported for the doped oxypnictide REO$_{1-x}$F$_x$FeAs, where RE is the rare earth metal Sm, Nd, Pr or Ce respectively [2].

Like in cuprates and other unconventional superconductors, doping of electrons or holes into the parent antiferromagnetic compound plays an important role in the superconducting mechanism. But unlike the parent compounds of the cuprates which are Mott insulators, the parent oxypnictides are poor metals and have delocalized electrons.

The REOFeAs compounds have a layered crystal structure with alternating Fe-As and RE-O layers. The compound becomes electron doped by replacing oxygen by fluorine, the superconductivity emerges while magnetic order is suppressed. This has been taken as evidence that the strong magnetic fluctuations arising due to a proximity to a magnetic quantum critical point (QCP) are important for the realization of superconductivity in the electron doped superconductors REO$_{1-x}$F$_x$FeAs [3].
In $LaOFeAs$ a structural transition from a tetragonal to an orthorhombic lattice structure at $T_{SC} = 150$ K \cite{4,5} and a magnetic transition to a long-range spin density wave ($SDW$) antiferromagnetic order with strongly reduced ordered moments below 134 K are found. The latter has been observed in neutron scattering and muon spin relaxation ($\mu$SR) experiments \cite{5,6}. In this $La$-system it is possible to study the magnetic and superconducting properties of the $FeAs$ system without possible interference effects due to the rare-earth magnetic moments. For the heavy rare-earth elements a single structural phase could not easily be formed and no superconducting state was observed above 2 K. Due to this, when superconductivity was found in the doped compounds of $GdOFeAs$, it attracted a lot of attention. At high temperature $GdOFeAs$ shows an anomaly at 138 K which can be related to a structural or a $SDW$ transition \cite{7}. Below 4 K the $Gd$ moments order.

Here we report thermal expansion measurement carried out in a capacitance dilatometer on polycrystalline samples of $LaOFeAs$, doped $LaO_{1-x}F_xFeAs$ ($x$=0.10) and $GdOFeAs$.

5.1.1 Crystallographic structure of REOFeAs

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Left: REOFeAs crystallizes in the ZrCuSiAs structure with space group P4/nmm. Right: Unit cell of REOFeAs with 8 atoms/unit cell. (Picture taken from Ref. 8)}
\end{figure}
The parent \( \text{REOFeAs} (\text{RE=La, Nd, Sm, Gd}) \) compounds are poor metals and exhibit Pauli-paramagnetism. The equiatomic quaternary parent compounds crystallize in the tetragonal \( \text{ZrCuSiAs} \) type structure [8] with space group \( P_{4/nmm} \) at high temperature. Fig. 1 shows the crystal structure and unit cell. The dimensions of the unit cell are roughly \( a = 4 \text{ Å} \) and \( c = 8-9 \text{ Å} \) [9]. There are two formula units per unit cell. The \( \text{Fe-As} \) layer is sandwiched between the \( \text{RE-O} \) layers. The \( \text{RE-O} \) layer acts as a charge reservoir when it is doped with fluorine. The electrons flow in the \( \text{Fe-As} \) layer. It is believed that superconductivity mainly takes place in the \( \text{Fe-As} \) layer. In the parent compounds the \( \text{Fe} \) moments order antiferromagnetically in a stripe pattern.

The antiferromagnetic (\( \text{AFM} \)) phase transition is associated with the crystallographic distortion from a tetragonal to an orthorhombic phase. For the parent compounds neutron-diffraction experiments have shown that the antiferromagnetic transition is of the spin density wave (\( \text{SDW} \)) type [9].

By doping electrons or holes in the parent compounds, the \( \text{SDW} \) and crystallographic transitions are suppressed, while superconductivity appears. Also, applying pressure on the parent compounds shows the increase in superconducting transition temperature. For example, superconductivity with \( T_{SC}= 43 \text{ K} \) appears in \( \text{LaOFeAs} \) at a pressure of \( \sim 4 \text{ Gpa} \). It has been concluded that pressure or chemical doping plays an important role for the appearance of superconductivity [10].

An increase in the number of charge carriers and a contraction of the lattice parameter appears in these systems in the case of oxygen deficiency [2]. To investigate how oxygen deficiency affects these systems, a series of \( \text{REFeAsO}_{1.8} \) samples has been prepared by high-pressure synthesis [2]. These illustrative results are discussed next.

Fig. 2a is a plot of the resistivity as a function of temperature for \( \text{REFeAsO}_{0.85} \) (\( \text{RE= La, Ce, Pr, Nd, Sm} \)). The doping of oxygen vacancies suppresses the \( \text{SDW} \) transition and superconductivity appears. Fig. 2b is a plot of the onset temperature for superconductivity as a function of the lattice parameter. The chemical pressure, due to
contraction of the basal-plane lattice parameter by 3.1% from La to Sm, results in an increase of the onset temperature $T_{\text{onset}}^{\text{SC}}$ from 26 K to 55 K.

(a)

![Graph showing temperature dependence of resistivity and lattice parameter](image)

**Fig. 2 a)** Temperature dependence of the resistivity for the oxygen deficient $\text{REFeAsO}_{1-\delta}$ samples. **b)** Lattice parameter dependence of $T_{\text{onset}}^{\text{SC}}$ for $\text{REFeAsO}_{1-\delta}$ samples. (Picture taken from Ref. 2).

5.1.2 **Phase diagram of RE(O$_{1-x}$F$_x$)FeAs series**

The superconducting transition temperature of the $\text{REOFeAs}$ compounds changes by doping of charge carriers. Neutron scattering experiments [12] have demonstrated the antiferromagnetic parent compound ($\text{REOFeAs}$) deforms from tetragonal to orthorhombic structure at high temperatures. This deformation is then followed by the spin density wave transition. As the doping concentration increases the antiferromagnetic order is destroyed. Superconductivity is observed at higher doping concentration. So far, no generic phase diagram can be reported.
For the $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$ system, the phase diagram (Fig. 3a) indicates magnetism vanishes continuously, as for a phase transition of the second order type [12]. The antiferromagnetic order due to the Fe moments vanishes at the fluorine content $x = 0.06$, above which superconductivity appears. At low temperatures the Ce moments order magnetically.

Fig. 3b shows the phase diagram for $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$. Already at low fluorine concentration ($x > 0.04$ content of fluorine) superconductivity is observed and antiferromagnetism is suppressed. This indicates antiferromagnetism vanishes in a first order fashion and superconductivity does not coexist with antiferromagnetic order. The $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ phase diagram is different from the one of the high temperature superconducting cuprates, where it is believed that antiferromagnetic spin fluctuation mediate superconductivity. However the phase diagram of $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$ is similar to the cuprates diagram. Clearly more research is needed to come to a generic phase diagram for $\text{REO}_{1-x}\text{F}_x\text{FeAs}$.

In fluorine doped $\text{GdOFeAs}$ the superconducting transition temperature is higher than in the La-systems. For $\text{Gd}(\text{O}_{0.83}\text{F}_{0.17})\text{FeAs}$ $T_{SC} = 37$ K [13]. Electrical resistivity measurement for $\text{Gd}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ with $x = 0.12, 0.15, 0.17$ indicates coexistence of antiferromagnetic order and superconductivity [14]. By using a high pressure synthesis method oxygen deficiency can be created which results in doping of hole carriers. In this way $T_{SC}$ of $\text{GdO}_{1-x}\text{FeAs}$ can be increased to 53.5 K [13]. By doping $\text{Th}^{4+}$ for $\text{Gd}^{3+}$, the system is doped by electron carriers in the $\text{REO}$ layer instead of in the FeAs layer, which leads to an increase in $T_{SC}$ to 56.5 K.
Fig. 3  

a) Electronic phase diagram of Ce(O\textsubscript{1-x}F\textsubscript{x})FeAs as a function of fluorine doping determined by neutron scattering experiments. {Picture taken from Ref. 12}.

b) Electronic phase diagram of La(O\textsubscript{1-x}F\textsubscript{x})FeAs as a function of fluorine doping determined by μSR experiments. {Picture taken from Ref. 11}.

5.2 Experimental results and discussion

5.2.1 Thermal expansion of LaOFeAs

The thermal expansion of polycrystalline LaOFeAs was measured on a pressed pallet with diameter 3 mm and height 1.6 mm. The sample was prepared by the two step solid-state reaction method [15] in the group of Dr. Rudiger Klingeler at the Leibniz-Institute for Solid State and Materials Research (IFW) in Dresden, Germany. At high T, the unit cell dimensions are \(a=4.03\ \text{Å},\ \ c=8.74\ \text{Å},\ \) and \(V=142.15\ \text{Å}^3\) with space group \(P4/nmm\). There are 2 formula units per unit cell. For low temperatures the unit cell dimensions are \(a=5.682\ \text{Å},\ \ b=5.71\ \text{Å},\ \ c=8.71\ \text{Å},\ \) and \(V=282.95\ \text{Å}^3\) with space group of \(C_{mma}\). There are 4 formula units per unit cell [16].
The coefficient of linear thermal expansion ($\alpha$) was measured in the bath cryostat system. At low temperature the thermal expansion was measured by step-wise heating and at high temperatures the continuous heating method was used (see chapter 3).

The sample was mounted in the capacitance dilatometer together with a copper spacer of 3.4 mm in order to make the total sample length 5 mm. The $\alpha(T)$ data obtained in this way are reported in Fig.4.

![Coefficient of linear thermal expansion, $\alpha$, for the LaOFeAs sample as a function of temperature. The red line represents an estimate of the lattice contribution. $T_S$ and $T_{SDW}$ are the structural and magnetic ordering transition temperatures.](image)

Fig. 4 Coefficient of linear thermal expansion, $\alpha$, for the LaOFeAs sample as a function of temperature. The red line represents an estimate of the lattice contribution. $T_S$ and $T_{SDW}$ are the structural and magnetic ordering transition temperatures.

In the neutron diffraction measurements [17] a structural transition is reported at $T_S= 156$ K. At $T_{SDW} = 138$ K an antiferromagnetic spin density wave transition is reported in optical measurements [16]. These transitions were also observed in other properties like the electrical resistivity and the magnetic susceptibility [17]. Fig. 5 is a plot of the electrical resistivity and magnetic susceptibility as a function of temperature for LaOFeAs. The temperature derivative of the resistivity and susceptibility are shown as well (filled circles,
right scale). Both data sets show the structural as well as the antiferromagnetic spin density wave transition in good agreement with our thermal expansion measurements.

Fig. 5 Temperature dependence of (top) the electrical resistivity and (bottom) the magnetization as a function of temperature and the respective derivatives. $T_S$ and $T_{SDW}$ are the structural phase transition temperature (156 K) and the SDW-transition temperature (138 K) respectively. {Picture taken from Ref. 15}.

The overall behavior of $\alpha(T)$ can be attributed to the thermal expansion of the lattice. At high temperatures two clear anomalies are observed, which we identify as the structural transition at $T_S = 156$ K and the antiferromagnetic transition at $T_{SDW} = 138$ K. The steps in $\alpha$, $\Delta\alpha$, at these transition temperatures are $\Delta\alpha_S = 2.77 \times 10^{-6}$ K$^{-1}$ and $\Delta\alpha_{SDW} = -1.56 \times 10^{-6}$ K$^{-1}$, respectively.

The specific heat of LaOFeAs was also measured by the Dresden group for the parent compound [19]. A plot of the specific heat as a function of temperature is shown in Fig. 6. The structural and the antiferromagnetic $SDW$ transitions can be observed in the data. The
step in the specific heat at the structural phase transition is \( \Delta c_S = 1.65 \text{ J/mol K} \) and for the \( SDW \) antiferromagnetic transition \( \Delta c_{SDW} = 2.28 \text{ J/mol K} \).

![Graph showing specific heat and anomaly at different temperatures](image)

**Fig. 6** The specific heat at constant pressure, \( c_p \) (left axis) and \( \Delta c_p \) (right axis) as a function of temperature \( T \) for \( LaOFeAs \). The inset shows \( c/T \) versus \( T^2 \). {Picture taken from Ref. 19}.

The hydrostatic pressure dependence of \( T_{SDW} \) is directly related to the steps in the coefficient of the linear thermal expansion, \( \Delta \alpha \), and the specific heat, \( \Delta c \). It can be calculated using the Ehrenfest relation for second order phase transitions:

\[
\frac{dT_{SDW}}{dP} = \frac{3V_m}{(\Delta c / T)} \frac{\Delta \alpha}{(\Delta c / T)}
\]

(Eq. 5.3)

where \( V_m = 4.23 \times 10^{-5} \text{ m}^3/\text{mol} \) is the molar volume. A negative jump in \( \Delta \alpha \) is observed at the antiferromagnetic \( SDW \) transition temperature (\( T_{SDW} = 134 \text{ K} \)). The calculated pressure dependence for \( T_{SDW} \) is \( dT_{SDW}/dp = -0.12 \pm 0.10 \text{ K/kbar} \).
Although a structural phase transition is often first order, the thermal expansion data show this is not the case for the transition at $T_S = 156$ K in LaOFeAs. The calculated pressure dependence is $dT_S/dp = 3.363 \pm 0.10$ K/kbar.

The low temperature specific heat has the following $T$ dependence.

$$\frac{c}{T} = \gamma + \beta T^2$$

(Eq. 5.1)

where $\gamma$ is the electronic coefficient and $\beta$ is the phononic coefficient. The inset of Fig. 6 shows a graph of $c/T$ as a function of $T^2$. The linear behavior gives $\gamma = 5.0 \pm 0.2$ mJ/mol K$^2$ for low temperature and the Debye temperature $\theta_D = 295$ K, as calculated from the formula;

$$\theta_D^2 = 4 \times \frac{12\pi^4 R}{5\beta}$$

(Eq. 5.2)

Here the factor 4 accounts for the 4 atoms in the formula unit LaOFeAs.

**5.2.2 Thermal expansion of La(O$_{1-x}$F$_x$)FeAs**

The phase diagram reported in Fig. 3b shows doping of fluorine in LaOFeAs, suppresses the SDW ordering and superconductivity in these materials is observed. To study the effect of doping on the thermal expansion we have examined a sample of La(O$_{1-x}$F$_x$)FeAs with $x = 0.10$ content of fluorine.

The pressed pallet of polycrystalline La(O$_{0.90}$F$_{0.10}$)FeAs (3 mm diameter, 1.9 mm height) was prepared by the group of Dr. Rudiger Klingeler at IFW Dresden. The dimension of the unit cell [16] are $a= 4.02$ Å, $c=8.69$ Å, $V=140.84$ Å$^3$ and the space group is $P_{4/nmm}$. There are 2 formula units per unit cell. The thermal expansion data as a function of temperature for La(O$_{0.90}$F$_{0.10}$)FeAs are plotted in Fig. 7. No anomalies are observed in the
high temperature regime. The thermal expansion anomaly near the superconducting transition temperature was too small to be observed in our measurements.

With an estimated pressure coefficient $dT_S/dp = 1 \text{K/kbar}$, one would expect $\Delta \alpha$ is $0.8 \times 10^{-6}$ K$^{-1}$. The experimental data show $\Delta \alpha < 0.5 \times 10^{-6}$ K$^{-1}$. This in turn indicates the pressure dependence is much less than $1 \text{K/kbar}$.

![Graph showing thermal expansion anomaly.](image)

**Fig. 7** The coefficient of linear thermal expansion, $\alpha$, as a function of temperature for La(O$_{0.90}$F$_{0.10}$)FeAs. The vertical line at $T_{SC} = 26$ K locates the superconducting transition temperature.

Fig. 8 shows the specific heat divided by temperature ($c/T$) as a function of temperature. The superconducting transition was observed at $T_{SC} = 26$ K where the idealized step in the specific heat is $\Delta c = 232 \pm 25 \text{mJ/(mol K)}$.

The effective Grüneisen parameter, $\Gamma_{eff}(T)$ [19], gives the relation between the volumetric thermal expansion, $\beta$, and the specific heat, $c$. When $\beta$ and $c$ have the same temperature dependence, the effective Grüneisen parameter, $\Gamma_{eff}(T)$, is quasi-constant.
Fig. 8  The specific heat in a plot of $c/T$ versus $T$ of $\text{La(O}_{0.90}\text{F}_{0.10})\text{FeAs}$. {Picture taken from Ref. 19}

We have calculated $\Gamma_{\text{eff}}(T)$ by

$$
\Gamma_{\text{eff}}(T) = \frac{V_m}{\kappa} \frac{\alpha_p(T)}{c(T)}
$$

(Eq.5.5)

where $\kappa = -V^{-1} \times dV/dT$ is the isothermal compressibility $\kappa = 14 \times 10^{-12}$ Pa$^{-1}$ [20]. The results are shown in Fig. 9.

For the $\text{LaOFeAs}$ compound we observe at high temperature an overall constant value of $\Gamma_{\text{ph}} = 1$. Small anomalies at $T = 138$ K and $T = 156$ K are due to the magnetic and structural transitions. This is a usual value for the characteristic energy scale for phonons:

$$
\Gamma_{\tau} = -\frac{d}{d \ln V} \ln \frac{T^*}{T}
$$

(Eq.5.4)
Below 30 K the Grüneisen parameter decreases and has a minimum near 10 K. The origin of these negative values is unknown.

Fig. 9 The plot shows the effective Grüneisen parameter as a function of temperature for LaOFeAs and La(O\textsubscript{0.90}F\textsubscript{0.10})FeAs. The inset shows the high temperature anomalies in LaOFeAs which are suppressed in La(O\textsubscript{0.90}F\textsubscript{0.10})FeAs.

For doped La(O\textsubscript{0.90}F\textsubscript{0.10})FeAs we observe no high temperature anomalies. For $T > 50$ K the effective Grüneisen parameter is constant and amounts to $\Gamma_{ph} = 1$. Near the superconducting transition temperature ($T_{SC} = 26$ K) the Grüneisen parameter increases and reaches a value of $\Gamma_{eff} = 5$ at $T = 4$ K.
5.2.3  Thermal expansion of GdOFeAs

![Graph showing thermal expansion vs temperature]

**Fig. 10** Coefficient of linear thermal expansion, $\alpha$, versus the temperature, of the GdOFeAs sample. $T_S$ is the structural and/or SDW transition temperature. The inset shows the magnetic ordering of Gd at $T_M = 3.8K$.

A pressed pallet of polycrystalline GdOFeAs (3 mm diameter, 1.9 mm height) was prepared by the two step solid-state reaction method [17] in the group of Dr. Rudiger Klingeler at IFW Dresden. The dimension of the unit cell are $a = 3.91 \text{ Å}$, $c = 8.44 \text{ Å}$, $V = 129.49 \text{ Å}^3$ at 300 K and space group is $P4/nmm$. There are 2 formula units per unit cell [21]. As shown in Fig. 10, we observe an anomaly in the thermal expansion at high temperature. This anomaly is showing similar characteristics as the magnetic transition in LaOFeAs. So we can argue it is due to the SDW antiferromagnetic transition at $T_{SDW} = 125 \text{ K}$. At low temperature, $T_M = 3.8 \text{ K}$, the magnetic ordering of the Gd moments can be observed.
5.3. Summary

In this study we reported the first thermal expansion data on LaOFeAs. The phase transition temperatures are in good agreement with those observed in the electrical resistivity, magnetic susceptibility and specific heat data. By using the Ehrenfest relation, we calculated the pressure dependence of LaOFeAs at $T_S$ and $T_{SDW}$. For the structural transition at $T_S = 156$ K it is $dT_S/dp = 3.36 \pm 0.10$ K/kbar and for the spin density wave antiferromagnetic transition at $T_{SDW} = 138$ K it is $dT_{SDW}/dp = -1.20 \pm 0.10$ K/kbar.

Thermal expansion experiments are also carried out on the doped LaO$_{0.90}$F$_{0.10}$FeAs compound. The structural and spin density wave transitions were suppressed. In specific heat measurement, the superconducting transition was observed at low temperature, but superconductivity was not resolved in the thermal expansion data.

For the GdOFeAs compound, the thermal expansion measurements revealed a high temperature anomaly which was similar to one of the LaOFeAs SDW phase transition. Magnetic ordering of the Gd moments at low temperature was observed.
References:

Summary

In recent years strongly correlated metals, heavy-fermion systems (HFS) based on f-electron elements Ce, Yb or U, have attracted much attention of both experimental and theoretical condensed matter scientists. These systems are good candidates to investigate magnetic to non-magnetic quantum phase transitions (QPT). HFS have low magnetic ordering temperatures and an exchange interaction which can be tuned to a quantum critical point by using a non-thermal control parameter. In the quantum critical regime the collective fluctuations result in a second-order phase transition at zero temperature. Near the quantum critical point (QCP) these systems may exhibit a novel ground state, the so-called the non-Fermi liquid (NFL) state, which is characterized by a strong deviation from the Landau Fermi liquid (FL) state. The study of QCPs has led to the discovery of unconventional superconducting states located near magnetic ordering of HFS.

In this thesis, we have mainly studied the Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$, LaOFeAs, LaO$_{0.90}$F$_{0.10}$FeAs and GdOFeAs systems. The heavy-fermion system, Ce(Ru,Fe)$_2$Ge$_2$, can be tuned to an antiferromagnetic QCP by using pressure or doping or external magnetic field. In this work we applied a magnetic field to tune the system to the QCP. The recently discovered high temperature superconductor REO$_{1-x}$F$_x$FeAs with RE = La, Gd is also studied.

The magnetic ordering is suppressed by applying a magnetic field $B_{cr} \approx 0.80$ T along the tetragonal axis of Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$. Thermal expansion and specific heat measurements are carried out in zero and applied magnetic field to calculate the effective Grüneisen ratio, $\Gamma_{eff}(T)$. $\Gamma_{cr}(T)$ attains very large values at low temperature. At $B_{cr} \approx 0.80$ T the thermal and transport properties show NFL temperature dependencies. The exponent $n$ of the resistivity $\rho \propto T^n$ has the maximum value of 1.5. For high magnetic field ($B > B_{cr}$) the system is pushed away from the QCP and the Fermi-liquid state $\rho \propto T^2$ is recovered.
For $REO_{1.3}F_xFeAs$ with $RE=La, Gd$, the thermal expansion measurements are carried out in the temperature range 2 – 200 K. In the pure compound we observed the structural ($T_S = 156$ K) and spin density wave ($T_{SDW} = 138$ K) phase transitions. The doped compound $LaO_{0.90}F_{0.10}FeAs$ was also examined in the high and low temperature regime. The structural and spin density wave transition were suppressed due to doping. The Ehrenfest relation was used to calculate the pressure dependence of $T_S$ and $T_{SDW}$. The $GdOFeAs$ system was also investigated by thermal expansion measurements. We observed the spin density wave transition at high temperature ($T_{SDW} = 125$ K) and the $Gd$ moments order at low temperature ($T_N = 3.8$ K).
Samenvatting

In de afgelopen jaren hebben sterk gecorreleerde metalen, met name zware fermion systemen gebaseerd op de f-elektron elementen Ce, Yb of U, veel aandacht getrokken van zowel experimentele als theoretische gecondenseerde materie natuurkundigen. Deze systemen zijn goede kandidaten om magnetisch niet magnetische kwantum fase overgangen te onderzoeken. Zware fermion systemen hebben lage magnetische ordenings temperaturen en een exchange interactie die gevarieerd kan worden naar een kwantum kritisch punt onder invloed van een niet thermische control parameter. In het kwantum kritisch regime resulteren de collectieve fluctuaties in een tweede orde fase overgang bij een temperatuur van 0 K. In de buurt van het kwantum kritisch punt kunnen deze materialen een nieuwe grondtoestand vertonen, de zogeheten niet-Fermi-vloeistof toestand, die gekarakteriseerd wordt door een sterke afwijking van de Landau Fermi-vloeistof toestand. Het onderzoek naar kwantum kritische punten heeft geleid tot de ontdekking van onconventionele supergeleidende toestanden in de buurt van magnetische ordening van zware fermion systemen.

In deze scriptie hebben we vooral de Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$, LaOFeAs, LaO$_{0.90}$F$_{0.10}$FeAs en GdOFeAs systemen bestudeerd. Het zware fermion systeem Ce(Ru$_x$Fe$_{1-x}$)$_2$Ge$_2$ kan gestuurd worden naar een antiferromagnetisch kwantum kritisch punt door druk, chemische substitutie of extern magnetisch veld. In dit werk legden we een magnetisch veld aan om het systeem af te regelen op het kwantum kritisch punt. De recentelijk ontdekte hoge temperatuur supergeleider REO$_{1-x}$F$_x$FeA met RE = La, Gd is ook onderzocht.

De magnetische ordening wordt onderdrukt door een magnetisch veld B$_{cr}$ ≈ 0.80 T langs de tetragonale as van Ce(Ru$_{0.24}$Fe$_{0.76}$)$_2$Ge$_2$ aan te leggen. Thermische uitzetting en soortelijke warmte metingen werden uitgevoerd met en zonder magnetisch veld met als doel het berekenen van de effectieve Grüneisen verhouding $\Gamma_{eff}(T)$. $\Gamma_{cr}(T)$ bereikt zeer hoge waarden bij lage temperatuur. Voor B$_{cr}$ ≈ 0.80 T vertonen de thermische en transport eigenschappen niet-Fermi-vloeistof gedrag. De exponent $n$ van de temperatuursafhankelijkheid van de weerstand $\rho \sim T^n$ heeft een maximale waarde van 1.5. Bij een hoog magnetisch veld
(B > B_{cr}) wordt het systeem weggedreven van het kwantum kritisch punt en de Fermi-vloeistof toestand $\rho \sim T^2$ herstelt zich weer.

Voor $\text{REO}_{1-x}\text{F}_{x}\text{FeA}$ met $\text{RE} = \text{La}, \text{Gd}$ worden thermische uitzetting metingen verricht tussen 2 en 200 K. In het zuivere materiaal zien we een structurele ($T_S = 156$ K) en een spin dichtheidsgolf ($T_{SDW}$) fase overgang. Het materiaal waarin F gesubsitueerd is voor O ($\text{LaO}_{0.90}\text{F}_{0.10}\text{FeAs}$) is ook onderzocht in het hoge en lage temperatuurgebied. De structurele en spin dichtheidsgolf overgangen werden onderdrukt door chemische substitutie. De Ehrenfest vergelijking werd gebruikt om de druk afhankelijkheid van $T_S$ en $T_{SDW}$ te berekenen. Het systeem GdOFeAs werd ook onderzocht met thermische uitzetting metingen. We namen de spin dichtheidsgolf waar bij een hoge temperatuur ($T_{SDW} = 125$ K). De Gd momenten ordenen bij lage temperatuur ($T_N = 3.8$ K).
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