1 Introduction

Heavy fermion (HF) systems belong to the group of strongly correlated electron systems and have attracted considerable attention because of their unusual physical behaviour at low temperatures. Only a few ytterbium-based heavy-fermion compounds were discovered in the past twenty years in comparison to Ce-based ones, because of the difficulty in synthesising Yb compounds due to its high vapour pressure. Thus the aim of this thesis was to synthesise and investigate new Yb-based heavy-fermion systems.

Only very little is known e.g. about RT_2X_2 compounds with X = Ge and a transition metal T from the Fe or Co columns. A few compounds like $YbNi_2Ge_2$ and $YbCo_2Ge_2$ have been investigated and both show a weakly intermediate-valent Yb state, at the border to the Kondo regime. Therefore, we looked for new RT_2Ge_2 systems, which are close to a quantum critical point (QCP), where the magnetic ordering temperature goes continuously to 0 K. Close to such a QCP, one often observes in these compounds unusual transport and thermodynamic properties, which differ from Landau-Fermi-liquid behaviour. These compounds are therefore called non-Fermi-liquid (NFL) systems. We grew polycrystalline and single crystalline $YbFe_2Ge_2$ and investigated its physical properties (chapter 3). Previously only the structure, but no physical properties of $YbFe_2Ge_2$ had been reported. Our results show a weakly intermediate-valent Yb state with a low characteristic 4*f* energy, at the border to the Kondo regime. The susceptibility shows an anomalous behavior and can be fitted at high temperatures (T > 100 K) with a Curie-Weiss law with a surprisingly high effective moment of $\mu_{eff} = 6.2\ \mu_B$ and a very large Curie-Weiss temperature. The results on $YbFe_2Ge_2$ will be discussed in comparison with the reference compound $LuFe_2Ge_2$, which shows an additional phase transition at $T_0 \approx 9$ K.

The HF system $YbRh_2Si_2$, has attracted strong attention because it is located very close to a QCP connected with the transition from a magnetically ordered ground state to a non-magnetic one. At ambient pressure it orders antiferromagnetically at a very low temperature, T_N = 70 mK. Upon

applying a small magnetic field (60 mT) or a slight negative chemical pressure using Ge doping, T_N disappears at a QCP where the effective mass of the quasiparticles diverges. The proximity to the QCP leads to pronounced NFL behaviour in the resistivity ρ(T) and the specific heat C(T). The low-temperature physics of this system can be explained within the local QCP scenario. The aim of this work was to reach and to cross the quantum critical point by using negative chemical pressure in doped $YbRh_2Si_2$. Already slight negative chemical pressure using 5 % nominal Ge doping leads to the extension of the NFL behaviour to the lowest investigated temperature T ≈ (10 - 20) mK. But this Ge content was not enough to cross the QCP. Since crystals with a higher Ge-content could not be obtained, we tried to replace Yb by the larger lanthanum, which should also lead to an increase of the unit-cell volume. Single crystals of pure and doped $YbRh_2Si_2$ were grown using a flux technique in closed Ta crucibles. We succeeded with the single-crystal growth of $Yb_{1-x}La_xRh_2Si_2$ with $0 < x < 0.3$, which allowed us to study the behaviour upon crossing the QCP (chapter 4).

The second reason to investigate more intensively $YbRh_2Si_2$ was the missing detailed analysis of the high-temperature properties, like e.g. the crystal electric field, which was not settled. We therefore analyzed the high-temperature specific heat to fix the energy of the first excited crystal electric field (CEF) level. From the analysis of the temperature dependence of the entropy we deduce the Kondo temperature of pure and La-doped $YbRh_2Si_2$.

The samples obtained from the reproducible crystal growth were used for many other investigations, like e.g. neutron-scattering experiments to study the magnetic excitations i.e., the higher excited CEF levels and magnetic fluctuations. Additionally ESR experiments were performed on pure and La-doped $YbRh_2Si_2$, which shows a very surprising result, because for the first time the ESR signal of the Kondo ion was found in a dense Kondo system.

Attempts to prepare the pure isoelectronic compound $YbRh_2Ge_2$ failed, instead single crystals of $Yb_4Rh_7Ge_6$ were obtained and studied (chapter 5).

The results evidence a stable Yb^{3+}state, which orders presumably antiferromagnetically at 0.49 K.
The main results of this thesis are summarised at the end in chapter 6.

2 Introduction to 4f-based heavy fermions

This chapter will give a short introduction into heavy-fermion systems, especially Yb-based ones. In comparison with Ce-based compounds, only a few Yb-based heavy fermions were discovered in the past twenty years. The main reason for this is the difficulty in synthesising Yb compounds because of the high vapour pressure of Yb.

Heavy-fermion systems belong to the group of strongly correlated electron systems and have attracted considerable attention because of their unusual physical behaviour at low temperatures. These systems are intermetallic compounds with elements from the group of lanthanides or actinides. Especially systems with elements having an instable f shell like cerium, ytterbium or europium are of interest, because of the transition from a magnetic to a non-magnetic ground state.

The following text will give a short introduction into intermetallic 4*f*-based systems with an instable 4*f* shell. First, a very general approach and phase diagrams for the transition from a magnetic to a non-magnetic state shall be presented, followed by a more detailed discussion of the difference between Ce-, Eu- and Yb-based compounds. Finally, two theoretical models, the localised-moment scenario and the spin-density-wave scenario, will be discussed at the end of this chapter.

The origin for the interesting physical properties is the hybridisation of the atomic 4f or 5f states (of the cerium, ytterbium or uranium atoms) with the valence-band states. Different ground states are occurring in dependence of the hybridisation between the 4f or 5f electrons and the valence electrons. Two types of interactions are important: the Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange and the Kondo [Kondo 1964] effect. The first one (RKKY) describes the indirect interaction between neighbouring magnetic moments through the conducting electrons and favours magnetic order. The second mechanism describes the interaction between a single

magnetic ion in the lattice with its metallic surrounding. The simplest description of the competition between a non-magnetic Kondo-state and a magnetically ordered state is given by the Doniach model [Doniach 1977], where only one parameter, the coupling parameter *g* is used (fig. 2.1).

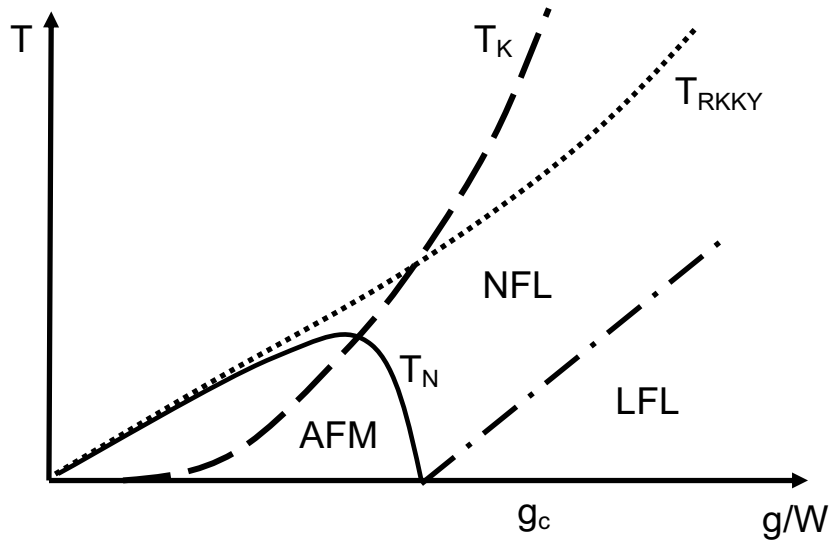

Figure 2.1: *This schematic phase diagram shows the effect of the competition between Kondo effect, T_K, and RKKY exchange, T_{RKKY}, in dependence of the hybridisation strength g. Antiferromagnetism occurs in the region, where $T_{RKKY} > T_K$. For $T_K > T_{RKKY}$ the non-magnetic ground state with enhanced effective mass of the quasiparticles is formed. This modified Doniach diagram [Doniach 1977] shows a QCP, where T_N goes to zero temperature at a critical value g_c. The area close to this point is dominated by non-Fermi-liquid behaviour. The blue line indicates the crossover temperature below which Landau-Fermi-liquid (LFL) behaviour is expected.*

This parameter *g* is determined by the exchange *J* between the 4f level and the conduction electrons and by the density of states at the Fermi edge $N(E_F)$: $g = |J| \cdot N(E_F)$. Large g values favour a nonmagnetic ground state and small g values a magnetically ordered ground state. The exchange strength *J*

can be tuned experimentally by applying pressure or by chemical doping. Upon increasing g beyond a critical value g_c, one observes the transition from a magnetically ordered to a paramagnetic state. Systems very close to the critical g_c are of special interest, because there the competition between Kondo and RKKY interaction results in very unusual low temperature properties.

The point, where the magnetic ordering temperature goes continuously to 0 K is called a quantum critical point (QCP). Systems, which are very close to such a QCP present properties which often differ from those expected for a Landau-Fermi liquid (LFL) and show abnormal transport and thermodynamic properties, so called non-Fermi-liquid (NFL) behaviour.

Landau-Fermi-liquid theory is very essential for solid-state physics and was originally developed to explain the behaviour of liquid ^{3}He. In comparison with the model of the free electron gas the Landau-Fermi-liquid theory includes the interaction between the fermions among each other. A short overview is given in [Landau 1957] and [Ashcroft 1976]. The electrons are colliding with each other and one expects a high scattering rate, but this is reduced because of the Pauli principle. Landau's theory describes the excitation states of single particles in a system of interacting particles. Those excitation states are called quasiparticles and one can visualise them as single particles surrounded by a distortion cloud, when moving inside the electron gas. Each quasiparticle (like electrons with spin $\frac{1}{2}\hbar$ and charge $\pm e$) corresponds to one excitation state in the free electron gas and obeys Fermi statistic. The effective mass of the electrons changes drastically, because of the interaction between the electrons. The specific heat of Fermi liquids is given by:

$$C(T) = \gamma T, \quad \text{with } \gamma = \gamma_0 \, m^*/m, \tag{1}$$

γ_0 being the Sommerfeld coefficient in the absence of interactions.

This is equivalent to the equation of a free electron gas, but with a renormalized electron mass m^*/m_0. In the special case of heavy-fermion systems, the effective mass of the quasiparticles m^* is about 100 to 1000

times larger than in normal Fermi-liquid systems. The electronic contribution of the resistivity follows

$\rho = \rho_0 + AT^2$, (2)

where the residual resistivity ρ_0 comes from the scattering of the quasiparticles with lattice defects and A^2 scales with γ.

In the last years a lot of systems have been discussed showing characteristic deviations from typical Landau-Fermi-liquid systems. Such compounds are so called non-Fermi liquids and show for example a resistivity dependence $\rho \propto T^n$ with $1 \leq n \leq 1.5$, like $CeCu_2Si_2$ with n = 3/2 [Steglich 1996] or $CePd_2Si_2$ close to its critical pressure of $p_c \approx 2.8\ GPa$ with n = 1.2 [Julian 1996]. The specific heat $C(T)/T$ towards low temperatures is not constant anymore, but shows different behaviours, such as a logarithmic increase, $C(T)/T \propto ln(T_0/T)$, for $CeCu_{5.9}Au_{0.1}$ [Löhneysen 1996], [Löhneysen 1999] and for $YbRh_2Si_2$ [Trovarelli 2000a, b, c] or a square-root-like increase of the form $C(T)/T = \gamma_0 - cT^{0.5}$ in $CeNi_2Ge_2$ [Steglich 1996].

Since this work is more focused on the experimental investigation and crystal growth of such compounds it is not the appropriate place for a detailed presentation of the theoretical aspects. A more detailed overview about non-Fermi-liquid behaviour is given in the proceedings of the 'International Conference on Non-Fermi-liquid Behaviour in Metals' [Santa Barbara 1996] or [Stewart 2001].

Before giving an overview on the different chapters in this work a comparison between Ce, Yb and Eu systems is necessary to underline the difference between heavy-fermion compounds based on those elements. The character of the 4f electrons determines the ground state properties of intermetallic rare-earth compounds. The 4f electrons have a very small radial extension and are therefore located within the Xe-core electrons. The influence of ligand atoms is very small and 4f electrons in solids have atomic-like character. Looking at the periodic table of elements within the row of the lanthanides and considering the trivalent state usually taken by the lanthanides in a metallic compound, Ce is sitting on the left side (just after La) with a configuration $4f^1 5d 6s^2$, while Yb is on the right side (before