1 Theoretical concepts

1.1 Heavy-fermion systems

Heavy-fermion (HF) systems are intermetallic compounds containing rare-earth or actinide elements with partially filled $4f$- and $5f$-electron shells, respectively. The name of this class of materials is connected to the high effective mass, m^*, of their conduction electrons. This heavy mass manifests itself, for example, in a large electronic specific heat or Pauli susceptibility at low temperatures. An interesting aspect of the HF systems is that a variety of unusual low-temperature properties can occur as a result of different ground states. In this chapter, the presentation of the complex properties of this class of materials is restricted to those that are important for the understanding of the materials studied in this work. For a more detailed discussion on HF compounds the reader is referred to review articles, e.g., Stewart 1984, Fulde 1988, Grewe and Steglich 1991, and Stewart 2001.

At elevated temperatures, HF metals exhibit properties resembling those of conventional metals with weakly interacting magnetic moments immersed in a sea of conduction electrons. The electronic transport properties are dominated by incoherent scattering of the conduction electrons off the local moments. As the temperature is reduced below a characteristic temperature, a crossover to a coherent scattering at low temperatures is observed. The low-temperature properties of HF metals display similarities to those of normal metals. Thus, the thermodynamic properties of the HF systems may be described in terms of the Landau Fermi-liquid (LFL) theory.

1.1.1 Single-impurity Kondo effect

In the early 1930's a minimum of the electrical resistivity, $\rho(T)$, followed by an increase toward lower temperatures, was observed in simple metals such as gold or copper with small amount of magnetic impurities (e.g., Fe). This phenomenon was theoretically not understood before Kondo's work in 1964 (Kondo 1964). His theory explains the upturn of the resistivity at low temperatures by considering the scattering of the conduction electrons off a single magnetic ion in an otherwise non-magnetic sea of conduction electrons. In general, the single-impurity Kondo effect is observed in diluted alloys with a small amount of $3d$ or $4f$ impurities, in which the magnetic moments do not interact, directly or indirectly, due to the large distance in between them. The important aspect of this scattering mechanism is that the resistance increases logarithmically upon lowering the temperature. The above-mentioned resistance minimum is caused by an interplay between the T^5-dependent resistivity, due to the electron-phonon interaction dominating the resistance at high temperatures, and the logarithmically increasing spin-dependent scattering at low temperatures. It turns out that the theoretical estimations made by Kondo are valid only above a characteristic temperature, which is known as the Kondo temperature, T_K. Below it, Kondo's prediction leads to an unphysical result, namely the resistance diverges as $T \rightarrow 0$. Known as the "Kondo problem", the behavior of $\rho(T)$ at low temperatures was solved by Wilson using the renormalization-group technique (Wilson 1975). Within this framework, the exact solution at $T = 0$ consists in a non-magnetic spin-singlet state formed by an antiparallel coupling between the impurity spin and the conduction electron spins. In the simplest model, the $s-d$ model (Wilson 1975), a single impurity spin $S = \frac{1}{2}$ is coupled by an exchange interaction J to the conduction electrons of the host metal. This model is also valid for systems containing a $4f$ impurity embedded in a non-magnetic metallic host. The classical exchange Hamiltonian can be written as

$$H = -Js \cdot S, \tag{1.1}$$

where s is the conduction electron spin. The exchange-coupling constant, J, depends on the hybridization strength or matrix element between the impurity spin and the conduction electron, V_{s-f}, and the binding energy of the $4f$ level, ϵ_{4f}, as $J = -\frac{V_{s-f}^2}{\epsilon_{4f}}$. The temperature dependence of the thermodynamic properties in the single Kondo impurity case was derived applying the Bethe-Ansatz on the classical exchange Hamiltonian (Desgranges 1982, Andrei 1983). The Coqblin-Schrieffer model generalizes the $s-d$ model for effective impurity spins larger than 1/2 (Coqblin 1969). Later, the spin-orbit coupling and crystalline electric field (CEF) effects were included in these models leading to a good agreement between the experiments and the theoretical estimations (Rajan 1983, Desgranges 1985, Desgranges 1986). Today, there exists a variety of theoretical models describing the single-impurity Kondo problem at different levels or complexity and a number of theoretical approaches have been used to solve these models (Hewson 1997).

The physical properties of diluted Kondo systems may be classified with respect to the Kondo temperature. T_K determines the characteristic energy scale of the interaction between the magnetic impurity and the conduction electrons. It is defined as

$$k_B T_K \propto \frac{1}{N(E_F)} \exp\left(-\frac{1}{|JN(E_F)|}\right), \tag{1.2}$$

where k_B is the Boltzmann constant and $N(E_F)$ represents the electronic density of states (DOS) at the Fermi level, E_F.

- At $T \gg T_K$ the temperature dependencies of the resistivity and specific heat resemble those of normal metals. The impurity spin behaves as free magnetic moment giving rise to a magnetic susceptibility, $\chi(T)$, displaying a Curie-Weiss-type behavior. As $T \to T_K$ the resistivity follows $\Delta\rho(T) = (\rho(T) - \rho_0) \propto -\ln T$, where ρ_0 is the residual resistivity.

- At very low temperatures, $T \ll T_K$, the transport properties are well described within the Landau Fermi-liquid formalism which is addressed in Section 1.2. As soon as the magnetic moments are completely compensated, $\chi(T)$ shows a temperature-independent Pauli susceptibility.

- At $T = 0$, the properties are characteristic of a non-magnetic spin-singlet state. The magnetic susceptibility and the electronic specific-heat coefficient are enhanced compared with those in a normal metallic behavior, while $\rho(T)$ saturates at a constant value ρ_0. Moreover, the hybridization between the $4f$ and the conduction electrons gives rise to two peaks in the DOS: one broad peak centered at the position of the $4f$ level, below E_F, and a narrow peak located at the Fermi level which has the width of the order of $k_B T_K$ and is known as the Abrikosov-Suhl or Kondo resonance peak.

1.1.2 Kondo-lattice systems and RKKY interaction

The single-impurity Kondo effect is caused by the antiferromagnetic (AFM) exchange interaction between a small amount of non-interacting magnetic impurities and conduction electrons. The situation changes, if the localized magnetic moments form a dense periodic array. Thus, the so-called Kondo-lattice systems can be viewed as a lattice of f electrons, each with a magnetic moment, embedded in a metallic host. At high temperatures the physical properties of these dense f-electron materials are similar to those of the single-impurity Kondo systems, but marked differences are observed at low temperatures. An alteration in physical properties can be clearly distinguished in the low-T resistivity, where due to the periodicity of the arrangement of the f electrons

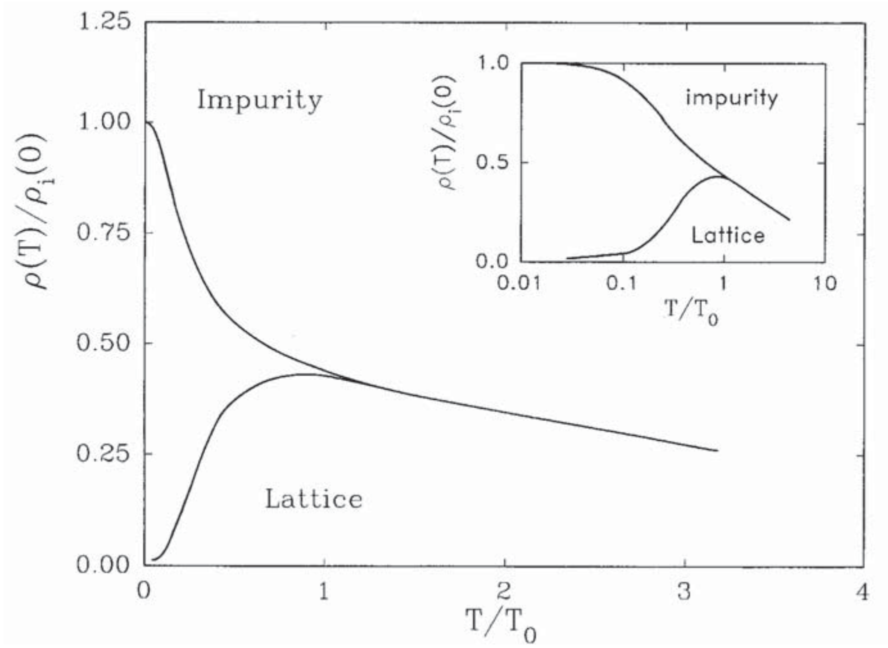

Figure 1.1: *Temperature dependence of the electrical resistivity in the case of a single-impurity Kondo system and a Kondo-lattice system. $\rho_i(0)$ is the zero-temperature resistivity per ion in the dilute limit. The same plot but on a semi-logarithmic scale is displayed in the inset. Figure taken from Ref. Cox and Grewe 1988.*

coherence effects appear. Figure 1.1 illustrates $\rho(T)$ of a single-impurity Kondo system and of a Kondo-lattice system (Cox and Grewe 1988). With decreasing temperature, the resistance shows a $-\ln T$ dependence, in both systems. A remarkable difference can be observed when the coherent scattering in the Kondo-lattice system sets in. Unlike in the single-impurity case, the resistivity of a Kondo-lattice system exhibits a pronounced maximum followed by a sharp decrease on lowering the temperature.

A consequence of the dense periodic array of the Kondo ions is that the distance between the neighboring magnetic moments is small compared to dilute Kondo systems. Although, the direct interactions between the $4f$ moments are still negligible, they interact via the conduction electrons. This indirect exchange interaction, the so-called Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, favors magnetic ordering at low temperatures (Ruderman and Kittel 1954, Kasuya 1956, Yosida 1957). Depending on the distance between the $4f$ moments, the order may be AFM or ferromagnetic (FM). The energy scale associated with this type of interaction is proportional to $J^2 N(E_F)\cos(2k_F r)/r^3$ for sufficiently large distances, r, between the moments. The strength of the interaction can be expressed by the characteristic temperature:

$$k_B T_{RKKY} \propto J^2 N(E_F). \tag{1.3}$$

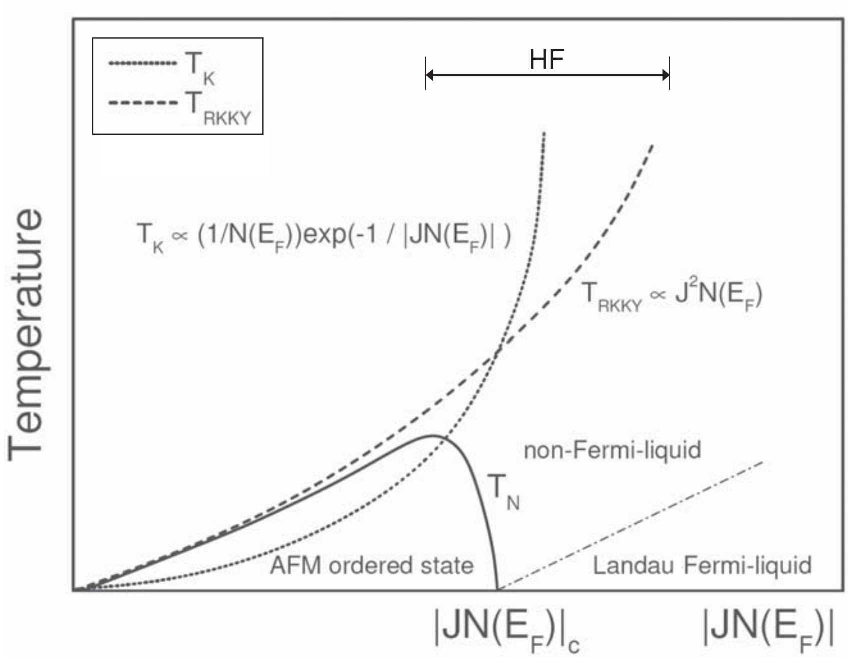

Figure 1.2: *Doniach phase diagram; T_K and T_{RKKY} are the characteristic temperatures of the Kondo and RKKY interaction, respectively. The solid line represents the magnetic-ordering temperature T_N. The dash-dotted line depicts the temperature below which LFL behavior is found.*

Considering the energy scales defined by T_K and T_{RKKY}, Doniach proposed that the ground state of a Kondo-lattice system is a direct consequence of the competition between the Kondo effect and the RKKY interaction (Doniach 1977). For the case of AFM inter-site interaction of the Kondo ions, the competition of the two effects as function of $|JN(E_F)|$ is qualitatively illustrated in the phase diagram displayed in Figure 1.2. HF metals are in general located close to the magnetic instability where the magnetism is suppressed to zero temperature. Here, the interplay between the RKKY interaction, which tends to mediate magnetic ordering between the rare-earth atoms and the Kondo effect, which, on the contrary, tends to suppress the individual magnetic moment of the rare-earth ions, is most important. For small $|JN(E_F)|$, the RKKY interaction dominates and, as a result, the system orders magnetically. Upon increasing the hybridization strength the Kondo effect overwhelms the RKKY interaction and the system becomes non-magnetic due to the Kondo screening of the magnetic moments of the rare-earth ions. The ordering temperature, T_N, increases initially with increasing $|JN(E_F)|$, then passes through a maximum and is then suppressed to zero at the critical value $|JN(E_F)|_c$. In the paramagnetic (PM) regime, $|JN(E_F)| > |JN(E_F)|_c$, the low-temperature properties can be described within the Landau Fermi-liquid theory. The basic concepts of this theory will be summarized in the following section.