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TO MY WONDERFUL FAMILY
CHAPTER 1

Superconductivity in Heavy Fermion Compounds

Superconductivity is a macroscopic quantum mechanical phenomenon which manifests itself in a large number of condensed matter systems from insulators to simple metals to complex materials and ceramics. Superconductivity was first observed by Dutch physicist Heike Kamerlingh Onnes in 1911, who noticed that the resistivity of a sample drops to zero when the sample was cooled below certain critical temperature, $T_c$. Almost 50 years after this discovery, three American physicists, John Bardeen, Leon Cooper, and J. Robert Schrieffer in 1957 proposed a consistent microscopic theory of superconductivity (BCS theory), which up to this day remains one of the most elegant theories in physics.

At the heart of the BCS theory is the concept of Cooper pairs: at low enough temperatures electrons form pairs with opposite spin and condense into a single quantum state with a macroscopic wave-function. In other words, the electrons form a superconducting condensate by binding into Cooper pairs. Furthermore, it was confirmed both experimentally and theoretically that the superconducting state remains surprisingly robust with respect to non-magnetic disorder present in the samples. Contrary to the case of non-magnetic disorder, superconducting critical temperature was quickly suppressed to zero by an addition of small
amounts of magnetic impurities. With the introduction of magnetic impurities, the local field of the impurity can flip the spin of one of the electrons which leads to a breaking of the Cooper pair. Thus within the BCS model it soon became clear that the presence of magnetic impurities is detrimental to superconductivity.

More than 20 years after the advent of BCS theory, there were two ground-breaking experimental discoveries of superconductivity in lanthanide- and actinide-based materials CeCu$_2$Si$_2$ [1] and UBe$_{13}$ [2]. These discoveries made a profound impact on the field of superconductivity for both of these materials have partially filled $f$-shells and, as a consequence, magnetic moments at each lattice site. What is more, thermodynamic properties of these materials in the superconducting phase appeared to be drastically different from those predicted by the BCS theory. For example, heat capacity at very low temperatures had power-law dependence on temperature in contrast with the exponential dependence in conventional superconductors. Importantly, theoretical analysis of the temperature dependence of the heat capacity showed that the superconducting order parameter in CeCu$_2$Si$_2$ and UBe$_{13}$ must depend on the direction of the electron’s momentum and, in fact, must change sign as the direction of momentum was changing. This and other observations were clearly at odds with the predictions of the BCS theory, which by that time was dubbed in the literature as conventional superconductivity. Hence, superconductivity in CeCu$_2$Si$_2$ and UBe$_{13}$ became known
as *unconventional superconductivity* and provided the first examples of unconventional superconducting pairing in crystalline environment.

Subsequent experimental research in the area of unconventional superconductivity has produced many materials with anisotropic nature of superconducting gap symmetry. Examples include not only actinide-based materials such as UPt$_3$, URu$_2$Si$_2$ and the family of the Ce-based ‘115’ systems to copper-oxide compounds LaBaCuO$_4$ and organic superconductors (TMTSF)$_2$PF$_2$. More importantly, the discovery of unconventional superconductivity not only triggered the development of new fundamental concepts such as quantum criticality and unconventional metallic behavior, but also provided insights into the formation of the novel phases of matter such as co-existence of magnetism and superconductivity.

The focus of this dissertation is on a ‘115’ family of cerium-based lanthanide superconducting alloys Ce$_{1-x}M_x$CoIn$_5$. These materials naturally provide an ideal playground for studying an interplay between quantum criticality, magnetism and superconductivity. We will specifically focus on the effects of alloying with either non-magnetic ions such as lanthanum (\(M = \text{La}\)) or magnetic ones such as ytterbium (\(M = \text{Yb}\)) as a probe for microscopic origin of unconventional superconductivity, unusual metallic behavior and the role of quantum fluctuations which driven by a system’s proximity to a magnetic quantum phase transition taking place at absolute zero temperature. Furthermore, recent theoretical insights into
1.1. Conventional theory of metals: Landau’s Fermi-liquid theory

the mechanism for topological superconducting states provide an intriguing possibility for realization of topological superconductivity in Ce$_{1-x}$Yb$_x$CoIn$_5$ alloys.

My goal for this chapter is to provide a general conceptual background for the physics of materials containing ions with partially filled $f$-shells. Strong electron-electron correlations between the $f$-electrons are the hallmark of the physics in these materials. In the what follows, I will briefly review the basic physical properties of the $f$-electron systems and introduce concepts, which I will later use for the analysis of the experimental and theoretical results.

1.1 Conventional theory of metals: Landau’s Fermi-liquid theory

Since the early experimental studies of transport properties of elementary metals such as copper and mercury, it became clear that electrons in metals behave as they were non-interacting, which was counterintuitive given that electrons interact with each other via long-range Coulomb forces. The resolution to this conundrum was provided by the Russian physicist Lev Landau. Landau hypothesized that there is one-to-one correspondence between the electrons in the Fermi gas and single particle excitations in a metal. Landau envisaged the ideal Fermi gas in which interactions between the constituent electrons are turned on very slowly. As a result, Landau showed that excitations of the interacting electrons behave as non-interacting fermions called quasiparticles. Thus, according to Landau the system of electrons in Fermi gas is equivalent to a Fermi gas of quasiparticles in
1.1. Conventional theory of metals: Landau’s Fermi-liquid theory

a metal. Microscopically, the long-range Coulomb forces in interacting electronic system can be dynamically screened so that electron-electron interactions become much smaller than the average kinetic energy.

The transformation of electrons to the quasiparticles conserves its spin, its electronic charge, and its momentum but Landau reasoned that due to dynamical screening processes, the effective magnetic moment and mass of the quasiparticle would be renormalized to new values \( \mu^* \) and \( m^* \) respectively. The specific heat, magnetic susceptibility and electrical resistivity for this Fermi liquid system are given by:

\[
\begin{align*}
\text{Specific heat:} & \quad \frac{C(T)}{T} = \frac{m^*}{m_e} \gamma_0 = \gamma \\
\text{Magnetic Susceptibility:} & \quad \chi(T) = \frac{m^*}{m_e} \frac{\chi_0}{1 + F_0^a} \\
\text{Electrical Resistivity:} & \quad \rho(T) = \rho_0 + AT^2
\end{align*}
\]

where \( F_0^a \) is a Landau parameter. For regular metals, the physical properties can be explained in terms of a linear sum of Fermi liquid and lattice contributions. Table 1 [3] shows some of the key properties of the Fermi liquid systems. Landau’s theory of Fermi liquids furnished the remarkable success in our understanding of the physical properties of elemental metals and semiconductors. For example, the state-of-the-art numerical techniques, such as density-functional theory (DFT) and the leading-density approximation (LDA) - also known as ‘band theories’ - are all based on the picture of a single electron moving in the self-consistent...
1.1. Conventional theory of metals: Landau’s Fermi-liquid theory

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<td>Charge Susceptibility</td>
<td>$\chi_c = N(0)$</td>
<td>$\chi_c = \frac{N^\star(0)}{1 + F_0^a}$</td>
</tr>
</tbody>
</table>

Table 1: Key Properties of the Fermi Liquid
1.2. Strongly Correlated Electron Systems

potential created by the other electrons. Band theories have been remarkably precise in predicting the electronic and magnetic properties for the wide class of materials.

1.2 Strongly Correlated Electron Systems

With the advances in materials physics many new materials have been synthesized with physical properties, which are completely opposite to what single-particle theories will predict. For example, NiO and $V_2O_3$ are predicted to be a band metals as they have odd number of electrons per unit cell. However, resistivity measurements show that these materials behave as insulators with fairly large insulating gap. Band theories fail here because in these materials electron-electron interactions greatly exceed the average kinetic energy: Coulomb repulsion hinders the electron hopping from site to site allowed otherwise by the laws of quantum mechanics. NiO and $V_2O_3$ are an example of ‘Mott insulators’ named after Sir Neville Mott who pioneered the field of metal-insulator transitions in correlated electronic systems.

Subsequent research of Mott insulators lead to the development of the whole area of strongly correlated electron systems (SCES). These systems are broadly defined as systems in which electron-electron interactions are not necessarily weak and therefore cannot be accurately described by single-particle theories. Some notorious examples of strongly correlated electronic systems are cuprate high-$T_c$ superconductors, heavy fermion materials, two-dimensional heterostructures and
1.3. Correlated Electrons Primer: Formation of Local Moments

Formation of the magnetic moments in a metallic environment is one of the primary examples of correlated electrons physics. Experimentally, it has been known that addition of a small amount of magnetic ions (such as iron) to a metallic host does not necessarily produce a magnetic moment. Sometimes the moments are formed beyond a certain critical concentration of magnetic ions added to the host. In 1963 Philip Anderson proposed a theoretical model [4] in order to provide the conditions for the formation of local moments. Below I will provide a brief review of the Anderson model.

Hamiltonian for the Anderson model includes three terms: the first term describes conduction electrons

\[ \hat{H}_c = \sum_{k, \sigma} \epsilon_k \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma}, \]

(2)

where \( \hat{c}_{k\sigma}^\dagger \) is a creation operator for an electron in a state with spin projection \( \sigma \) and energy \( \epsilon_k \). Similarly, the second term is an atomic Hamiltonian which accounts for the states on impurity:

\[ \hat{H}_d = E_f \sum_{\sigma} \hat{f}_{\sigma}^\dagger \hat{f}_{\sigma} + U \hat{f}_{\uparrow}^\dagger \hat{f}_{\uparrow} \hat{f}_{\downarrow}^\dagger \hat{f}_{\downarrow}. \]

(3)

Here \( \hat{f}_{\sigma} \) is a fermionic creation operator on impurity with spin projection \( \sigma \) and
1.3. Correlated Electrons Primer: Formation of Local Moments

energy $E_f$, while $U$ accounts for the local Coulomb repulsion between the electrons on impurity. Note that the Coulomb interactions between the conduction electrons can be neglected due to the effects of screening. Finally, the third term accounts for the hybridization of the conduction electrons with a magnetic impurity electrons:

$$\hat{H}_V = \sum_{k,\sigma} \left[ V(k) \hat{c}_k^{\dagger} \hat{f}_\sigma + V^*(k) \hat{f}_\sigma^{\dagger} \hat{c}_k \right]$$

where $V(k)$ is the hybridization matrix element describing the overlap between a localized $f$-state and the Bloch wave of conduction electrons sea [3]. In passing I note that the momentum dependence of the $V(k)$ arises from the difference in the orbital quantum numbers for the conduction and atomic orbitals: for example, in Ce-based materials the conduction electrons predominantly occupy the $d$-orbitals ($l = 2$) so that hybridization with the $f$-electron necessarily incorporates the angular momentum transfer $\Delta l = \pm 1$. Lastly, Coulomb interaction $U$ sets up the largest energy scale in the problem and serves as a primary source of correlations in the system.

Let me first consider the atomic limit first, since this discussion is important in order to get insight into the physics of the local moment formation. We consider the Hamiltonian (3). It has four eigenstates: two eigenstates correspond to a doubly occupied or empty atomic orbital

$$|f^2\rangle: \quad E(f^2) = 2E_f + U, \quad |f^0\rangle: \quad E(f^0) = 0$$

while the remaining two are singly occupied and are energetically degenerate with
1.3. Correlated Electrons Primer: Formation of Local Moments

respect to the spin projection

\[ |f^1 \uparrow \rangle, \ |f^1 \downarrow \rangle : \ E(f^1) = E_f \]  

Clearly, to obtain the magnetic ground state, i.e. the state with nonzero magnetization

\[ m = \langle \hat{f}^\dagger \hat{f} \rangle - \langle \hat{f}^\dagger \hat{f} \rangle \neq 0 \]  

we first need to require that the singlet state is the most energetically favorable one out of all other states. The simple counting of the corresponding energy costs to add/remove an electron yields

\[ E(f^2) - E(f^1) = U + E_f \quad \text{for adding an electron} \]  

\[ E(f^0) - E(f^1) = -E_f \quad \text{for removing an electron.} \]

Thus, two conditions must be satisfied for singly occupied state to become energetically favorable (see Fig. 1)

\[ E_f < 0, \ U > |E_f| \].

The situation changes when we now consider the remaining two terms in the Hamiltonian for the Anderson model. In the limit, when hybridization amplitude exceeds the strength of the local Coulomb repulsion between the \( f \)-electrons, the \( f \)-electrons from the core of the magnetic ion, hybridize with the Bloch states of surrounding conduction electron sea to form a resonance [5]. In absence of any Coulomb interactions, the localized \( f \)-state is broadened by the hybridization, and
1.3. Correlated Electrons Primer: Formation of Local Moments

Figure 1: Phase diagram showing the possible ground states in the atomic limit. For $U > |E_f|$, the ground-state is a magnetic doublet. When $U < 0$, the ground-state is degenerate charge doublet provided $E_f = 0$. 
produces a resonance. No moment formation would be possible in this case since the moment is simply dissolved into the conduction sea. However, in the case, when $U$ is large enough, i.e. when

$$U \rho_d(\varepsilon_F) > 1$$

(10)

the Hartree-Fock analysis of the Anderson model shows that the magnetic moment indeed forms [4]. In Eq. (10) above, $\rho_d(\varepsilon_F)$ is the density of states for conduction electrons at the Fermi level. Thus, the physics of the local moment formation necessarily requires somewhat enhanced density of states of the conduction electrons to ensure nonzero value $m$, (7). Anderson’s discovery of the local moment formation is quite remarkable, since it shows that time-reversal symmetry can be broken locally without a phase transition. However, as we will show below, although magnetic moments can form, they will never survive if a system is cooled down to lower temperatures. The physical effect, which describes how magnetic moments get dissolved into conduction sea, is known as Kondo effect and presents another hallmark of correlated electron physics.

1.4 Kondo Effect

The fate of the magnetic moment as system is being cooled down to lower and lower temperatures has been elucidated in the seminal paper by J. R. Schrieffer and P. Wolff [6]. Specifically, they showed that at low energies the Anderson impurity model is, in fact, equivalent to the spin-exchange model or what became later
1.4. Kondo Effect

known in the literature as the Kondo model. Thus, when system is cooled down to low temperatures the magnetic entropy of the impurity atoms gets fully dissolved into the sea of the conduction electrons via macroscopic quantum mechanical effect known as Kondo effect.

Generally, Kondo effect can be described as the variation in certain physical properties of a metallic host when impurity ions with the partially filled $d$- or $f$-electron shells are introduced in it. These temperature dependent anomalies in physical properties are a result of the screening of the free magnetic ions (resulting from the partially filled electron shells of impurity) by the spins of the conduction electron sea of host due the spin-exchange interaction $J_K$. This screening is a continuous process and takes place below a characteristic temperature called the Kondo temperature $T_K$. The term Kondo effect was coined in 1964 when Jun Kondo successfully explained decades old problem of resistivity minimum observed in many of the metals diluted with a minimal amount of localized $d$- or $f$-electron magnetic impurities [7]. Kondo used a perturbative calculation within the $s-d$ model framework in which the magnetic impurity is described by a local spin $\vec{S}$ ($|\vec{S}| = 1/2$), coupled to the conduction electron spin density. The magnetic impurity contribution to resistivity appears in form of a logarithmic temperature increase as the temperature is lowered. In Kondo’s description, this impurity
1.4. Kondo Effect

contribution both to resistivity and magnetic susceptibility are given by

\[
\rho_{\text{imp}}(T) \propto \rho_0 (1 + \nu_F J_K \log(T/T_K)), \quad \chi_{\text{imp},0} \propto \chi_0 (1 + \nu_F J_K \log(T/T_K))
\]  

which very well explains experimental data for \( T \sim T_K \).

Although Kondo's theory was very successful in describing the physics at temperatures \( T \sim T_K \) it clearly predicted an infinite resistance at further lower temperatures, while experimentally the resistivity reached the constant value. It was soon realized that the results of Kondo and others were based on perturbation theory in powers of the spin-exchange coupling \( J_K \). As it turns out, the effective exchange coupling constant grows logarithmically with decrease in temperature invalidating the perturbative analysis. Thus, the Kondo's theory works only above a certain low temperature \( T_K \), below which the results of the theory were unphysical.

How can one claim then that as temperatures approach absolute zero, the impurity entropy goes to zero? Indeed, since perturbation theory does not work the only controllable theory must be based on the exact solution for the Kondo problem. Fortunately such an exact solution indeed can be found and in 1970’s two independent groups - A. Tsvelick and P. Wiegmann in Russia and N. Andrei in USA - have independently solved the Kondo problem by providing an exact solution for the more general Anderson impurity model. Specifically, they showed
1.4. Kondo Effect

that

$$\rho_{\text{imp.}}(T \to 0) \to \text{const.}, \quad \chi_{\text{imp.}}(T \to 0) \to \mu_B^2 \nu_F. \quad (12)$$

Furthermore, in 1976 the method of the renormalization group treatment was applied to the Kondo problem by K. Wilson who confirmed the results from the exact solution.

As we can see from our discussion above, Anderson impurity model has only one electron with energy level $E_f$. When introduced in the host metal, this electron co-exist with the conduction electron sea of the host (Fermi sea). The impurity electron spin lies at energy $E_f$ below the Fermi level and can not be coupled with a second electron due to the coulomb barrier $U$ (see Fig. 2). However the impurity electron can quantum mechanically through the Coulomb barrier but another electron must tunnel from the Fermi sea back towards the impurity. The spin of this new electron may point in the opposite direction. The energy spectrum of the system changes qualitatively due to this spin flip and many such events taken together give rise to the phenomenon of Kondo resonance, with exactly the same energy as Fermi level. Thus the electrons with energies close to the Fermi energy are very effectively scattered due to Kondo resonance. The way to get the resonance is to cool down the system to sufficiently low temperatures below the Kondo temperature $T_K$. Kondo temperature is related with the parameters of
1.4. Kondo Effect

Figure 2: (a) The Anderson model of a magnetic impurity assumes that it has just one electron level with energy $\epsilon_0$ below the Fermi energy of the metal (red). This level is occupied by one spin-up electron (blue). Adding another electron is prohibited by the Coulomb energy, $U$, while it would cost at least $\epsilon_0$ to remove the electron. Being a quantum particle, the spin-up electron may tunnel out of the impurity site to briefly occupy a classically forbidden “virtual state” outside the impurity, and then be replaced by an electron from the metal. This can effectively “flip” the spin of the impurity. (b) Many such events combine to produce the Kondo effect, which leads to the appearance of an extra resonance at the Fermi energy. Since transport properties, such as conductance, are determined by electrons with energies close to the Fermi level, the extra resonance can dramatically change the conductance. From Ref. [8]
1.4. Kondo Effect

Anderson model by the formula[8]:

\[ T_K = \frac{1}{2} (\Gamma U)^{1/2} \exp \left[ \frac{\pi E_f (E_f + U)}{\Gamma U} \right] \]  

(13)

where \( \Gamma = \pi \nu_F |V|^2 \) is the width of the impurity, \( \nu_F \) is the density of state at the Fermi level, \( E_f \) is an impurity energy level, which is broadened by electrons tunnelling from it, and \( U \) is the Coulomb repulsion energy between two electrons at the site of the impurity.

Also note that as shown in Fig 1, in region of the phase diagram where local interaction is attractive (\( U < 0 \)), the ground state could be a doubly occupied or empty and an interesting effect called the “charge Kondo effect” takes place when the ground state becomes degenerate for \( E_f + U/2 = 0 \).

Apart from the phenomenon of superconductivity, Kondo effect provides another example of how quantum mechanical correlations between magnetic degrees of freedom lead to a complete reconstruction of the underlying metallic state. Indeed, the typical length scale for this reconstruction can be estimated as

\[ \xi_K \approx \frac{\hbar v_F}{k_B T_K} \sim 10^{-6} \text{ m.} \]

(14)

where \( v_F \) is the Fermi velocity. In the following Section, I will discuss how the Kondo physics manifests itself when there are enough magnetic impurities - disordered Kondo lattice. This case will be important to setup our discussion of the case when magnetic moments occupy each lattice site - Kondo lattice environment.
1.5 From a system of Kondo impurities to Kondo lattice

With large amount of magnetic impurities, the theoretical description of system gets complex as the impurities could interact via exchange interaction mediated by conduction electrons. This interaction is known in the literature as Ruderman-Kittel-Kasuya-Yosida (or RKKY) exchange interaction. It is expected that Kondo exchange interaction will compete with the RKKY interaction and this competition essentially determines the nature of the ground state. Indeed when the Kondo exchange interaction is dominant, all moments will get screened and the ground state is nonmagnetic. In the opposite limit, one can expect a magnetic ground state as impurity moments are ordered, either ferromagnetically or antiferromagnetically. We also note that alloys with dilute concentration of magnetic transition metal ions usually exhibit frustrated, glassy magnetic state known as a spin glass (in spin glass state the magnetic moments freeze into a fixed, but random orientation). On the other hand the dense systems, are typically found to result in an ordered antiferromagnetic ground state.

The type of magnetic ordering depends on the distance between impurities as well as the Fermi momentum. Introduction of a magnetic moment into a metallic or semiconducting host induces Friedel oscillations in the free electron spin density around the magnetic ion. These oscillations depict a characteristic exponential decay in the fermionic density near the impurity followed by an
1.5. From a system of Kondo impurities to Kondo lattice

Figure 3: Schematic picture of a magnetic impurity induced Friedel oscillations in a metallic host and the role of Friedel oscillations in inducing an RKKY interaction between the spins. From Ref. [3].

ongoing sinusoidal decay. These oscillations are written as:

$$\langle \tilde{M}(x) \rangle = -J \chi(\tilde{x} - \tilde{x}') \langle \tilde{S}(\tilde{x}') \rangle$$  \hspace{1cm} (15)$$

where $J$ is the strength of the Kondo coupling and $\chi(\tilde{x} - \tilde{x}')$ is the non-local susceptibility of the metal[3]. A second local moment introduced at location $x$ couples to the oscillations due to the first moment $\langle \tilde{M}(x) \rangle$. Such a mechanism results in establishing a long range magnetic order in the system and is termed Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction,

$$H_{RKKY} = -J^2 \chi(\tilde{x} - \tilde{x}') \tilde{S}(x) \cdot \tilde{S}(x')$$ \hspace{1cm} (16)$$

Thus, as the perturbation caused by the magnetic ions are oscillatory in nature, the RKKY interactions also oscillate in sign depending upon the distance between the two impurities. The approximate size of the RKKY interaction is given by $E_{RKKY} \approx J^2 \rho$, where $\rho$ is the conduction electron density of state.
1.5. From a system of Kondo impurities to Kondo lattice

1.5.1 Heavy Fermions

Heavy fermion materials form a large class of strongly correlated electron systems. The characteristic property of these materials is that the quasiparticle excitations have exceptionally high effective mass - often of the order of 1000 bare electron mass, hence the name ‘heavy fermions’. This large effective electronic mass is reflected in anomalously large, low-temperature Sommerfeld coefficient ($\gamma$) and correspondingly large Pauli paramagnetic susceptibility ($\chi$). Heavy-fermion materials contain elements with 4$f$ or 5$f$ electrons and their properties are derived from the partially filled $f$-electron orbital which often are predominately localized (see Fig. 4) forming magnetic moments.

It is important to note that many of the Kondo anomalies in the normal state physical properties of Kondo lattice systems closely resemble those of the dilute Kondo systems e.g., the resistivity minimum and logarithmic-in-temperature increase of resistivity with decreasing temperature. Note that this resemblance is possible for two reasons: a negligible overlap of neighboring 4$f$ wave-functions (as the inter-atomic spacing is almost 10 times larger than the spatial extent of 4$f$ wave-function) results in negligible direct exchange coupling and a relatively weak indirect exchange between the local moments via the conduction electron spin (the magnitude of the exchange interaction between the 4$f$ and the conduction...
1.5. From a system of Kondo impurities to Kondo lattice

Figure 4: Square of the radial wavefunctions for the 4f, 5s, 5p and 6s energy levels calculated for Gd$^+$, by Freeman and Watson using Hartree-Fock method. From Ref. [10].
1.5. From a system of Kondo impurities to Kondo lattice

electrons is only 0.1eV)[9].

Similar to dilute Kondo systems, heavy fermions show different magnetic properties in high and low temperatures. For example, at high temperatures the magnetic susceptibility shows a Curie temperature dependence characteristic of a lattice of non-interacting moments:

\[ \chi = \frac{g_J^2 \mu_B^2 J (J + 1)}{3T}, \]  

where \( J \) is the total angular momentum and \( g_J \) is the gyromagnetic ratio. The magnetic entropy at high temperatures extracted from the specific heat is:

\[ S_m = k_B \log(2J + 1), \]  

which is expected for a system of non-interacting magnetic moments. Quite remarkably, in canonical heavy-fermion materials like UPt\(_3\) or UBe\(_{13}\) which show conventional metallic behavior at very low temperatures magnetic susceptibility becomes essentially temperature independent. This fact can be interpreted as if all magnetic entropy got dissolved into an electronic subsystem giving rise to the high mass of the carriers.

In a wide class of heavy-fermion materials, which also includes Ce-based ‘115’ compounds, the low-temperature metallic state is unconventional, which is manifested in anomalous temperature dependence of various thermodynamic quantities and transport coefficients. For example, the Sommerfeld coefficient shows
1.5. From a system of Kondo impurities to Kondo lattice

logarithmic temperature dependence, inverse magnetic susceptibility shows sub-linear temperature dependence and resistivity shows significant deviations from the standard $T^2$ dependence at very low temperatures. In passing, I would like to emphasize that understanding of the anomalous behavior of the Sommerfeld coefficient remains one of greatest challenges in condensed matter physics and reminiscent of a famous “puzzle of specific heats” a century ago, which ultimately gave rise to the emergence of quantum mechanics.

On a qualitative level, the low-temperature anomalies described above can be understood as being governed by the remaining magnetic entropy $\delta S_m \ll S_m$. Then, the system may release this entropy by ordering magnetically. In fact, many heavy-fermion systems indeed show tendency towards magnetic ordering. The ordering is driven by interacting magnetic moments which have not been fully dissolved into the conduction sea. Intriguingly, the overwhelming amount of experimental data clearly suggest that in some materials like CeCoIn$_5$, the magnetic transition can only take place at absolute zero temperature, i.e. there simply not enough magnetic entropy to drive the transition to temperatures above zero. Thus the system releases this remaining entropy by developing unconventional superconductivity.

The transition from magnetic to non magnetic phase can be tuned to take place at absolute zero temperature, giving rise to a quantum phase transition. Different novel states of matter emerge from the resulting quantum critical point.
1.5. From a system of Kondo impurities to Kondo lattice

Pressure, chemical doping or magnetic field can be used as the tuning parameter. The study of HF superconducting materials is particularly important, as the spin fluctuations originating from the quantum critical point are believed to be a likely mechanism of superconducting pairing in unconventional superconductors.

1.5.2 Quantum Criticality

A quantum phase transition is defined as the phase transition taking place at absolute zero temperature. Similar to the classical case, a quantum phase transition can either be first order or second order. A quantum critical point (QCP) is point in a phase diagram where the quantum phase transition is of second order. In heavy fermion materials the quantum fluctuations emanating from QCP has profound effects on material properties.

In many of the cases a superconducting region develops around QCP on the suppression magnetic phase. It has also been observed in recent measurements that the quasiparticle mass diverges in the approach to an antiferromagnetic quantum critical point. This divergence of quasiparticle mass is indicative of the fact that the anti ferromagnetism causes a break-down in the Fermi liquid concept and indeed the normal state of materials in such a case exhibit non Fermi liquid behavior. Based on these observations, it is being suggested that the emerging picture of pairing in unconventional superconductors is not the conventional phonon pairing. Rather, the pairing mechanism appears to be mediated by excitations that are related to the QCP, such as spin fluctuations.
1.6. Non-Fermi Liquid behavior due to Quantum Criticality

A schematic phase diagram based on Sebastian Doniach’s proposal for heavy fermion compounds provides a conceptual understanding of how the QCP is formed in heavy fermion compounds. Doniach’s argument is based on two competing energy scales (the Kondo temperature $T_K$ and the RKKY interaction $T_{RKKY}$) in the heavy fermion compounds. Strength of these interactions depend on the value of $J\rho$ as:

$$T_K = D e^{-1/2\rho}, \quad T_{RKKY} = J^2 \rho$$  \hspace{1cm} (19)

Recall that the Kondo interaction favors the non magnetic ground state while the RKKY interaction favors the antiferromagnetic ground state. For small values of $J\rho$, $T_{RKKY} >> T_K$ and an antiferromagnetic state is formed (see Fig. 5). On the other hand for large $J\rho$, $T_{RKKY} << T_K$, dense Kondo lattice ground state is formed, which is non-magnetic. For a critical $J\rho$ value, these two scales cross each other and the 0K point for this value of $J\rho$ results in a quantum phase transition from a magnetic to a nonmagnetic phase. The value of $J\rho$ can be tuned across the critical value using chemical substitutions, magnetic field or pressure as the tuning parameter, as discussed earlier.

1.6 Non-Fermi Liquid behavior due to Quantum Criticality

Non-Fermi liquid behavior refers to the case when the standard Fermi liquid properties are not observed. There are several proposals of the situations in which non-Fermi-liquid behavior could be observed in the heavy fermion systems.
1.6. Non-Fermi Liquid behavior due to Quantum Criticality

Figure 5: A schematic Doniach phase diagram for Kondo lattices: energy scales $T_K$, $T_{RKKY}$ and $T_N$, and $T_{FL}$ as a function of the exchange-coupling parameter $J$. For $T_K < T_{RKKY}$, magnetic order sets in below $T_N$. For large $J$, magnetic order dissolves and system exhibits Fermi liquid properties. Magnetic and non-magnetic phases are separated by a quantum phase transition occurring for $J=J_c$. This point serves as a quantum critical point (QCP) if the transition from magnetic to non-magnetic phase is of second order at 0 K.
1.6. Non-Fermi Liquid behavior due to Quantum Criticality

Quantum critical fluctuations are one of the readily observed mechanism of non
Fermi liquid behavior and is experimentally verified for many of the heavy fermion
systems. Some of the other popular mechanisms are:

1. Quantum Spin Fluctuation

2. Kondo disorder model

3. Griffiths phase model

4. Quadrupolar Kondo model

5. Quantum Valence Fluctuations

A number of researchers have investigated the quantum critical phenomena using
the renormalization-group theory[11, 12, 13, 14, 15]. These theories provide the
temperature dependence of various physical quantities in the low temperature
limits, for systems exhibiting quantum criticality. The results of these models
depend on the nature of the magnetic phase, the dimension ‘d’, critical exponent‘z’
and a control parameter $\delta$. The results from some of these theories are summarized
in Table 2.

It is important to note that the experiments can only be performed to study
the behavior of systems at finite temperatures $T \neq 0$, many times the presence of
a quantum critical point in the phase diagram is identified by the scaling behavior
of different dynamical variables as suggested in theoretical models [17, 18]. Two
### 1.6. Non-Fermi Liquid behavior due to Quantum Criticality

#### (a)

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<td>$T^{4/3}$</td>
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Table 2: Non-fermi liquid behaviors in terms of temperature dependencies of different physical quantities from (a) Millis/Hertz theory, (b) Moriya et al., theory, and (c) Lonzarich theory. $\delta_c$ is the critical parameter in Millis-Hertz theory. From Ref. [16]
1.7. Superconductivity in heavy-fermion systems

such scaling behaviors for the specific heat and magnetization are:[16]

\[
\frac{C(H,T)}{T} - \frac{C(0,T)}{T} = f_1\left(\frac{H}{T^{\beta_b}}\right), \quad \left[\frac{H}{M} - \frac{1}{\chi_0}\right]^{-1} = \frac{1}{T^\nu} f\left(\frac{H}{T^\beta}\right)
\]

(20)

1.7 Superconductivity in heavy-fermion systems

As we have already discussed above, most of the heavy fermion compounds studied until now are Cerium (Ce), Uranium (U) and Ytterbium (Yb) based materials. These compounds have been observed in variety of different phases and provide rich physics of many body systems. The table from Ref. [19] provides the examples of some of the selected heavy fermion systems, but one should note that the actual number of heavy fermion compounds exhibiting non Fermi liquid behavior alone is well over 50 [16].

It would be an impossible task to discuss all categories of these heavy fermion compounds in this dissertation. However, in what follows, I will provide some examples of Cerium based heavy fermion superconductors, as these materials are the most relevant ones for the purpose of the current dissertation.

1.7.1 CeM\textsubscript{2}X\textsubscript{2} (M = Ni, Cu, Rh, Pd; X = Si, Ge)

The first discovered heavy fermion superconductor (CeCu\textsubscript{2}Si\textsubscript{2} [1]) belongs to this isostructural series, which have ThCr\textsubscript{2}Si\textsubscript{2} crystal structure. Superconductivity in CeCu\textsubscript{2}Si\textsubscript{2} was observed in ambient pressure but in some other members, superconductivity only appears after the suppression of their magnetic ground state to 0 K by using pressure (see Fig. 6). Examples of compounds with pressure
1.7. Superconductivity in heavy-fermion systems

induced superconductivity are CeCu$_2$Ge$_2$ [20], CePd$_2$Si$_2$ [21], and CeRh$_2$Si$_2$[22]. Studies on this series provides the understanding of a generic phase diagram for the Ce based heavy fermion superconductors (see Fig. 7). The phase diagram is generated on the observed behavior of the members of this series. The ambient pressure superconductivity in CeCu$_2$Si$_2$ exhibits some very interesting pressure dependence. Under applied pressure the $T_c$ in this material grows and reaches a maximum at about 4 GPa of pressure, and then decreases with increasing pressure. On introduction of a small amount of Ge, results in appearance of a second dome of superconductivity at higher pressure that is associated with a valence

![Figure 6: Temperature-pressure phase diagram for CePd$_2$Si$_2$. A dome of superconductivity appears with the suppression of AFM phase to 0 K. The inset displays electrical resistivity data which exhibits a non Fermi liquid temperature dependence, suggesting the presence of a QCP. From Ref. [23]](image)
1.7. Superconductivity in heavy-fermion systems

Figure 7: Schematic phase diagram of temperature vs. lattice density for a generic Ce-based compound. For low lattice density, localized magnetic moments order antiferromagnetically below a Néel temperature (the red line). The AFM order is suppressed to 0 K with applied pressure and unconventional superconductivity (the red dome), facilitated by magnetically-mediated pairing develops around critical pressure $p_{c1}$. Further increasing the lattice density takes the compound from heavy-fermion behavior to an intermediate valence region. This cross over could take place through a first-order phase transition (green dashed line) and is accompanied by a concomitant volume collapse of the unit cell. Another dome of superconductivity may form around the quantum phase transition associated with unit cell volume collapse at $p_{c2}$ (the green dome). From Ref. [26]

transition of the Ce ions (see Fig. 7) [24, 25]. This intriguing result suggests two different mechanisms for supporting superconductivity in CeCu$_2$Si$_2$ i.e., a magnetically-mediated pairing mechanism and an interaction based on spatially-extended density fluctuations [26].

1.7.2 CeIn$_3$, CeMIn$_5$ (M = Co, Rh, Ir) and related Compounds

These superconductors are members of a larger family of layered, tetragonal compounds with compositions Ce$_n$M$_m$In$_{3n+2m}$, where M is a transition metal. For
1.7. Superconductivity in heavy-fermion systems

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ground State</th>
<th>$T_N$, $T_c$ (K)</th>
<th>$\gamma$ (mJ mol$^{-1}$K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeCoIn$_5$</td>
<td>SC</td>
<td>2.3</td>
<td>250</td>
</tr>
<tr>
<td>CeRhIn$_5$</td>
<td>AFM/SC</td>
<td>3.8/2.4 (2.3 GPa)</td>
<td>430</td>
</tr>
<tr>
<td>CeIrIn$_5$</td>
<td>SC</td>
<td>0.4</td>
<td>750</td>
</tr>
<tr>
<td>CePt$_2$In$_7$</td>
<td>AFM/SC</td>
<td>5.5/2.3 (3.1 GPa)</td>
<td>340</td>
</tr>
<tr>
<td>Ce$_2$CoIn$_8$</td>
<td>SC</td>
<td>0.4</td>
<td>500</td>
</tr>
<tr>
<td>Ce$_2$RhIn$_8$</td>
<td>AFM/SC</td>
<td>2.8/2.0 (2.3 GPa)</td>
<td>400</td>
</tr>
<tr>
<td>Ce$_2$PdIn$_8$</td>
<td>SC</td>
<td>0.7</td>
<td>550</td>
</tr>
<tr>
<td>Ce$_3$PdIn$_1$</td>
<td>AFM + SC</td>
<td>1.6+1.5+0.4 (SC)</td>
<td>300</td>
</tr>
<tr>
<td>PuCoIn$_5$</td>
<td>SC</td>
<td>2.5</td>
<td>200</td>
</tr>
<tr>
<td>PuRhIn$_5$</td>
<td>SC</td>
<td>1.6</td>
<td>200</td>
</tr>
<tr>
<td>PuCoGa$_5$</td>
<td>SC</td>
<td>18.5</td>
<td>80</td>
</tr>
<tr>
<td>PuRhGa$_5$</td>
<td>SC</td>
<td>8.7</td>
<td>80-150</td>
</tr>
</tbody>
</table>

Table 3: Basic properties of members of the Ce$_n$M$_m$In$_{3n+2m}$ family as well as of the PuMX$_5$ materials. From Ref. [26]
1.7. Superconductivity in heavy-fermion systems

the series CeMIn$_5$, n = 1, m = 1 and M = Co, Rh, Ir. CeIn$_3$ is the basic structural building block of the family. CeIn$_3$ is layered, cubic compound exhibiting superconductivity induced under pressure. The members of the CeMIn$_5$ series crystallize in a HoCoGa$_5$ crystal structure with alternating layers of CeIn$_3$ and MIn$_2$.

Similar to CeIn$_3$, the ground state of CeRhIn$_5$ is also antiferromagnetic and superconductivity is induced on application of pressure [23]. On the other hand, CeCoIn$_5$ and CeIrIn$_5$ exhibit superconductivity under ambient pressure [27, 28]. Superconductivity is also found in other related materials of the series with n = 1, 2 or 3 and m = 1 or 2 and in Pu-based analogs PuMX$_5$. Table 3 lists the basic properties of members of the series and the related Pu based compounds. Readers are referred to a recent article by White et. al., [26], and the references therein for a more in depth and wide discussions of the properties of this series.

1.7.3 Heavy-fermion alloys Ce$_{1-x}$R$_x$CoIn$_5$ System (R = Rare Earth)

CeCoIn$_5$ is the parent compound of Ce$_{1-x}$R$_x$CoIn$_5$ family. Under ambient conditions CeCoIn$_5$ does not exhibit any magnetic ground state but evidence suggest that the magnetic order in this material develops inside the vortex core in the mixed state. CeCoIn$_5$ have been shown to reveal quantum criticality on tuning with either pressure or field. The critical behavior is attributed to the presence of strong spin fluctuations inside the vortices. With the presence of quantum spin fluctuations, CeCoIn$_5$, continues to be a very intriguing heavy fermion material
1.7. Superconductivity in heavy-fermion systems

Figure 8: Dependence of superconducting transition temperature, $T_c$, and Kondo-lattice coherence temperature, $T_{coh}$, of Ce$_{1-x}$R$_x$CoIn$_5$ on rare-earth concentration. The horizontal axis is plotted as residual resistivity with ($\rho_{0} \sim x$) From Ref. [29]
1.7. Superconductivity in heavy-fermion systems

to study the interplay between magnetism and superconductivity.

Thus a universal suppression of $T_{coh}$ and $T_c$ is observed for $R$ being magnetic or non magnetic (see Fig. 8).

The study of electric transport in Ce$_{1-x}$R$_x$CoIn$_5$ series suggests that the unconventional superconductivity and the Kondo-lattice coherence of the family is independent of the nature of the rare earth substituents.

Later experiments on this series of materials found that Ytterbium (Yb) substitution for Ce was distinctively different from the any other members of the series in the sense that both the coherence temperature and the superconducting transition temperatures for Ce$_{1-x}$Yb$_x$CoIn$_5$ were very robust and the system exhibited a strange non Fermi liquid behavior in terms of temperature dependence of resistivity [30]. The spectroscopic and bulk property measurements on Ce$_{1-x}$Yb$_x$CoIn$_5$ show that Yb appears in a mixed valence state in this system. The average Yb valence depends on doping level and exhibits an intermediate valence of +2.3 for $x > 0.2$. For lower doping ($x \leq 0.2$), the average Yb valence increases rapidly with decreasing $x$ from +2.3 towards +3 [31]. Furthermore, for smaller Yb concentrations, there is a proposal for Yb impurity correlations, providing the healing effect on suppression of coherence with the introduction of disorder [32].
CHAPTER 2

Experimental Techniques

In this chapter I will provide a snapshot of different measurement techniques and experimental setups, used for the purpose of investigation of electronic and thermal transport properties of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals. Detailed description of the experimental techniques used are readily available from various other sources.

2.1 Physical Properties Measurement System

In study of the single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$, we utilized the data obtained from the measurements of electrical resistivity, magnetoresistance, and heat capacity. The measurements were performed in Physical Property Measurement System (PPMS) designed by Quantum Design Inc. PPMS is a variable temperature-magnetic field system optimized to perform a variety of automated measurements. With the basic setup, the PPMS can used to perform measurements in the temperature range $1.8 \text{ K} \leq T \leq 300 \text{ K}$ and magnetic fields as high as 14 T.

Figure 9, shows a vertical cross section of PPMS with the basic components involved in controlling the temperature and magnetic field. PPMS probe insert is designed to maintain a uniform temperature at the bottom of the probe where the sample mounting system (the puck) is housed. The bottom of the sample chamber
2.2. Sample Growth

consists of a 12-pin connector wired to the electronics of the system. The bottom of the puck firmly plugs in to this connector, thereby providing pin connections for flow of current and recording of signals. In the proximity to the sample puck, there are two thermometers and a heater which provide close thermal contact with the puck and sample during experiments. Multiple set of wire running from bottom of the probe to the top provide necessary connections for the puck heater and the thermometers.

The cooling annulus is the region where Helium is pulled through the impedance tube in a controlled fashion to heat and cool the sample chamber uniformly. The flow of Helium in annulus is controlled by the impedance assembly.

Surrounding the sample chamber is a superconducting magnet which provides magnetic field in vertical direction.

2.2 Sample Growth

Excellent quality single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$, with several doping level ($0 \leq x_{nom} \leq 0.775$) were obtained from our collaborators (Prof. Brian Maple and group) at University of California, San Diego. We note that the actual Yb doping differ from the nominal concentration and a detailed analysis of the relationship between actual and nominal doping has been discussed in Ref. [33]. A table relating the nominal and actual concentrations is provided in the appendix A. The self flux method was utilized in growing the crystals, with In used as the
2.2. Sample Growth

Figure 9: Schematic picture of PPMS sample probe (left) and the vertical cross section of the bottom of the probe (right) showing assembly of the puck and the various components used in controlling the temperature and magnetic field in an experiment.
2.3. Sample Preparation

Starting materials Ce, Co and Yb were mixed in stoichiometric amount with excess of In in an alumina crucible. The crucible was encapsulated in an evacuated quartz ampoule. The mixture was heated rapidly to 1150°C to obtain a homogeneous mixing of molten materials. The solidification of single crystals was obtained through a two-stage cooling process including an initial rapid cooling from 1150°C to 750°C followed by a slower cooling to 450°C. Typical dimensions of the crystals obtained were $0.5 \times 0.25 \times 0.1\text{mm}^3$ with the c-axis oriented along the smallest dimension.

2.3 Sample Preparation

Before utilizing the crystals for measurements, we followed a cleaning routine to get rid of the excess Indium flux and to obtain uniform surfaces. Thus the single crystals were etched in concentrated HCl to remove any leftover Indium on the surface. The crystals were then cleaned using ethanol. Occasionally the surfaces were made smooth by sanding with SiC sanding sheets of super fine grade. The samples were flushed with ethanol and dried, after every cleaning.

2.4 Electronic Transport Measurements

For the purpose of electronic transport measurements, long thin samples were chosen carefully. The care was made to make sure that the samples are free of any defect and have uniformity in size and flatness of the surface. Four parallel gold leads were attached to the surface of the sample. The gold wire used had 99.995% purity with a diameter of 0.05 mm. The leads were attached using a conductive
2.4. Electronic Transport Measurements

Figure 10: Schematic picture of the single crystal with four parallel gold leads attached to the top surface of the crystal using a silver based epoxy H20E.

silver based epoxy named H20E Fig. 10. The epoxy was then cured at 200°C for 5 minutes to ensure that it sets completely on the surface of the sample. The sample is then mounted on Quantum Design standard resistance puck by soldering the four gold leads to the pins provided on the puck. The sample is supported horizontally on a thin MgO crystal placed on puck’s base. This crystal provides for a uniform distribution of temperature around the sample by maintaining a good thermal contact between the sample and the puck and without risking an electrical short between them. Uniform temperature distribution is additionally warranted by placing generous amounts of thermally conducting “GE-varnish” in the surrounding of the mounted sample.

The resistance measurement is performed using the standard four-wire method.
2.4. Electronic Transport Measurements

The four wire method eliminates undesired contributions to resistance which might come due to various factors. These factors include the resistance of the gold leads and contact resistance due to the epoxy. For these reasons, the four lead method allows for the measurement of lower resistances when compared with the two lead geometry. The two outer leads on the sample serve as the current leads and the two middle ones are used as the voltage leads. A known amount of low frequency alternating current is passed through the current leads and a very high impedance voltmeter is used to record the voltage and current drop across the sample. AC measurements is preferred over DC measurements to avoid the buildup of a large thermopower voltage along the measurement wires in going from room temperature to ultra low temperatures.

**Magnetoresistance:** Magnetoresistance (MR) is the change in the electrical resistance of a material under the application of external magnetic field. MR is defined by the formula:

\[
\frac{\Delta R}{R} = \frac{R(H) - R(0)}{R(0)}
\]  

(21)

where \( R(H) \) and \( R(0) \) are the electrical resistances with and without the external field respectively. Depending upon the direction of applied magnetic field relative to the current carrying surface of the sample, MR can either be transverse (\( H \perp \) surface) or longitudinal (\( H \parallel \) surface). The MR presented in this dissertation
2.5. Heat Capacity Measurements

follows from the transverse geometry, and for convenience can be denoted as:

\[
\frac{\Delta R_a^\perp}{R_a} \equiv \frac{R_a^\perp(H) - R_a(0)}{R_a(0)} \quad (22)
\]

Magneto-resistance of the samples is measured by scanning the magnetic field at fixed temperatures. A slight misalignment of the voltage leads may cause the measured MR on \(ab\)-plane to acquire some of the resistance along direction transverse to current. A symmetry analysis on MR data, for two different orientations of field \((H \parallel c \text{ and } H \parallel -c)\), is performed to get rid of this geometrical effect. Thus the MR can be correctly obtained from the measured data using:

\[
R_a^\perp(H) = \frac{R_a^\perp(\text{measured})(H) + R_a^\perp(\text{measured})(-H)}{2} \quad (23)
\]

2.5 Heat Capacity Measurements

Heat capacity data was obtained using a semi-adiabatic calorimeter, utilizing a heat pulse technique. The measurements were performed for temperatures as low as 0.5 K using separate pucks provided by Quantum Design for He-4 and He-3 options respectively. There are a few sources of background signal in the measured data. These include the specific heat of the platform and the “Apiezon N-grease” used to stick the sample to the platform. This cryogenic grease is specially formulated to exhibit craze-free performance characteristics at low temperatures and withstand frequent cycling between cryogenic temperatures as low as -273C and +30C. These background contributions were subtracted to obtain the heat capacity of sample. Figure 11 shows the expanded view of the puck assembly to
2.5. Heat Capacity Measurements

Figure 11: Schematic picture of puck assembly used in measurement of sample heat capacity with standard He-4 option in PPMS. (a) Parts of the puck assembly, (b) Top view of the sample platform consisting of a Cernox thermometer and a heater, and (c) Cross section of sample chamber, showing the loading of heat capacity puck to the bottom of the chamber.

Figure 11: Schematic picture of puck assembly used in measurement of sample heat capacity with standard He-4 option in PPMS. (a) Parts of the puck assembly, (b) Top view of the sample platform consisting of a Cernox thermometer and a heater, and (c) Cross section of sample chamber, showing the loading of heat capacity puck to the bottom of the chamber.

measure heat capacity using He-4 option. The basic design of the heat capacity puck contains an alumina platform with a cernox thermometer and a heater attached to the back of it. Eight wires coming out of the platform (as shown in Fig. 11(a)), are soldered to the puck and provide required connection between the puck and the heater and thermometer on the platform. The sample is glued to the top surface of the platform using Apiezon N-grease. When inside the sample chamber, the bottom of the puck fits to the keyed bottom connector inside the
2.6. He-3 Option

The operation of PPMS with He-4 provides the temperatures as low as 1.8 K. For further lower temperatures we utilized He-3 option which takes us comfortably to temperatures as low as 0.5 K. A continuous, closed cycle circulation of He-3
2.7 Measurements under Pressure

in a sealed system is utilized to obtain these extreme low temperatures. The low
temperatures obtained through He-3 option can be utilized in usual ways for the
purpose of electronic transport and heat capacity measurements.

2.7 Measurements under Pressure

Some of the transport studies, presented in this dissertation were performed by
putting the samples under hydro-static pressures up to 1.0 GPa. These pressures
were achieved by using Almax-easyLab high pressure cell module, Pcell 15/30,
designed to achieve an operating pressure of 2.6 GPa. The details of the module
can be found in the brochure published by Almax-easyLab.

For the purpose of transport measurements under pressure we prepared the
wires-and-platform assembly from bare feed-through. The prepared feedthrough
had the option to support the sample with four leads to be inserted in a pressure
transmitting fluid contained in a teflon cap. A 50:50 mixture of n-pentane and
iso-pentane was used as hydrostatic pressure transmitting medium. The tin wire
is attached to the back of the sample platform. The superconducting transition of
tin under pressure is used as reference to estimate the actual pressure inside the
pressure cell at low temperatures, when the pressure transmitting fluid freezes. The
electrical connections were made through the four pairs of twisted wires attached
on the puck provided with the assembly to hold the pressure cell. An internal
pressure of about 2 GPa was achieved using this assembly.
2.7. Measurements under Pressure

For the detailed description of the operating principles of PPMS options readers are referred to the operation manuals available from Quantum Design Inc. [34, 35, 36, 37]
2.7. Measurements under Pressure

Figure 12: Photographs of feedthrough prepared for the purpose of resistivity measurements under pressure. (a)(Top) Feedthrough cap with set of four pairs of wires for connections. Each set contains two wires twisted together to minimize the induced magnetic field. (Bottom) Feedthrough with sample on the platform as seen under the microscope and (c) Magnified side view of the sample platform showing the sample on the right and the twisted tin wire to the back of the platform.
CHAPTER 3

Non Fermi Liquid Regimes with and without Quantum Criticality in $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$\textsuperscript{1}

3.1 Introduction

One of the greatest challenges to Landau’s Fermi liquid theory - the standard theory of metals - is presented by complex materials with strong electronic correlations. In these materials, non-Fermi liquid transport and thermodynamic properties are often explained by the presence of a continuous quantum phase transition which happens at a quantum critical point (QCP). A QCP can be revealed by applying pressure, magnetic field, or changing the chemical composition. In the heavy-fermion compound $\text{CeCoIn}_5$, the QCP is assumed to play a decisive role in defining the microscopic structure of both normal and superconducting states. However, the question of whether QCP must be present in the material’s phase diagram to induce non-Fermi liquid behavior and trigger superconductivity remains open. Here we show that the full suppression of the field-induced QCP in $\text{CeCoIn}_5$ by doping with Yb has surprisingly little impact on both unconventional superconductivity and non-Fermi liquid behavior. This implies that the

\textsuperscript{1}This chapter is based on following article: T. Hu, Y. P. Singh, L. Shu, M. Janoschek, M. Dzero, M. B. Maple and C. C. Almasan, Proc. Nat. Acad. Sci. \textbf{110}, 7160-7164 (2013)
non-Fermi liquid metallic behavior could be a new state of matter in its own right rather than a consequence of the underlying quantum phase transition.

The heavy-fermion material CeCoIn$_5$ is a prototypical system in which strong interactions between conduction and predominantly localized f-electrons give rise to a number of remarkable physical phenomena [19, 38]. Unconventional superconductivity emerges in CeCoIn$_5$ out of a metallic state with non-Fermi-liquid (NFL) properties: linear temperature dependence of resistivity below 20 K, logarithmic temperature dependence of the Sommerfeld coefficient, and divergence of low temperature magnetic susceptibility [39, 27, 40, 41]. These anomalies disappear beyond a critical value of the magnetic field and the system recovers its Fermi liquid properties. The crossover from non-Fermi-liquid to Fermi-liquid behavior is thought to be governed by a quantum critical point (QCP), which separates paramagnetic and antiferromagnetic (AFM) phases and is located in the superconducting phase [42, 43]. Neutron scattering studies [44] and more recent measurements of the vortex-core dissipation through current-voltage characteristics [45] provide direct evidence for an antiferromagnetic QCP in CeCoIn$_5$ that could be accessed by tuning the system via magnetic field or pressure.

Nevertheless, a growing number of f-electron systems do not conform with this QCP scenario; for example, the NFL behavior in some systems occurs in the absence of an obvious QCP [46, 47, 48, 49]. An intriguing candidate is the alloy
3.2 Magnetoresistance of Ce$_{1-x}$Yb$_x$CoIn$_5$

Yb-doped CeCoIn$_5$ that exhibits an unconventional $T - x$ phase diagram without an apparent QCP, while the onset of coherence in the Kondo lattice and the superconducting transition temperature $T_c$ are only weakly dependent on Yb concentration and prevail for doping up to $x = 0.65$ [30]. Yet, the presence of a QCP in the parent CeCoIn$_5$ compound and the logarithmic temperature dependence of the normal state Sommerfeld coefficient in lightly doped Ce$_{1-x}$Yb$_x$CoIn$_5$ crystals [50] show that this system is in the vicinity to a QCP. Therefore, we are presented with the remarkable opportunity to elucidate the nature of the NFL behavior and unconventional superconductivity in such a system, to search for possible QCPs, and to determine the specific role QCP plays in defining the low-temperature properties of this material and, in particular, to determine the degree to which quantum criticality and superconductivity are coupled to each other.

3.2 Magnetoresistance of Ce$_{1-x}$Yb$_x$CoIn$_5$

To uncover the field-induced QCP and its evolution on Yb concentration we study the magnetic field ($H$) and temperature ($T$) dependence of the transverse ($H \perp ab$) in-plane magnetoresistivity $\Delta \rho_a^\perp/\rho_a \equiv [\rho_a^\perp(H)-\rho_a(0)]/\rho_a(0)$, for $H \leq 14$ T and $2 \leq T \leq 70$ K. Fig. 13(a) and its inset display the field dependence of $\Delta \rho_a^\perp/\rho_a$ measured at different temperatures for the $x = 0$ and $x = 0.40$ samples, respectively. We note that the data for these samples fall under two groups: (i) non-monotonic field dependence of magnetoresistivity (MR) [main panel] with
positive MR at low fields and negative quadratic MR at high fields, typical for $x \leq 0.20$ and (ii) negative and quadratic MR over the whole measured field range [inset], typical behavior for the high Yb doping ($0.25 \leq x \leq 0.65$).

Positive MR in heavy-fermion materials at low fields marks the departure from the single-ion Kondo behavior and is determined by the formation of the coherent Kondo-lattice state for systems in or close to their Fermi-liquid ground state [51, 52, 53, 54, 55, 56]. The maximum in the MR of a Kondo-lattice Fermi liquid at a certain field value is a result of the competition between a $T$-independent residual resistivity contribution that increases with increasing $H$, and a $T$-dependent term that decreases with increasing $H$ [56, 57]. Thus, in conventional Kondo-lattice systems, the peak in the field-dependent MR moves toward lower $H$ with increasing $T$ since a lower field is required to break the Kondo lattice coherence.

### 3.3 Quantum Criticality in Ce$_{1-x}$Yb$_x$CoIn$_5$

To determine the nature of the positive MR in Ce$_{1-x}$Yb$_x$CoIn$_5$ for $x \leq 0.20$, we extract the temperature dependence of the peak ($H_{\text{max}}$) in the field-dependent MR and plot these data in Fig. 13(b). This figure shows that $H_{\text{max}}$ vs $T$ of the $x \leq 0.20$ samples is non-monotonic, with a maximum around 20 K, and a linear behavior at low-$T$ values. The positive MR measured at $T > 20$ K [for which $H_{\text{max}}(T)$ decreases with increasing $T$] could reflect the presence of the coherent Kondo lattice state at low field values as discussed in the previous paragraph. In
3.3. Quantum Criticality in Ce\textsubscript{1-x}Yb\textsubscript{x}CoIn\textsubscript{5}

contrast, the behavior below 20 K is strikingly different from what one would expect for conventional Kondo-lattice systems. The increase of $H_{\text{max}}$ with increasing $T$ at these lower temperatures had previously been observed in CeCoIn\textsubscript{5} and has been attributed to field quenching of the AFM spin fluctuations responsible for the NFL behavior [58]. Therefore, we conclude that the positive MR measured at $T < 20$ K in Ce\textsubscript{1-x}Yb\textsubscript{x}CoIn\textsubscript{5} with $x \leq 0.20$ reflects the dominant role played by the AFM quantum spin fluctuations. An important next goal is to identify the $H_{QCP}$ associated with these quantum fluctuations. One option is to extrapolate the low temperature linear $H_{\text{max}}(T)$ behavior to $T = 0$ K and identify this $H_{\text{max}}(0)$ with $H_{QCP}$. However, since there is a certain error associated with the determination of $H_{\text{max}}$, we adopted a more accurate procedure to unambiguously determine $H_{QCP}$ for different Yb doping. This procedure is discussed in detail in the Materials and Methods section (see below). We show in Fig. 13(c) the values of $H_{QCP}$, obtained using this procedure, as a function of Yb concentration. As expected, the value of $H_{QCP}$ of 4.1 T for CeCoIn\textsubscript{5} [see Fig. 13(c)] coincides with the value of $H_{QCP}$ determined previously from both resistivity measurements done in the normal state [60] and $I - V$ characteristics measured in the mixed state [45]. Therefore, the measurement of $\Delta \rho_{a}/\rho_{a}$ along with the analysis used here constitutes an excellent experimental technique to determine the field-induced QCP in the NFL regime. The $H_{QCP} = 0$ points for $x > 0.20$ correspond to the case when there is no positive MR, i.e., the maximum in MR shifts to zero field [see inset to
3.3. Quantum Criticality in Ce$_{1-x}$Yb$_x$CoIn$_5$

Figure 13: (a) Magnetic field $H$ scans of transverse magnetoresistivity $\Delta \rho_a / \rho_a$ measured at different temperatures on Ce$_{1-x}$Yb$_x$CoIn$_5$ for $x = 0$ (main panel) and $x = 0.40$ (inset). (b) Temperature $T$ dependence of the characteristic field $H_{\text{max}}$ corresponding to the maximum of transverse magnetoresistivity $\Delta \rho_a / \rho_a$. The solid lines are linear fits of the low-$T$ data for the $x = 0, 0.10$ and 0.20 samples. (c) Evolution of the field induced quantum critical point $H_{\text{QCP}}$ as a function of rare-earth concentration $x$. Inset: Coherence temperature $T_{\text{coh}}$ and superconducting critical temperature $T_c$ (from Ref. [30]) of Ce$_{1-x}$Yb$_x$CoIn$_5$ and the corresponding temperatures (from Ref. [59]) of Ce$_{1-x}$La$_x$CoIn$_5$ as a function of rare-earth concentration $x$. Region I is where superconductivity coexists with antiferromagnetism at 0 K, while in region II the system is superconducting without magnetic order.
3.4. Quantum Critical Point and Gyromagnetic Factor

Fig. 13(a).

The inset to Fig. 13(c) shows the suppression with doping of $T_c$ (from [30]) and $T_{coh}$ for Ce$_{1-x}$Yb$_x$CoIn$_5$ and of the corresponding temperatures (from [59]) for Ce$_{1-x}$La$_x$CoIn$_5$. These doping-dependent $H_{QCP}$ and temperature phase diagrams for Ce$_{1-x}$Yb$_x$CoIn$_5$ show that, while superconductivity (SC) is robust and survives over the whole Yb doping range, the field-induced QCP is strongly suppressed with Yb doping and disappears for $x > 0.20$. This implies that SC and quantum criticality are likely to be decoupled in this system, i.e., unconventional superconductivity is not triggered by spin fluctuations.

3.4 Quantum Critical Point and Gyromagnetic Factor

The experimental technique used to determine $H_{QCP}$ also permits the determination of the gyromagnetic factor $g$. There is a significant change in the value of the $g$ factor at QCP. For CeCoIn$_5$, this change is from $g \approx 2.2$ (g-factor of free electrons in a metal) just below $H_{QCP}$ to $g \approx 1.3$ just above $H_{QCP}$. Similarly, for the $x = 0.10$ sample, the change is from $g \approx 2.5$ just below $H_{QCP}$ to $g \approx 1.0$ just above $H_{QCP}$. The experimentally observed changes in the $g$-factor reflect the transformations that the electronic system undergoes with the change in the external magnetic field. Therefore, we conclude that for $H < H_{QCP}$ the conduction electrons are only weakly coupled to the local spins (i.e., there is a small amount of admixture between the $f$-electron and the conduction-electron states). However, for $H > H_{QCP}$, given that the values of 1.3 and 1.0 are only slightly larger than
3.5 Origin of Non Fermi Liquid behavior in Ce$_{1-x}$Yb$_x$CoIn$_5$

the value of $g \approx 0.83$ for the crystal field configuration of Ce ions [61], the conduction states are strongly hybridized with the $f$-states since the antiferromagnetic fluctuations between the local moments are suppressed, which is reflected in the reduction in the value of the $g$-factor [62]. The change in the value of $g$ at $H_{QCP}$ can be interpreted using the phenomenological theory of “Kondo breakdown” at $H_{QCP}$ [62]. Within this theory, the changes in the $g$-factor are governed by the changes in the size of the Fermi surface: larger values of the $g$-factor correspond to small Fermi surface so that the conduction electrons are effectively decoupled from the localized $f$-states. In the opposite limit of smaller $g$-values, the Fermi surface is large, reflecting the strong coupling between the conduction and $f$-electrons. More importantly, the jump in the size of the Fermi surface at $H_{QCP}$ corresponds to the divergence of the quasiparticle’s effective mass.

3.5 Origin of Non Fermi Liquid behavior in Ce$_{1-x}$Yb$_x$CoIn$_5$

A very interesting and puzzling behavior of the Ce$_{1-x}$Yb$_x$CoIn$_5$ system is that, even though the QCP disappears for $x > 0.20$, the system continues to display NFL behavior, as evidenced by the sublinear $T$-dependence of its resistivity [30]. This means that this non-Fermi liquid behavior at higher Yb doping could be a new state of matter in its own right rather than a consequence of the underlying quantum phase transition. We further investigated the origin of this NFL behavior by studying in more detail the $T$ dependence of the resistivity measured in different magnetic fields. The resistivity of all the Yb-doped single crystals studied follow
3.5. Origin of Non Fermi Liquid behavior in Ce$_{1-x}$Yb$_x$CoIn$_5$

Figure 14: (a) Fits of the resistivity data with $\rho_a(H) = \rho_0 + AT + B\sqrt{T}$ for different doping levels of Yb. (b) Doping $x$ dependence of the linear in temperature $T$ contribution divided by the total contribution to the resistivity (left axis) obtained from fits of the resistivity data shown in panel (a), along with the evolution of the field-induced QCP $H_{QCP}(x)$ (right axis). (c) Variation of the average Yb valence with doping (data from Ref. [63]). (d) Field dependence of the linear in $T$ contribution over the total contribution to the resistivity (left axis) and magnetoresistivity (right axis) measured at 3 K for pure CeCoIn$_5$. 
remarkably well the expression

\[ \rho_a^\parallel(H, x, T) = \rho_0 + AT + B\sqrt{T} \] (24)

for temperatures up to about 15 K [see Fig. 14(a) for the fitting results] and in fields up to 14 T; here \( \rho_0, A, \) and \( B \) are doping- and field-dependent fitting parameters. We show in Figs. 14(b) and 14(d) the doping and magnetic field dependences, respectively, of the ratio of the \( T \)-linear contribution to the total \( T \)-dependent contribution of the resistivity. These results show that the linear in \( T \) term in resistivity is present for low Yb doping (\( x \leq 0.20 \)) in the quantum critical regime (\( T \leq 20 \) K). The percentage of the linear in \( T \) term decreases with increasing \( x \) and \( H \) and disappears for \( x > 0.20 \) and at fields at which the MR is only negative, where only the \( \sqrt{T} \) dependence is present.

It is noteworthy that the average Yb valence decreases with increasing Yb and saturates to a value of about 2.3 for \( x > 0.20 \) [63]. This result along with the data of Figs. 14(b) and 14(d) and the fact that both the superconducting transition and coherence temperatures remain weakly dependent on doping indicate that Yb atoms form a cooperative mixed-valence state that significantly reduces the pair-breaking effects, which could also play an important role in the origin of the NFL behavior at these higher Yb concentrations (\( x > 0.20 \)). This idea is supported by the observed scaling of \( T_{coh} \) vs \( T_c \) (see Fig. 15 and the following discussion).

Figure 15 shows that the normalized Kondo lattice coherence temperature
3.5. Origin of Non Fermi Liquid behavior in Ce_{1-x}Yb_xCoIn_5

Figure 15: Plot of the Kondo coherence temperature $T_{coh}$ vs. the superconducting critical temperature $T_c$ normalized by the corresponding values of the undoped sample, for Yb and La doped (from Ref. [59] samples.)
3.6. Role of Correlated Impurities in Ce$_{1-x}$Yb$_x$CoIn$_5$

$T_{coh}(x)/T_{coh}(0)$ (from this work) scales with the normalized superconducting critical temperature $T_c(x)/T_c(0)$ (from Ref. [30]) over the whole Yb concentration range studied here ($x \leq 0.65$) (black squares) and up to about 10% La doping (red circles, data from Ref. [59]). The linear scaling function is

$$\frac{T_{coh}(x)}{T_{coh}(0)} = \alpha \frac{T_c(x)}{T_c(0)} + \beta,$$

where

$$\alpha = 0.70 \pm 0.04, \quad \beta = 0.30 \pm 0.03. \quad (26)$$

The fact that both $T_{coh}$ and $T_c$ are suppressed at the same rate for both types of substitutions, i.e., $\alpha_{Yb} \simeq \alpha_{La}$, is notable.

We interpret it as an indication that the onset of the many-body coherence in the Kondo lattice and emergence of superconductivity have the same physical origin in both systems: hybridization between conduction and localized $f$-electron states. In particular, this suggests that Cooper pairing develops primarily on the “heavy” (i.e., large) Fermi surface.

### 3.6 Role of Correlated Impurities in Ce$_{1-x}$Yb$_x$CoIn$_5$

In addition, it is intriguing that, while the scaling of these two temperatures for Yb and La conforms with that of the other rare-earth substitutions on the Ce site [29], the nature of the scaling distinguishes the Yb substitution from the other rare-earth substitutions since both $T_{coh}$ and $T_c$ remain much more robust with respect to disorder for Yb, while a non-linear and quite rapid suppression
3.6. Role of Correlated Impurities in Ce$_{1-x}$Yb$_x$CoIn$_5$

of both temperatures is observed for the other rare earth substituents, with a suppression of $T_c$ to zero at around $x = 17.6\%$ of rare-earth substitution [29] (see inset to Fig. 13(c), data from Refs. [30, 59]). This observation could be explained by noting that Yb atoms are in a mixed valence state and, therefore, must be correlated. The correlation may arise via local lattice deformations. The Materials and Methods section below gives a scenario on how the Yb impurity correlations may slow down the suppression of the coherence temperature.

All of the above observations show that the field-induced QCP governs the normal-state transport and thermodynamic properties. While the proximity of many heavy-fermion superconductors to a magnetic instability indicates that the exchange of spin-fluctuations between the conduction electrons is a primary mechanism for the Cooper pairing [64, 23, 65], our experimental results strongly suggest that an alternative mechanism for Cooper pairing may be at play in Ce$_{1-x}$Yb$_x$CoIn$_5$: following the full suppression of the QCP, the normal state is fully reconstructed by the ytterbium substitution, while the superconducting critical temperature is reduced only by a factor of two at $x \approx 65\%$. One possible resolution of this conundrum lies in the hypothesis that superconducting pairing is spatially inhomogeneous and must necessarily involve local Ce $f$-moments. Specifically, when magnetic ions in a lattice exchange a spin with their metallic environment in two distinct symmetry channels, they become overscreened, forming a condensate of composite pairs. In this picture, both the local moments and
3.7. Determination of Field-induced Quantum Critical Point

The electron pairs are involved in the formation of the superconducting condensate - hence the name composite pairing [66, 67]. Therefore, within the framework of composite pairing theory, it is natural to expect that the magnetic quantum critical point will have little effect on the origin of unconventional superconductivity.

3.7 Determination of Field-induced Quantum Critical Point

Here we describe the procedure we used to identify the $H_{QCP}$ associated with the quantum fluctuations. Based on the data of Fig. 13(a) we conclude that the MR for low Yb doping has two main contributions: one negative and quadratic in $H$, which we denote $\Delta \rho_{\text{orb}}^a / \rho_a$ [black symbols in Fig. 16(a) at high fields] and the other is positive denoted $\Delta \rho_{\text{spin}}^a / \rho_a$ [green symbols in Fig. 16(a)], with the latter one obtained by subtracting for all field values the negative quadratic MR from the measured MR. This latter contribution to the MR is isotropic since the green data follow quite well the longitudinal magnetoresistivity $\Delta \rho_{\text{spin}}^a / \rho_a$ [red data in Fig. 16(a)]. Also, $\Delta \rho_{\text{spin}}^a / \rho_a$ is linear in $H$ at low fields [Fig. 16(b)] and saturates at high fields [Fig. 16(c)].

We define the characteristic fields $H_{max}$ where $\Delta \rho_{\text{spin}}^a / \rho_a$ is 100%, 95%, 80%, 75%, etc. of the saturation value $\text{MR}_{\text{spin}}^{max}$. We show the $T$ dependence of these characteristic fields in Fig. 16(d) by the black, red, green, and blue solid circles, respectively. We then fit the linear low-$T$ behavior of these $H_{max}(T)$. Figure 17 is a plot of the slopes $K$ (closed symbols), obtained from these linear fits of the different curves with different percentages of $\text{MR}_{\text{spin}}^{max}$ [Fig. 16(d)], and the
3.7. Determination of Field-induced Quantum Critical Point

Figure 16: (a) In-plane transverse $\Delta \rho_a^\perp / \rho_a$ (black) and longitudinal $\Delta \rho_a^\parallel / \rho_a$ (red) magnetoresistivity (MR) of the $x = 0$ (solid symbols) and $x = 0.40$ (open symbols) samples vs $H^2$ measured at 5 K. The green data are denoted $\Delta \rho_a^{\text{spin}} / \rho_a$ and represent the component of MR obtained by subtracting the high field quadratic MR, denoted $\Delta \rho_a^{\text{orb}} / \rho_a$, from the measured transverse MR. (b) $\Delta \rho_a^{\text{spin}} / \rho_a$ vs $H$ (for low $H$ values) for the $x = 0$ sample measured at different temperatures. (c) $H$ dependence of the isotropic component $\Delta \rho_a^{\text{spin}} / \rho_a$ of the transverse magnetoresistivity of CeCoIn$_5$ measured at different temperatures and up to 14 T. (d) Temperature $T$ dependence of the characteristic field $H_{\text{max}}$ determined for different percentages of the maximum isotropic component of magnetoresistance $M R_{\text{max}}^{\text{spin}}$ (main panel) and low-$T$ linear behavior of $H_{\text{max}}$ for $0 \leq x \leq 0.20$ samples (inset).
3.7. Determination of Field-induced Quantum Critical Point

Figure 17: Slopes $K$ (solid symbols) and percentage of $MR_{\text{spin}}^{\text{max}}$ (open symbols) as a function of the corresponding values of the intercept fields $H_{\text{max}}(0)$ for doping $x = 0$ and $x = 0.10$.

Figure 17: Slopes $K$ (solid symbols) and percentage of $MR_{\text{spin}}^{\text{max}}$ (open symbols) as a function of the corresponding values of the intercept fields $H_{\text{max}}(0)$ for doping $x = 0$ and $x = 0.10$. 
3.8. The Effect of the Correlation between the Yb Impurity on the Suppression of $T_{coh}$ and $T_c$

corresponding percentage of MR$^{spin}_{max}$ (open symbols) vs the corresponding values of the intercept fields $H_{max}(0)$ for the $x = 0$ and 0.10 samples. We note the sharp increase of the slope $K$ at a certain $H_{max}(0)$ value, that we identify as the quantum critical field $H_{QCP}$ for reasons given below.

The origin of the sharp increase in the values of $K$ can be interpreted as follows.

For a system in the quantum critical regime [i.e., low $H$ and $T$ data of Fig. 16(d)], the only energy scale is the Boltzmann energy $\mathcal{E}_T = k_B T$. We compare this energy scale $\mathcal{E}_T$ to the quasiparticle Zeeman energy, i.e.,

$$k_B T = g\mu_B (H - H_{QCP}).$$

(27)

From Eq. (27) we see that the slope $K$ must be inversely proportional to the gyromagnetic factor $g$. So, the sharp increase in $K$ is a result of the sharp decrease in $g$. Previous studies [68] have shown that abrupt changes in the values of the gyromagnetic factor occur at the quantum critical point. Therefore, using this procedure we are able to unambiguously determine $H_{QCP}$ as the value of $H_{max}(0)$ at which there is the sharp change in the $g$ factor.

3.8 The Effect of the Correlation between the Yb Impurity on the Suppression of $T_{coh}$ and $T_c$

To see how the impurity correlations may slow down the suppression of the coherence temperature, we consider the characteristic length scale $R$ on which the impurity distribution function significantly deviates from unity. The impurity
distribution function determines the probability with which one can find one impurity at a certain distance from another. Within the Born approximation, one can show that there will be two contributions to the self-energy of the conduction electrons. One contribution, $\Sigma_{ii}$, corresponds to the scattering of electrons on the same impurity and, upon the averaging over disorder, this contribution is proportional to the concentration of impurities ($n_{imp}$). The second contribution, $\Sigma_{ij}$, describes the scattering of electrons on two different impurities and, therefore, is proportional to $n_{imp}^2$. In the presence of impurity correlations, however, $\Sigma_{ij}$ becomes proportional to $n_{imp}^2 R^3$. Thus, if the radius of correlations is large enough, $n_{imp} R^3 \sim 1$, $\Sigma_{ij}$ becomes comparable with the first, linear in $n_{imp}$, self-energy correction $\Sigma_{ii}$. Consequently, within the large-$N$ mean field theory, one can show that impurity correlations may provide the “healing effect”: the rate of suppression of the coherence temperature becomes strongly dependent on the impurity correlation length $R$ [32].

3.9 Summary

To summarize, we have experimentally investigated the evolution of the field-induced QCP in the heavy-fermion alloy Ce$_{1-x}$Yb$_x$CoIn$_5$ upon Yb concentration. In particular, we have shown that the linear temperature dependence of resistivity is governed by the system’s proximity to the QCP, while the emergence of superconductivity and Kondo lattice coherence remain weakly dependent on the presence of the QCP. Finally, we proposed a novel technique to probe the interplay...
3.9. Summary

between quantum criticality and superconductivity, which can be used to analyze
a variety of strongly correlated electronic materials.
CHAPTER 4

From Local Moment to Mixed-valence Regime in Ce$_{1-x}$Yb$_x$CoIn$_5$

alloys$^1$

4.1 Introduction

In recent years, there has been a remarkable upturn in experimental work reporting the formation of highly unusual correlated many-body states in materials with partially occupied $f$-orbitals. Examples include observation of the topologically protected metallic surface states in canonical Kondo insulator SmB$_6$,[69, 70, 71] violation of the Wiedmann-Franz law in YbRh$_2$Si$_2$,[72] intrinsic non-Fermi liquid behavior and unconventional superconductivity in $\beta$-YbAlB$_4$,[46] rotational symmetry breaking inside the hidden-order phase in URu$_2$Si$_2$,[73, 74] and cooperative states in superconducting alloys Ce$_{1-x}$Yb$_x$CoIn$_5$[30]. Despite many years of experimental and theoretical research, however, many of these phenomena—with the possible exception of metallic states with Dirac spectrum in SmB$_6$—are still poorly understood and are often a subject of controversy.

What is common to all these phenomena is that they are driven not only by

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$^1$This chapter is based on following article:
4.1. Introduction

the strong local correlations between the $f$-electrons, but also by the non-local interactions between the conduction and $f$-electrons[19]. In particular, large enough repulsion between the $f$-electrons may lead to a significant energy separation between the two ionic configurations $f^n$ and $f^{n+1}$, thus leading to the formation of the local magnetic moments [75]. At the same time, in other cases, even in the presence of strong Coulomb interactions, the energy of the two ionic configurations becomes comparable, so that the local moments do not form and the $f$-ions are in an intermediate valence state [76, 77, 78]. How unconventional superconductivity emerges in the $f$-orbital materials that appear to be either in the local moment or mixed valence regime still remains one of the most fundamental problems.

One way to tune the relevant energy scales in order to study the physics of the crossover from Kondo-lattice to Kondo-impurity behavior is to introduce substitutional disorder on the $f$-electron sites. In the case of the unconventional superconductor CeCoIn$_5$—a member of the family of Ce-based ‘115’ compounds [38]—it is done by replacing a Ce ion with a non-magnetic one (La). [79, 39, 29] As another possibility, the substitution of magnetic (Yb) ions on the Ce sites provides an extra dimension to the problem:[80, 81] since Yb ions are in the mixed valence state of Yb$^{2+}$ (non-magnetic valence configuration) and Yb$^{3+}$ (magnetic valence configuration),[80, 63, 31] one can study not only how normal and superconducting states evolve as the alloy crosses over from the predominantly local-moment ($x < 0.6$) to the mixed-valence ($x > 0.6$) regime, but also the problem of the Kondo
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impurity in the heavy-fermion metal when \( x \sim 1 \).

Strong hybridization between the conduction and \( f \)-orbitals leads to the significant enhancement of the effective mass of the charge carriers at low-temperatures as well as emergence of the effective energy scale \( T_F^* \), which is much smaller then the conduction electron Fermi energy. Thus, the onset of unconventional superconductivity at a superconducting transition temperature (\( T_c \)) around 2.3 K in CeCoIn\(_5\) relegates this material to the class of high-temperature superconductors since \( T_F^*/T_c \sim 20 \) only. The origin of such a high (compared to \( T_F^* \)) transition temperature is thought to be due to system’s proximity to a magnetic field induced quantum phase transition, so that strong antiferromagnetic fluctuations provide the source of strong superconducting coupling for the heavy electrons and consequently yield the relatively high value of the superconducting transition temperature [82, 65].

Recently, the idea of unconventional superconductivity induced by the proximity to a magnetic quantum critical point in CeCoIn\(_5\) has been challenged by the systematic study of the superconducting alloys Ce\(_{1-x}\)Yb\(_x\)CoIn\(_5\) [81]. In particular, the evolution of the critical field (\( H_{QCP} \)) along the \( c \)-axis at which the quantum phase transition between the antiferromagnetic and paramagnetic phases takes place [42, 83, 84, 43, 44, 60, 45] has been studied as a function of Yb concentration. It is interesting to note that the value of \( H_{QCP} \) can be extracted from both normal
and superconducting states. The authors [81] found that the value of $H_{QCP}$ is significantly reduced for $x > 0.10$ and vanishes as $x \to 0.20$. Yet, at the same time, the value of the superconducting critical temperature is reduced by only about 15% at $x \approx 0.20$. Furthermore, the critical temperature is reduced only by half at $x \approx 0.5$; this is completely unexpected for an unconventional superconductor given the fact that ytterbium ions are in a mixed valence state with the average valence of $v_{Yb} \approx 2.3$, [63, 31] so that the magnetic valence state of $Yb^{3+}$ together with essentially unscreened cerium moments should provide enough scattering to completely suppress superconductivity. Thus, previously reported robustness of the unconventional superconductivity in $Ce_{1-x}Yb_xCoIn_5$ for intermediate values of Yb concentrations [30] represents a major challenge to our understanding of the physics of this $f$-electron alloy.

In this paper, we report the results of a systematic transport and thermodynamic study of the $Ce_{1-x}Yb_xCoIn_5$ alloy, mostly focusing on the intermediate range of concentrations, $0.40 \leq x \leq 0.775$. As we have already mentioned above, the effect of relatively small Yb substitution ($x \leq 0.20$) is very dramatic on the physics related to the presence of the magnetic quantum critical point [81]. In the intermediate doping range, however, we observe a crossover from coherent cerium Kondo lattice behavior to a coherent many-body state formed by the strong hybridization between conduction electrons and ytterbium $f$-electrons. We note that the temperature ($T_{coh}$) at which resistivity reaches its peak, erred to as coherence
temperature in the text, has a minimum as a function of Yb concentration at $x \sim 0.6$, signaling the reconstruction of the Fermi surface, in agreement with the recent quantum oscillations experiments [85]. On the other hand, the monotonic dependence[30] of $T_c$ on $x$ suggests that the onset of many-body coherence in the lattice of Yb ions diluted with Ce $f$-moments is decoupled from unconventional superconductivity. Moreover, our observation of the single impurity Kondo behavior of Ce ions in magneto-transport for $0.40 \leq x \leq 0.70$ points toward an intriguing possibility that unconventional superconductivity has purely local origin and is driven by the presence of Ce $f$-moments.

4.2 Experimental Results

4.2.1 Resistivity

Figure 18(a) shows the $T$ dependence of the electrical resistivity ($\rho_a$) normalized to its value at 300 K of the single crystals used in the present study ($0 \leq x \leq 0.775$). In the inset to Fig. 18 we plot the dependence of $T_{coh}$ on Yb doping. We notice that $T_{coh}$ decreases linearly with increasing $x$ up to $x \approx 0.65$ and then it increases with further increasing $x$. This indicates that the cerium Kondo lattice coherence initially becomes weaker, due to the dilution of the Ce Kondo lattice with increasing Yb doping, and then the coherence in the system is re-established for Yb doping higher than 65%. Therefore, this suggests that
Figure 18: (a) Temperature $T$ dependence of electrical resistivity $\rho_a$ normalized to its value at 300 K for single crystals with different Yb doping ($0 \leq x \leq 0.775$). The arrow on the top marks the coherence temperatures $T_{coh}$, corresponding to the maximum of resistivity. Inset: Coherence temperature $T_{coh}$ vs Yb doping $x$. 

$$\rho_a / \rho_a(300 \text{ K})$$

$$T (\text{K})$$
4.2. Experimental Results

the coherent many-body state formed by the conduction electrons and cerium $f$-moments is fully destroyed at $x \approx 0.65$ and a new coherent state emerges due to the interaction between the conduction electrons and ytterbium $f$-electrons as if it becomes energetically favorable for the conduction electrons to start hybridizing strongly with ytterbium ions in the lattice. It is also important to note, that our subsequent analysis in section III.C. reveals that cerium ions for the $x = 0.75$ sample are not fully in a single-impurity regime either, while the resistivity decreases with temperature—a clear sign of a coherent metallic state. Keeping in mind the results of the recent cyclotron resonance data,[85] which show substantial reconstruction of the Fermi surfaces for $x > 0.5$, we conclude that the coherence is re-established for $x > 0.65$ due to the onset of strong hybridization between the conduction electrons and Yb $f$-electrons, while the Ce moments become decoupled from the conduction band.

4.2.2 Residual Resistivity

At small concentrations $x$ of ytterbium ions, the Kondo lattice coherence temperature appears to be only slowly suppressed with increasing $x$. This implies that the correlations between Yb impurities play an important role. It has been shown through a combination of x-ray absorption and photoemission spectroscopy techniques[63, 31] that the average Yb valence in $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ decreases monotonically from $v_{\text{Yb}} = 3$ to $v_{\text{Yb}} = 2.3$ with increasing Yb from $x = 0$ to $x = 0.20$ and then it remains constant for $x > 0.20$. Therefore, upon the substitution of
4.2. Experimental Results

ytterbium on cerium sites, an ytterbium ion finds itself in a mixed valence state. It is important to keep in mind, however, that the process during which an ytterbium ion changes its valence is a dynamical one. Yb has thirteen $f$-electrons in its magnetic state, while it has fourteen $f$-electrons in its non-magnetic state. Thus, a transition of Yb from its magnetic to non-magnetic state results in an extra $f$-electron and hence an increase in the local volume around Yb. Theoretically, this increase in the local volume is naturally described by introducing the strain dependent hybridization between the conduction and $f$-states of ytterbium [32]. Of course, the conduction electrons may induce Yb-Yb correlations via an analog of the famous Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. However, theoretical estimates by Dzero and Huang show that the lattice strain serves as a mediator between two ytterbium ions and leads to an increase in the pair correlation radius between Yb impurities[32]. In addition, they have shown that the presence of Yb-Yb correlations in a mixed valence alloy must result in a non-linear dependence of the residual resistivity ($\rho_{a0}$) on $x$, with a positive quadratic increase of $\rho_{a0}(x)$, indicating that the effective interactions between ytterbium ions are predominantly attractive. Also, their theory predicts that the impurity correlations have a healing effect on the formation of the many-body states; i.e., both the Kondo lattice coherence temperature and superconducting critical temperature are expected to decrease at a much lower rate compared to the case when Yb ions are uncorrelated or repel each other. [32] This conclusion is consistent with
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the slow suppression of coherence and superconductivity[30] in Ce$_{1-x}$Yb$_x$CoIn$_5$ compared with other rare-earth substitutions on the Ce-site [39, 29].

To further test these ideas, we studied the dependence of $\rho_{a0} \equiv \rho_a(0 \text{ K})$ on $x$. We extracted $\rho_{a0}$ of all the single crystals studied by fitting $\rho_a(T)$ in the temperature range $3 \text{ K} \leq T \leq 15 \text{ K}$ with

$$
\rho_a(x, T) = \rho_{a0}(x) + a(x)T + b(x)\sqrt{T}.
$$

(28)

The right inset to Fig. 19 shows the excellent agreement between the $\rho_a(T)$ data and the fitting curves.

The main panel of Fig. 19 shows the results of $\rho_{a0}(x)$. The solid line is a quadratic polynomial fit of the residual resistivity data at low-$x$ values, with a positive quadratic term, while the dotted curve is a guide to the eye for the higher $x$ values. This result is in excellent agreement with the theory of Dzero and Huang,[32] indicating that, indeed, the effective interactions between ytterbium ions are predominantly attractive. We note that the non-monotonic $\rho_{a0}(x)$ is expected since the increase in $\rho_{a0}(x)$ and the corresponding maximum for $x \approx 0.55$ appear as a consequence of introducing disorder by the Yb substitution into the ordered host.

Lastly, we note that the reason for choosing the temperature dependence given by Eq. (1) was discussed in details elsewhere [81]. Here we want to mention that the presence of critical fluctuations at lower Yb doping ($x \leq 0.20$) gives rise to the
4.2. Experimental Results

Figure 19: Plot of residual resistivity $\rho_{a0}(x)$ as a function of Yb doping, for single crystals with $0 \leq x \leq 0.75$. The error bars of $\rho_{a0}(x)$ are the standard errors given by the fitting routine and they are within the symbols size. The solid line is a quadratic polynomial fit of the residual resistivity data at low-$x$ values, while the dotted curve is a guide to the eye for the higher $x$ values. Right Inset: Fit of temperature $T$ dependent resistivity data (as discussed in the text). Left inset: Doping dependence of the linear-in-temperature contribution divided by the total contribution to resistivity, obtained from fits of the resistivity data (right inset) for $0 \leq x \leq 0.75$ (the fit of resistivity data is in accordance with Eq. (1) discussed in the text).
4.2. Experimental Results

linear $T$-dependent contribution, while the $\sqrt{T}$ contribution is attributed to the cooperative mixed valence state of Yb. The left inset to Fig. 19 gives the ratio of the $T$-linear contribution to the total $T$-dependent contribution of the resistivity, i.e., $|a|/(|a| + |b|)$, which lects the percentage of the linear in $T$ term. This inset shows that the linear-in-$T$ contribution decreases with increasing $x$ and become almost zero for $x \geq 0.20$. This indicates that, indeed, the system is predominately in the quantum-critical regime only up to $x \approx 0.20$.

4.2.3 Magnetoresistivity

Magneto-transport measurements are an excellent tool to probe the physics of heavy-fermion materials; they can provide insight about many-body coherence, single-ion Kondo behavior, and quantum criticality [81]. In order to further verify the ideas developed while performing the in-plane resistivity measurements, we performed transverse ($H \perp ab$) in-plane magnetoresistivity (MR), $\Delta \rho_a^\perp/\rho_a \equiv (\rho_a^\perp(H) - \rho_a(0))/\rho_a(0)$, measurements as a function of $T$ and applied magnetic field ($H$). The data for all the doping studied fall under three groups: (i) a positive contribution to MR for low $H$ values followed by a negative $H^2$ dependence at higher $H$ values for $x \leq 0.20$ [Fig. 20(a)], (ii) a negative and quadratic in $H$ contribution to MR, typical of a dilute Kondo system, for the intermediate doping range, $0.20 < x \leq 0.70$, [Fig. 20(b)], and (iii) the re-appearance of the positive contribution to MR for $x \geq 0.75$ [Figs. 20(c) and 20(d)].

The positive in-plane magnetoresistivity (MR) is a result of antiferromagnetic
4.2. Experimental Results

Figure 20: Magnetoresistivity $\Delta \rho_a/\rho_a$ as a function of magnetic field squared $H^2$ for the (a) $x = 0.10$, (b) $x = 0.65$, (c) $x = 0.75$ single crystals, and for (d) $x = 0.75$ single crystals for two temperature and low field values.
4.2. Experimental Results

critical spin fluctuations[81] or, according to the standard theory of Kondo lattice systems,[19] a result of the formation of the coherent Kondo lattice state,[86, 87, 88] in heavy fermion materials measured at $T < T_{coh}$ and at low $H$ values. Therefore, the results of Figs. 20 are consistent with the non-monotonic $T_{coh}(x)$ dependence (inset to Fig. 18) and confirm that the coherence effects are stronger in low- and high-Yb-doped samples, while incoherent scattering dominates the contribution to MR for the intermediate Yb doping range.

A further analysis of the magnetoresistivity data based on Schlottmann scaling [89] confirms the above findings. Specifically, with increasing Yb concentration, one expects to observe the crossover from the cerium Kondo lattice to cerium Kondo impurity behavior. In the single-impurity Kondo limit, a plot of the $\rho_+^\prime(H)/\rho_a$ data vs $H/H^*$, where

$$H^* = k_B(T + T_K)/g\mu_B$$

and $T_K$ is the single impurity Kondo temperature, must display Schlottmann scaling [89]. This universal scaling shows that the underlying physics of the Kondo impurity in the single-ion regime is dominated by a single energy scale related to $T_K$. Figures 21(a), 21(b), and 21(c) show the results of this universal scaling for the $x = 0.40$, 0.65 and 0.70 samples, respectively, for $4 \text{ K} \leq T \leq 30 \text{ K}$. The Schlottmann curve (solid lines in Figs. 21) on which the experimental data scale is for $S = 1/2$ case. Choosing $S = 1/2$ is appropriate in the present case as Ce$^{3+}$
4.2. Experimental Results

follows the Kondo impurity model for $J = 5/2$ ion under the tetragonal crystalline field [39]. Notice that the scaling works very well for all these Yb concentrations, with a linear dependence of $H^*$ on $T$ [Figures 21(d), 21(e), and 21(f)], as expected based on Eq. (2), confirming that, indeed, the system is in the single Ce Kondo impurity limit for this intermediate Yb doping range.

The Kondo temperature, obtained from this linear relationship [see Eq. (2)], has the same value $T_K = 14.6 \pm 0.4$ K for these three Yb doping. The temperature scale of 14 K is most likely an intermediate energy scale separating the purely single ion behavior of cerium with $T_K \approx 2$ K and purely coherent behavior of cerium Kondo lattice with $T_{coh} \approx 45$ K. In other words, it reflects some degree of hybridization with conduction electrons as well as the antiferromagnetic exchange interaction between the Ce ions.

Schlottmann’s scaling does not work for any $H^*$ value for $x \geq 0.75$. Figure 21(g) shows an example with $H^*$ corresponding to $T_K = 14.6$ K. This lack of Schlottmann’s scaling indicates that the Ce ions are not fully in a single impurity regime and that the dominant contribution to scattering for these higher doping is coming from the itinerant Yb $f$-electronic states strongly hybridized with the conduction electrons.

4.2.4 Magnetoresistivity under Pressure

As discussed above, for $x \geq 0.75$, the scaling for the single-ion Kondo behavior of Ce moments does not work, $T_{coh}(x)$ increases with increasing $x$, and the positive
4.2. Experimental Results

Figure 21: (a), (b), (c), and (g): Plot of normalized magnetoresistance $\rho^s_a(H)/\rho_a$ data vs $H/H^*$ for the single crystals in the doping range $0.40 \leq x \leq 0.75$, measured at different temperatures $T$. Inset to (c): Same data as in the main panel zoomed at lower $H$ values. The solid curves are the Schlottmann’s theoretical magnetoresistance curve. The scaling field $H^*$ has been adjusted at each temperature to optimize the scaling of the experimental data and Schlottmann’s theoretical magnetoresistance curve. Panel (g) shows that Schlottmann scaling does not work for $x \geq 0.75$. The panels (d), (e) and (f) show scaling parameter $H^*$ vs $T$ for all three doping for which Schlottmann’s scaling works.
4.2. Experimental Results

Figure 22: (a) Temperature $T$ dependence of normalized electrical resistivity $\rho_a/\rho_a(300 \text{ K})$ for the $x = 0.75$ single crystal measured at ambient pressure and at 1 GPa. Inset: Pressure $P$ dependence of coherence temperature $T_{coh}$. The data for $x = 0.00$, 0.20, and 0.40 samples are taken from Ref. [90]. The data for the $x = 0.75$ sample are from the present work. (b) Magnetoresistivity $\Delta \rho_a^+/\rho_a$ of the $x = 0.75$ single crystal measured at different temperatures and under 1 GPa. Inset: Comparison of magnetoresistivity $\Delta \rho_a^+/\rho_a$ of the $x = 0.75$ single crystal measured at 30 K in ambient pressure and at 1 GPa.
4.2. Experimental Results

Figure 23: Specific heat $C$ divided by temperature $T$ for single crystals with different Yb concentrations ($0.10 \leq x \leq 0.775$), measured over the temperature range 1.9 to 5 K. Inset: Value of Sommerfeld coefficient $\gamma$ vs $x$ for $T = 2.15$ K and $T_{coh}$ vs $x$. The Ce and Yb sides are delineated on the figure as the local moment regime and the mixed valence regime, respectively.
4.2. Experimental Results

contribution to MR reappears in this higher doping range. All these results reflect
the strengthening of coherence in the high Yb doping range. Recent results on
Ce$_{1-x}$Yb$_x$CoIn$_5$ [solid symbols in the inset to Fig. 22(a)] have shown that $T_{coh}$
increases linearly with pressure ($P$) with the same slope for different Yb doping.
[90]

To study the effect of pressure on the coherence developing at high Yb dop-
ing, we performed MR measurements under pressure on the $x = 0.75$ sample.
Figure 22(a) shows that an applied pressure of 1 GPa increases the coherence
temperature from 39 K to 62 K [half filled symbols in the inset to Fig. 22(a)].
This increase is quantitatively in agreement with the recently published results[90].
Figure 22(b) shows the MR data measured under 1 GPa and at different temper-
atures. The positive contribution to MR clearly becomes stronger under pressure
[inset to Fig. 22(b)] for all the temperatures, which indicates that pressure in-
creases coherence.

4.2.5 Heat Capacity

The previously discussed transport measurements show that there is a crossover
between Kondo lattice behavior driven by the hybridization between the conduction
band and cerium $f-$moments to coherent state governed by the hybridization
between the conduction states and ytterbium $f-$orbitals for Yb concentrations
larger than 65%. As a final test of this finding, we performed heat capacity mea-
urements on all the single crystals studied. Figure 23 shows specific heat ($C$)
4.3 Conclusions

data divided by temperature measured for \(1.9 \text{ K} \leq T \leq 5 \text{ K}\). The value of the Sommerfeld coefficient \(\gamma \equiv C/T\) obtained at 2.15 K is shown in the inset. All Yb doping levels give large values of \(\gamma\) \((260 \text{ mJ/mol-K}^2 \leq \gamma \leq 380 \text{ mJ/mol-K}^2)\), which confirms the heavy fermion nature and strong electronic correlations for all Yb concentrations. In addition, \(\gamma(x)\) and \(T_{coh}(x)\) show the same behavior [inset to Fig. 23], i.e., they decrease monotonically with increasing Yb concentration up to \(x = 0.65\) and then they increase with further increasing \(x\). This behavior of \(\gamma(x)\) reflects the fact that the quasiparticles are stabilized easily with strengthening coherence in the system at higher Yb doping, which in turn yields a larger effective mass. This shows that the coherence effects, indeed, are strengthened for \(x > 0.65\).

4.3 Conclusions

In this paper we have reported transport and thermodynamic studies of the heavy-fermion superconducting alloys \(\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5\) focusing on the intermediate range of concentrations, i.e., \(0.40 \leq x \leq 0.775\). We observed a crossover from the local moment regime, driven by the hybridization between the conduction electrons and cerium \(f\)-moments, to a coherent many-body state formed by the strong hybridization between conduction electrons and ytterbium \(f\)-electrons. The temperature \(T_{coh}\) at which resistivity reaches its peak has a minimum as a function of Yb concentration at \(x \approx 0.65\), while \(T_c\) decreases linearly with \(x\) over the whole range [30]. This implies that the onset of the many-body coherence in
4.3. Conclusions

the lattice of Yb ions diluted with Ce $f$-moments and unconventional superconductivity are decoupled from each other. The signature of the Ce single-impurity Kondo behavior is revealed by the magneto-transport data for $0.4 \leq x \leq 0.70$. This suggests the likelihood that unconventional superconductivity has purely local origin and is driven by the presence of cerium $f$-moments. Our present results as well as previous transport, thermodynamic, and spectroscopic results show a systematic change in the properties of Ce$_{1-x}$Yb$_x$CoIn$_5$ for $0 \leq x < 0.8$. The fact that superconductivity exists in alloys with $x \sim 0.8$ clearly implies that superconductivity is driven by the presence of Ce ions as though they effectively act as negative-$U$ centers. Given the complete suppression of the antiferromagnetic fluctuations for $x > 0.20$, superconductivity may either be mediated by the electron-phonon interaction [91] or may be due to a more unconventional mechanism involving virtual fluctuations into higher lying Ce crystalline field multiplets [67].
CHAPTER 5

Evidence for Re-entrant, Zero Field Quantum Critical Point, with
Chemical Tuning in Ce$_{1-x}$Yb$_x$CoIn$_5$

We experimentally investigate the properties of high Yb doping in single crystalline alloys Ce$_{1-x}$Yb$_x$CoIn$_5$ (0.65 $\leq x \leq 0.775$). Specifically, we performed electronic transport and magnetoresistance measurements on Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals in order to study the origin of the unconventional behavior in this system that is observed in high doping. In particular, our motivation was to resolve the mysteries of re-entrant coherence in high Yb doping crystals, robust superconductivity, non-Fermi liquid behavior, and the possibility of quantum criticality in higher doping. Our analysis of resistivity, and magneto-resistance data unveils the presence of a crossover from non-Fermi liquid behavior at higher temperatures to Fermi liquid behavior at low temperatures for the $x = 0.75$ doping and provides evidence for a quantum critical point without any field tuning in the $x = 0.75$ doping.

5.1 Introduction

One of the most interesting problems in physics of $f$-electron materials is the quantum critical behavior. Quantum criticality in these materials reflects in a
5.1. **Introduction**

transition, taking place between a magnetically ordered to a disordered phase at 0
K, resulting in a quantum critical point (QCP) in \( T - \delta \) (‘\( \delta \)’ is a tuning parameter) phase diagram. The fluctuations originating from resulting QCP severely affect
the finite temperature properties of materials, in the vicinity of QCP. For instance
heavy fermion materials exhibit deviation from their fermi liquid (FL) properties
in presence of a QCP. For many of the heavy fermion materials, these fluctuations
are also believed to be providing the glue for superconducting pair of electrons.
In these materials, superconductivity originates from the QCP together with a
suppression of the ordered phase.

Many of the studies have reported the \( f \)-electron systems to exhibit the break-
down of FL theory, due to the quantum spin fluctuations. The common feature
of these compounds is that they all are Kondo lattice systems with the integral
valence. The fact that quantum criticality has also been observed in mixed va-
lence compound \( \beta \)-YbAlB\(_4\), provides a motivation to study Kondo lattice system
CeCoIn\(_5\), diluted by Yb which appears in an intermediate valence state.

The motivation behind our study of high Yb doping crystals of \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \)
comes from a few recent developments in physics of this material and also from
some of our previous study of this family of heavy fermion compounds.

From our recent work we proposed that the mechanism of superconducting
pairing in this \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) system does not appear to be mediated by spin
fluctuations. In other words although this system is clearly in the quantum critical
5.1. Introduction

regime, unlike the popular belief, the development of superconductivity is not the result of the quantum fluctuations. Our conclusions find excellent support in a subsequent theoretical proposal of composite pairing mechanism [92], which suggests that superconductivity in this material essentially involves both, the Ce local moments and the conduction electrons. Among the other results of composite pairing theory, there is proposal of two Lifshitz transitions of Fermi surface (one at low Yb doping and other at higher Yb doping), resulting in change in SC gap symmetry and QCPs at these two doping levels. Based on our recent work, the first such critical doping appears to be the $x = 0.20$, where the QCP is very close to $H = 0$ T. Another recent experimental report also finds the doping level $x = 0.20$ to be critical and suggests a transition of SC gap from nodal to nodeless across $x = 0.20$ [93].

Additionally, in one of our recent magnetoresistance (MR) measurements on Ce$_{1-x}$Yb$_x$CoIn$_5$ we have shown a re-entrant positive contribution (and hence a peak) to MR appears for higher Yb doing ($x > 0.70$). This contribution is in addition to the usual negative contribution which is observed for the intermediate Yb doping range $0.20 < x \leq 0.70$. We attributed this positive contribution to MR, reappearing for the higher Yb doping, to the hybridization of magnetic valence state of fluctuating valence Yb, with the conduction electron, which, in turn gives rise to an increased coherence effects in the system. Extending our study in view of the above findings, the goal of the present work is to look for the possibility
5.2 Experimental Results

Heavy fermion materials exhibit a characteristic resistivity behavior in which a logarithmic increase is observed due to the Kondo effect below a certain low temperature. In Kondo lattice materials, the increase in resistivity is followed of an additional QCP, attributed to the intermediate valence Yb, which would explain some of the unresolved issues in the series.

Figure 24: (a) Temperature $T$ dependence of electrical resistivity $\rho_a$ normalized to its value at 300 K for single crystals with different Yb doping ($0.65 \leq x \leq 0.775$). The dashed vertical lines indicate the coherence temperature $T_{coh}$, corresponding to the maximum of resistivity.

$\rho_a / \rho_a(300K)$

$T (K)$

$\rho_a / \rho_a(300K)$

$T (K)$

$\rho_a / \rho_a(300K)$

$T (K)$
5.2. Experimental Results

by a sharp drop due to the development of coherence effects. Consequently a resistivity peak is observed in Kondo lattice materials at a temperature called coherence temperature ($T_{coh}$). Figure 24 shows the temperature dependence of the normalized electrical resistivity of the single crystals used in the present study ($0.65 \leq x \leq 0.775$). $T_{coh}$ increases for Yb doping around $x = 0.38$ and above, as indicated in the inset of Fig. 24. This increase in $T_{coh}$ is attributed to the coherence effect developing in the system due to the intermediate valence state of the Yb atoms and involves participation of Yb $f$-electrons and the conduction electrons [94]. Kondo screening involves the screening of a magnetic moment with the conduction electron spin. This observation suggests that for Yb concentrations $x = 0.70$ and above, Yb $f$-electrons contributes to the coherent scattering of quasiparticles by participating in hybridization with conduction electrons.

The low temperature resistivity data for single crystals with doping $0.65 \leq x \leq 0.75$ exhibit interesting behavior. A $\sqrt{T}$ dependence of resistance is seen for all the doping in the temperature range $3 \text{ K} \leq T \leq 15 \text{ K}$. For further low temperatures $0.5 \text{ K} \leq T \leq 3 \text{ K}$, we find that resistance of $x = 0.75$ crystal crosses over to FL behavior with a $T^2$ dependence. The crossover temperature (termed $T_{FL}$ in the text) from FL to NFL resistance is field dependent and is indicated in Fig. 25(a) by the arrows on temperature dependent resistance data in different fields $6 \text{ T} \leq H \leq 14 \text{ T}$. Note that the resistance is plotted as a function of $T^2$ and a linear fit is performed on the low temperature data as shown by the solid lines
5.2. Experimental Results

in Fig. 25(a). The arrows in the figure mark the points where the data deviates from the fit line \( (T_{FL}) \).

The same low temperature resistance measurement on other single crystals \((x = 0.65\) and \(0.70\)) do not show a crossover to the FL state but instead show a linear-in-T resistance. One such data for temperature dependence of resistance of \(x = 0.70\) doping in 14 T is shown in Fig. 25(b) where the solid line is the linear fit to the data. Note that the low Yb doping crystals in Ce\(_{1-x}\)Yb\(_x\)CoIn\(_5\) \((0 \leq x \leq 0.20)\) exhibit a \(\sqrt{T}\) dependence for temperatures \(T < 3\) K due the presence of superconducting fluctuations \([95]\). One possible reason for the linear-in-T dependence of resistance in present case could be the change in the anisotropy of the system at higher Yb doping. This can be understood by considering the contribution to resistance from superconducting fluctuations, which depends on the dimension ‘d’ as: \([97]\)

\[
R(T) = R_0(T_c) + A(H)T^{(4-d)/2}
\]  

Thus an increased anisotropy will result in a transition from \(\sqrt{T}\) to linear-in-T dependence of resistivity. Our analysis for resistivity anisotropy \((\rho_c/\rho_{ab})\)data (see Fig. 26) suggests that indeed there is a big change in anisotropy at Yb concentration \(x = 0.65\).

The field dependence of crossover temperature \(T_{FL}\) for \(x = 0.75\) is plotted in Fig. 27(a) as black squares (along with other data which would be discussed
5.2. Experimental Results

![Graph](image)

Figure 25: (a) Resistance of $x = 0.75$ single crystals plotted as function of square of temperature $T^2$. The resistance was measured in the temperature range $0.5 \text{ K} \leq T \leq 3 \text{ K}$ and in magnetic fields in the range $6 \text{ T} \leq H \leq 14 \text{ T}$. The solid lines are the linear fit to the low temperature data and the arrows indicate the position where the data deviate from fit lines. (b) Resistance of $x = 0.70$ crystal, measured at $H = 14 \text{ T}$ and plotted as a function of temperature. The solid line is the linear fit to the data.
5.2. Experimental Results

Figure 26: Ratio of out-of-plane $\rho_c$ and in-plane $\rho_{ab}$ resistivities for Ce$_{1-x}$Yb$_x$CoIn$_5$ ($0 \leq x \leq 0.775$) crystals. The data was obtained using 8-lead configuration and the formula developed in reference [96].

Later). The solid lines connecting these data points are the linear fit to the data and extrapolate to zero field for $T = 0$ K. For HF systems such an extrapolation gives the quantum critical field corresponding to absolute zero temperature [42, 60]. Thus the present evidences, as shown in Fig. 27(a) suggest that doping level $x = 0.75$ is quantum critical doping without external tuning. To further verify the critical nature of this doping level, we perform a fit to the resistance data of Fig. 25(a) according to the expression:

$$R = R_0 + A(H)T^2$$

(31)
5.2. Experimental Results

The slope of the fitted $R$ vs $T^2$ curves is a measure of the strength of electron-electron interactions and, according to the FL theory, it is proportional to the effective electronic mass. We plot the field dependence of this slope $A(H)$ in Fig. 27(b). As can be seen in this figure, parameter $A$ diverges at lower field, indicating the enhanced effective electronic mass at some low field. To obtain the value of the field where $A$ diverges, we further fit the field dependence of $A$ with the expression:

$$A(H) = B(H)(H - H_{QCP})^{-n}$$

(32)

This is the same expression which has been used previously in HF materials to extract information about quantum critical field. The parameter $A(H)$ diverges at the quantum critical field as the effective mass diverges. We find that $H_{QCP} = 0$ and $n = 1.33$ provides an excellent fit to $A(H)$ data. Thus from this analysis we conclude that $x = 0.75$ is indeed a critical doping with $H_{QCP} = 0$ T. This conclusion is further supported by the observation of low temperature MR maximum extrapolating to zero field (blue circles in Fig. 27(a)). The solid line indicating the SC phase is a guide to eye based on $T_c$ measurements under field for $x = 0.75$ crystal. In the next paragraph we describe the procedure to obtain the $H_{max} - T$ line plotted in the phase diagram of Fig. 27(a).

Magnetoresistance measurements in HF materials provide a lot of insight into the physics of the system. In particular, MR data has proved to be a useful tool in discussing the quantum physics of $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ system [81]. In order
5.2. Experimental Results

Figure 27: (a) Field-Temperature ($H$-$T$) phase diagram for $x = 0.75$ crystals. The solid line marking the SC phase is obtained from resistivity measurements. Black squares are the temperatures obtained from Fig. 2(a) and are the points where the resistance deviate from $T^2$ behavior. Blue circles are the fields corresponding to maximum in MR at different temperatures, corresponding to Figs. 28 and 29. Solid line connecting black squares and the one connecting blue circles are the linear extrapolation of the respective data. (b) Field dependence of the quadratic coefficient $A$ of $R(T)$ the solid line is a fit of the data points to the displayed formula.
5.2. Experimental Results

Figure 28: Magnetoresistivity $\Delta\rho_a^\perp/\rho_a$ as a function of magnetic field squared $H^2$ for (a) $x = 0.65$, (b) $x = 0.70$ single crystal. (c) Main panel: magnetoresistivity $\Delta\rho_a^\perp/\rho_a$ as a function of magnetic field $H$ for $x = 0.75$. Inset: The data of main panel zoomed in at lower field values.
to further verify the ideas developed while performing the in-plane resistivity measurements, we performed transverse ($H \perp ab$), in-plane MR measurements as a function of temperature ($T$) and applied magnetic field ($H$) over all Yb concentrations discussed here. In what follows, we will use the following notation for MR: $\Delta \rho_x^\perp / \rho_a \equiv \rho_x^\perp (H) / \rho_a(0)$.

Figure 28 shows MR vs $H^2$ data for the $x = 0.65$, 0.70 and MR vs $H$ data for $x = 0.75$ single crystals. As can be seen from Fig. 28(a) and 28(b), doping levels $x = 0.65$ and 0.70 exhibit a negative, quadratic-in-field MR which is observed in Kondo systems when scattering is primarily incoherent. This MR behavior is characteristic of single impurity type behavior of Ce in a diluted Ce lattice [94]. The behavior observed for these intermediate doping is as expected in a diluted Kondo system.

However, MR data for the $x = 0.75$ Yb doping (Fig. 28(c)) is found to be significantly different from the data for $x = 0.65$ and 0.70 doping. Although the major part of MR is still negative and quadratic in field (indicating substantial amount of incoherent scattering at high fields), low field data clearly shows small positive contributions for all temperatures below $T_{coh}$ (recall that $T_{coh}$ is defined from the peak of the resistivity data as shown in Fig. 24). This behavior indicates the strengthening of coherence effects for $x = 0.75$ crystals, since the positive contribution to MR in Kondo lattices is attributed to the development of a coherent state. Indeed, as seen in Fig. 24, resistivity measurements clearly indicates a
5.2. Experimental Results

A strong increase in coherence temperature for $x = 0.75$.

![Graph showing the position of magnetoresistivity peak $H_{max}$ plotted as a function of temperature $T$ for single crystal with doping level $x = 0.75$. The solid line shows the linear extrapolation of the data to $T = 0$ K.](image)

Figure 29: The position of magnetoresistivity peak $H_{max}$ plotted as a function of temperature $T$ for single crystal with doping level $x = 0.75$. The solid line shows the linear extrapolation of the data to $T = 0$ K.

For Kondo systems, magnetoresistance behavior is quite well explained, and is governed, primarily, by two competing energy scales, i.e., the Kondo temperature $T_K$ favoring a non-magnetic coherent state and the Ruderman-Kittel-Kasuya-Yosida (RKKY) scale favoring a magnetic ground state. In our recent works [81, 94, 98, 95] we have discussed that temperature dependence of MR peak can be used to obtain information regarding the nature of the ground state in HF materials. To confirm the quantum critical nature of $x = 0.75$ doping we extract the temperature dependence of MR peak $H_{max}$ from Fig. 28(c) and plot it in Fig. 29. According to the standard theory of Kondo lattice systems the peak in
5.3. Conclusions

the field-dependent MR for a Kondo lattice moves to lower fields with increasing temperatures due to the fact that at higher temperatures, a smaller field is required to break the ‘Kondo singlets’. However, in the present MR data (Fig. 29) this standard Kondo lattice behavior is observed only for $T > 15$ K, while the opposite behavior takes place for $T < 15$ K, i.e., the MR peak moves to higher field with increasing temperature. In view of our previous reports[81, 94, 98, 95] this unusual temperature dependence of $H_{\text{max}}$ can be attributed to quantum spin fluctuations originating from a quantum critical point at 0 K.

5.3 Conclusions

In this chapter, we have performed transport and thermodynamic studies of the heavy-fermion superconducting alloys $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ focusing on the high concentrations of Yb, i.e., $0.65 \leq x \leq 0.775$. Our findings indicate the presence of a zero field QCP at $x = 0.75$ Yb doping. We do not have a conclusive proof of the nature of this higher doping QCP but Yb valence fluctuations and quadrupolar effects are the possible mechanisms which can result in such a quantum critical behavior. Although our findings are in line of the recent theoretical proposal of additional zero field quantum critical doping, additional experimental studies would be required to understand the mechanism at play. Our finding explains many of the earlier unresolved issues in $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ system, i.e., enhanced coherence at higher Yb doping levels and a robust NFL behavior for the whole doping range.
5.3. Conclusions

and provides a possible explanation for robust $T_c$ due to spin fluctuations present in low and high Yb doping levels.
CHAPTER 6

Pressure Effects in Composite Pairing Superconductivity

Composite pairing theory has recently emerged as a prominent microscopic mechanism for superconducting pairing in heavy-fermion materials [99, 66, 67, 100]. At the heart of the theory is the idea that virtual fluctuations of an \( f \)-electron ion between magnetic (say \( f^1 \)) and non-magnetic (\( f^0 \) and \( f^2 \)) valence states become resonant [101] and, in principle, can promote superconducting pairing [99]. It is crucial that the emerging superconducting amplitude is anisotropic in momentum, signaling an onset of unconventional superconductivity. This in turn implies that the composite pairing can only be realized in the lattice of magnetic moments. It is also worth mentioning that, initially, the idea of the composite pairing has been developed in the context of odd-frequency Cooper pairing and its realization in heavy-fermion materials [102, 103, 104]. Subsequently, it was realized that even-frequency composite pairing can be regarded as an alternative to odd-frequency pairing with the order parameter given by the expectation value, which also contains a local spin operator [104].

In this Section we theoretically study the effect of hydrostatic pressure on

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Figure 30: Schematic presentation for the virtual charge fluctuations between magnetic $f^1$ and non-magnetic valence configurations: $f^1 \iff f^0 + e$ via the first conduction channel and $f^1 \iff f^2 - e$ via the second conduction channel. Since the change in the ionic radius is opposite for the two channels, we expect the opposite behavior for the change in the corresponding coherence temperatures with pressure.
6.1. Model

composite pairing. Specifically, we evaluate the pressure dependence of $T_{\text{coh}}$ and $T_c$. For simplicity we will ignore the presence of disorder, so strictly speaking for the arguments presented below we assume the presence of a spatially homogeneous lattice. Our primary goal here is to show that the microscopic mechanism for the composite pairing necessarily implies opposite behaviors of $T_{\text{coh}}$ and $T_c$ with pressure, which can be traced to the opposite changes in the ionic sizes as the resonance valence fluctuations take place.

6.1 Model

We consider the two-channel Kondo lattice Hamiltonian, which is obtained from the Anderson lattice model by formally integrating out high-energy states by means of the Schrieffer-Wolff transformation [101, 99, 66]. We have:

$$H = \sum_{k\sigma} \epsilon_k \hat{c}^\dagger_{k\sigma} \hat{c}_{k\sigma} + \frac{1}{2} \sum_{\kappa,\rho,\beta} \sum_j J_{k,p} \hat{c}^\dagger_{\kappa\alpha} \hat{c}^\dagger_{\rho\beta} \left( \vec{\sigma}\alpha\beta \cdot \vec{S}_f(j) \right) e^{i(p-k)\cdot \vec{R}_j}, \quad (33)$$

where $\hat{c}^\dagger_{k\sigma}$ is a fermionic creation operator, $k$ is a momentum, $\sigma = \uparrow, \downarrow$, $\epsilon_k = -\frac{t}{2}(\cos k_x + \cos k_y) - \mu$, $t$ is a hopping amplitude, $\mu$ is a chemical potential, and $\vec{S}_f(j) = \frac{1}{2} f_{j\sigma} \vec{\sigma} f_{j\sigma}$, written using the Abrikosov fermionic representation, accounts for the localized cerium $f$-moments at site $\vec{R}_j$. Note that, for simplicity, we choose the two-dimensional spectrum for the conduction electrons. The momentum dependent exchange couplings $J_{p,k} = J_1 \phi_{1k}\phi_{2p} + J_2 \phi_{2k}\phi_{2p}$ include exchange couplings $J_{1,2} > 0$ for the electrons in the first and second conduction channels, while $\phi_{1,2}$ are the corresponding form-factors. Without loss of generality,
we choose them in the following form $\phi_{1k} = 1$ (s-wave) and $\phi_{2k} = \cos k_x - \cos k_y$ (d-wave). The mean-field analysis of the model (33) shows that at $T_{coh}$ the heavy-fermion state forms. Within the mean-field approximation, the formation of the heavy-fermion state is governed by the development of the non-zero expectation value $\langle c_{j\alpha}^\dagger f_{j\alpha} \rangle$ at each site. Interestingly, for $J_2 < J_1$ an anomalous expectation value can develop, signaling the onset of either a charge-density wave state or superconductivity. The proper choice of the phase stabilizes the superconducting state with a critical temperature $[99] T_c \sim T_{coh} \exp (-1/\nu_F J_2)$ where $\nu_F$ is the density of states at the chemical potential. This expression is reminiscent of the BCS weak-coupling expression for the critical temperature. As we will show below, $T_c$ shows a strong pressure dependence. Finally, we note that the mean-field theory results at ambient pressure are reproduced by various numerical approaches [105, 106, 104]. More importantly, the composite pairing mechanism for superconductivity can be extended to systems with mixed-valence [100]. However, to this date, the mean-field theory of the composite pairing state for the $f$-electron systems in the mixed-valence regime has not been numerically confirmed.

### 6.2 Mean-field theory: Effect of Hydrostatic Pressure

The mean-field theory is formulated by performing the decoupling in the interacting part of the Hamiltonian (33). This is an approximation which becomes exact in the limit when the number of fermionic flavors $N$ goes to infinity. Therefore, to make our mean-field approximation controlled, we generalize our model from
6.2. Mean-field theory: Effect of Hydrostatic Pressure

SU(2) to symplectic-\(N\) [66] by replacing the Pauli spin operators \(\sigma_{\alpha\beta} \rightarrow (\sigma_N)_{\alpha\beta}\).

At ambient pressure we find:

\[
\mathcal{F}_0 = -NT \sum_{k,\pm} \log[2 \cosh(\beta \omega_{k\pm}/2)] + N N_s \sum_{\Gamma=1,2} \frac{v_{\Gamma}^2}{J_{\Gamma}},
\]

(34)

where \(\beta = 1/k_B T\), \(N_s\) is a number of lattice sites, \(v_{1,2}\) are corresponding mean-field amplitudes that describe the onset of coherence and superconductivity, while \(\omega_{k\pm}\) account for dispersion of newly formed electron bands \(\omega_{k\pm} = \sqrt{\alpha_k \pm (\alpha_k^2 - \gamma_k^2)^{1/2}}\), where we have introduced functions \(\alpha_k = v_{k+}^2 + \frac{1}{2} (c_k^2 + \lambda^2), \gamma_k^2 = (\epsilon_k \lambda - v_{k-}^2)^2 + 4(v_1v_2k)^2, v_{1k} = v_1\phi_{1k}, v_{2k} = v_2\phi_{2k}\), and \(v_{k\pm}^2 = v_{1k}^2 \pm v_{2k}^2\).

For the Ce ions, the change in the \(f\)-shell occupation is positive due to its electronic nature, so that the leading resonance scattering involves conduction electrons in the first channel and a zero-energy boson with amplitude \(v_1\), and an electron: \(f^1(j, m) \Rightarrow f^0(j, m) + e\). In contrast, the resonance scattering in the second conduction channel involves a zero energy boson with an amplitude \(v_2\) and a hole: \(f^1(j, m) \Rightarrow f^2(j, m) + e - 2e\). When resonance develops in both channels, for the total volume of the system within the mean-field theory, we write: [107]

\[
\Omega_t = \Omega(f^0)v_1^2 + (1 - v_1^2 - v_2^2)\Omega(f^1) + \Omega(f^2)v_2^2,
\]

(35)

where \(\Omega(f^n)\) are the cell volumes for the singlet \((n = 0, 2)\) states and a doublet \((n = 1)\) state.

It is convenient to introduce the change in the cell volumes: \(\delta \Omega_{1ch} = \Omega(f^0) - \Omega(f^1)\) is negative and accounts for the difference in cell volumes between two \(f\)-ion
6.2. Mean-field theory: Effect of Hydrostatic Pressure

Figure 31: Plots of the pressure dependence of the Kondo lattice coherence temperature $T_{coh}$ and superconducting critical temperature $T_c$ from the solution of the mean-field theory for the two-channel Kondo lattice model. The first screening channel corresponds to the fluctuations between $f^1$ and $f^0$ cerium valence states, so that the change in the ionic volume is negative $\delta\Omega_{1ch} = \Omega(f^0) - \Omega(f^1) < 0$. The amplitude $v_1$ becomes non-zero at $T = T_{coh}$ as the resonance $f^1 \approx f^0 + e$ develops. Similarly, the superconductivity is driven by the hybridization of the conduction electrons with the $f$-states in the second channel corresponding to the fluctuations between $f^1$ and doubly occupied singlet $f^2$: $f^1 \approx f^2 + e - 2e$. Since the $f^2$ state has a larger ionic volume $\delta\Omega_{2ch} = \Omega(f^2) - \Omega(f^1) > 0$. Here we define $\delta\Omega_{Ce} = -\delta\Omega_{1ch} = \delta\Omega_{2ch}$. We use the following set of parameters: $\mu = -0.125t$, $D = t$ and $J_1 = 0.5t$. Panel (a): $J_2 = 1.05J_1$. Panel (b): $J_2 = 0.7J_1$. 
6.2. Mean-field theory: Effect of Hydrostatic Pressure

configurations for the resonance in the first channel. Similarly, \( \delta \Omega_{2ch} = \Omega(f^2) - \Omega(f^1) \) is positive and yields the difference in volume between ionic configurations for the resonance in the second channel, Fig. 30. In what follows, we assume that \( \delta \Omega_{2ch} \approx -\delta \Omega_{1ch} = \delta \Omega_{Ce} \). For the free energy we find:

\[
\mathcal{F} = \mathcal{F}_0 + P\Omega_t. \tag{36}
\]

The mean-field equations are obtained by minimizing the free energy \( \mathcal{F} = \mathcal{F}_0 + P\Omega_t \) with respect to \( \lambda \) and \( (v_T)^2 \) \((\Gamma = 1, 2)\). This yields:

\[
\frac{1}{N_s} \sum_{k \pm} \frac{\tanh(\omega_{k \pm}/2T)}{2\omega_{k \pm}} \left( \lambda \pm \frac{\lambda \epsilon_k - \epsilon_k \lambda - v_k^2}{\sqrt{\alpha_k^2 - \gamma_k^2}} \right) = 0,
\]

\[
\frac{1}{N_s} \sum_{k \pm} \phi_{1k}^2 \frac{\tanh(\omega_{k \pm}/2T)}{2\omega_{k \pm}} \left( 2 \pm \frac{(\epsilon_k + \lambda)^2}{\sqrt{\alpha_k^2 - \gamma_k^2}} \right) = \frac{4}{J_1} + 4P\delta \Omega_{1ch},
\]

\[
\frac{1}{N_s} \sum_{k \pm} \phi_{2k}^2 \frac{\tanh(\omega_{k \pm}/2T)}{2\omega_{k \pm}} \left( 2 \pm \frac{(\epsilon_k - \lambda)^2}{\sqrt{\alpha_k^2 - \gamma_k^2}} \right) = \frac{4}{J_2} + 4P\delta \Omega_{2ch}.
\]

In the normal phase either \( v_1 \) or \( v_2 \) is nonzero, corresponding to the development of the Kondo effect in the strongest channel. Here we will consider two cases: the first one corresponds to the choice of \( J_1/J_2 \) such that resonances in both channels develop simultaneously, while in the second case the condensation occurs in the first channel. From the mean-field equations (37) we can already see that the pressure has an opposite effect on the condensation temperatures in two channels: since \( \delta \Omega_{1ch} < 0 \) it means that the effective exchange coupling \( \tilde{J}_1(P) > J_1(P = 0) \), signaling an increase of the Kondo lattice coherence temperature. In contrast, \( \tilde{J}_2(P) < J_2(P = 0) \), implying a decrease in \( T_c \) with pressure. We compute the
corresponding dependences of $T_c$ and $T_{\text{coh}}$ on pressure by solving Eqs. (37) numerically. The results are shown on Fig. 31. We note also that while opposite tendencies in $T_{\text{coh}}$ and $T_c$ in response to pressure appears to be a universal feature for the composite pairing mechanism, the rates with which $T_{\text{coh}}$ and $T_c$ change with pressure are not universal and depend on the microscopic features of the model.

6.3 Summary

We have established that within the mean-field theory approach for the composite pairing scenario, $T_c$ decreases while $T_{\text{coh}}$ increases with increasing $P$. These results are at odds with the experimental data in $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$, which show that both $T_{\text{coh}}$ and $T_c$ initially increase with pressure. By examining $T_c \sim T_{\text{coh}} \exp \left(-1/\nu_F J_2\right)$ we see that one possible way to reconcile the composite pairing theory [67, 92] with the experimental data would be to assume that quantum valence fluctuations may effectively renormalize the spin exchange coupling $J_2$ to compensate for the effect caused by the change in the ionic volume. In this case, only $T_{\text{coh}}(P)$ will have a pronounced pressure dependence and $T_c(P) \sim T_{\text{coh}}(P)$, in agreement with experimental observations. However, a detailed study of this problem clearly goes beyond the scope of this paper and will be addressed elsewhere.
 CHAPTER 7

Effect of pressure on Electronic Transport Properties in a Disordered Kondo Lattice

In this Section, we will formulate a general approach to Kondo alloys diluted with magnetic dopants that will help us to interpret our experimental results. In what follows, we first introduce the model in order to study the effects of pressure in disordered Kondo lattice. Then, we will employ the coherent potential within the mean-field theory for the disordered Kondo lattice to compute the pressure dependence of the Kondo lattice coherence temperature and residual conductivity.

7.1 Model

We consider the following model Hamiltonian, which we write as a sum of three terms

\[ \hat{H} = \hat{H}_0 + \hat{H}_{Kh} + \hat{H}_V. \] (38)

The first term describes the kinetic energy of the conduction and \( f \)-electrons in the unperturbed (i.e. spatially homogeneous) Kondo lattice:

\[ \hat{H}_0 = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} \tilde{\varepsilon}_f \tilde{f}_{k\sigma}^\dagger \tilde{f}_{k\sigma}. \] (39)

---

1This chapter is based on following article:
7.1. Model

where \( \epsilon_k = -(t_c/2)(\cos k_x + \cos k_y) - \mu_c \) is the single particle energy taken relative to the chemical potential \( \mu_c \) (here we will ignore the transport along the \( z \)-axis).

The second term in Eq. (38) accounts for the Kondo holes, i.e., it prohibits the \( f \)-electrons from occupying an impurity site, and it also describes the impurity \( f \)-electrons denoted by \( \hat{p} \):

\[
\hat{H}_{Kh} = \sum_{i \sigma} (1 - \xi_i)(\xi_{\sigma} + \xi_{\bar{\sigma}})\hat{f}_i^{\dagger}\hat{f}_{i\sigma} + \sum_{\sigma} \hat{\epsilon}_f\hat{p}_\sigma\hat{p}_\sigma + \\
\frac{U_f}{2} \sum_{i \sigma} \xi_i\hat{f}_i^{\dagger}\hat{f}_i\hat{f}_{i\sigma}\hat{f}_{i\sigma} + U_p\hat{p}_\sigma\hat{p}_\sigma\hat{p}_\sigma\hat{p}_\sigma,
\]

where summation goes over all lattice cites, and

\[
\xi_i = \begin{cases} 
0, & i = 0 \\
1, & i \neq 0
\end{cases}
\]

with \( i = 0 \) denoting the position of an impurity site. The first term in Eq. (40) accounts for an \( f \)-electron state on an impurity site. Physically, this process cannot happen. Therefore, at the end of the calculation, the energy of the \( f \)-electron on the impurity site will be taken to infinity, \( \xi_{0f} \rightarrow \infty \), to ensure \( \langle \hat{f}_{i=0\sigma}^{\dagger}\hat{f}_{i=0\sigma} \rangle = 0 \).

Lastly, the third term in Eq. (38) accounts for the hybridization between the conduction electrons and both cerium \( f \)-electrons and ytterbium \( f \)-holes:

\[
\hat{H}_V = \sum_{i \sigma} \xi_i \left( V_f\hat{c}_i^{\dagger}\hat{f}_{i\sigma} + h.c. \right) + \sum_{k \sigma} \left( V_p\hat{c}_k^{\dagger}\hat{p}_\sigma + h.c. \right).
\]

Clearly, the theoretical analysis of this model is hindered by the presence of the Hubbard interaction terms with both \( U_f \) and \( U_p \) being the largest energy scales in
7.1. Model

the problem. To make progress, we will adopt the slave-boson mean-field theory (SBMF) approach. Thus, we will set $U_f$ and $U_p$ to infinity:

$$U_f \to \infty, \quad U_p \to \infty.$$  \hspace{1cm} (43)

The double occupancy on the $f$-sites is excluded by introducing the slave-boson projection operators:

$$\hat{f}_{i\sigma} \to \hat{b}_{i\sigma}^\dagger \hat{f}_{i\sigma}, \quad \hat{f}_{i\sigma}^\dagger \to \hat{f}_{i\sigma}^\dagger \hat{b}_{i\sigma},$$

$$\hat{p}_{\sigma} \to \hat{a}_{\sigma}^\dagger \hat{p}_{\sigma}, \quad \hat{p}_{\sigma}^\dagger \to \hat{p}_{\sigma}^\dagger \hat{a}_{\sigma},$$  \hspace{1cm} (44)

supplemented by the following constraint conditions:

$$\sum_{\sigma} \hat{f}_{i\sigma}^\dagger \hat{f}_{i\sigma} + \hat{b}_{i\sigma}^\dagger \hat{b}_{i\sigma} = 1, \quad \sum_{\sigma} \hat{p}_{\sigma}^\dagger \hat{p}_{\sigma} + \hat{a}_{\sigma}^\dagger \hat{a}_{\sigma} = 1.$$  \hspace{1cm} (45)

Thus, the phase space is reduced to the set of either singly occupied states $|b^0 f^1\rangle$ or empty states $|b^1 f^0\rangle$ for the $f$-electrons and, similarly, $|a^0 p^1\rangle$ or $|a^1 p^0\rangle$ for $f$-holes. Clearly, the hybridization part of the Hamiltonian in Eq. (42) always acts only between these two states. Thus, for the kinetic energy terms, we find

$$\hat{f}_{i\sigma}^\dagger \hat{f}_{i\sigma} |b^0 f^1\rangle \to \hat{f}_{i\sigma}^\dagger \hat{b}_{i\sigma}^\dagger \hat{f}_{i\sigma} |b^0 f^1\rangle = \hat{f}_{i\sigma}^\dagger \hat{f}_{i\sigma} |b^0 f^1\rangle.$$  \hspace{1cm} (46)

In the mean-field approximation, the projection (slave-boson) operators are replaced with their expectation values:

$$\hat{b}_{i} \to \langle \hat{b}_{i} \rangle = b, \quad \hat{a} \to \langle \hat{a} \rangle = a.$$  \hspace{1cm} (47)
7.1. Model

The corresponding mean-field Hamiltonian is

\[ \hat{H}_{mf} = \sum_{k\sigma} \epsilon_k \hat{c}_k^{\dagger} \hat{c}_{k\sigma} + \sum_{k\sigma} \xi (1 - \xi)(\epsilon_{0f} - \epsilon_f) \hat{f}_{i\sigma}^{\dagger} \hat{f}_{i\sigma} + \sum_{\sigma} \tilde{\epsilon}_f \hat{p}_{\sigma}^{\dagger} \hat{p}_{\sigma} \]

\[ + \sum_{i\alpha \sigma} \xi_i \left( V_{f} b^* \hat{c}_{i\alpha}^{\dagger} \hat{f}_{i\sigma} + \text{h.c.} \right) + \sum_{k\sigma} \left( V_p a^* \hat{c}_{k\sigma}^{\dagger} \hat{p}_\sigma + \text{h.c.} \right) \]

\[ + \sum_i \xi_i \lambda_b \left( \sum_{\sigma} \hat{f}_{i\sigma}^{\dagger} \hat{f}_{i\sigma} + |b|^2 - 1 \right) + \lambda_a \left( \sum_{\sigma} \hat{p}_{\sigma}^{\dagger} \hat{p}_{\sigma} + |a|^2 - 1 \right). \]

(48)

where \( \lambda_{a,b} \) are Lagrange multipliers, which will be computed self-consistently. Let us introduce the following parameters:

\[ E_f = \lambda_b + \epsilon_f, \quad E_{0f} = \epsilon_{0f} - \epsilon_f, \quad \epsilon_f = \tilde{\epsilon}_f + \lambda_a. \]

(49)

In addition, I introduce \( z = 1 - x \) with \( x \) being the concentration of Yb ions:

\[ z = \frac{1}{N_s} \sum_i \xi_i. \]

(50)

In this expression \( N_s \) is the total number of sites. After re-arranging the terms in Eq. (48) and using Eq. (49) we obtain:

\[ \hat{H}_{mf} = \hat{H}_{mf}^{(b)} + \hat{H}_{mf}^{(a)}, \]

\[ \hat{H}_{mf}^{(b)} = \sum_{k\sigma} \epsilon_k \hat{c}_k^{\dagger} \hat{c}_{k\sigma} + \sum_{k\sigma} E_f \hat{f}_{k\sigma}^{\dagger} \hat{f}_{k\sigma} + E_{0f} \hat{f}_{0\sigma}^{\dagger} \hat{f}_{0\sigma} \]

\[ + \sum_{i\alpha \sigma} \xi_i \left( V_{f} b^* \hat{c}_{i\alpha}^{\dagger} \hat{f}_{i\sigma} + \text{h.c.} \right) + z N_s \lambda_b \left( |b|^2 - 1 \right), \]

(51)

\[ \hat{H}_{mf}^{(a)} = \sum_{\sigma} \tilde{\epsilon}_f \hat{p}_{\sigma}^{\dagger} \hat{p}_{\sigma} + V_p \sum_{k\sigma} \left( a^* \hat{c}_{k\sigma}^{\dagger} \hat{p}_\sigma + a \hat{p}_{\sigma}^{\dagger} \hat{c}_{k\sigma} \right) \]

\[ + \lambda_a \left( |a|^2 - 1 \right). \]
7.2. Coherent Potential Approximation

Because ytterbium ions are in the mixed valence state, the hybridization amplitude $V_p \ll V_f$. Moreover, we assume that the condensation temperature $T_{Yb}$ for the bosons $a$ is significantly smaller than the Ce Kondo lattice coherence temperature $T_{coh}$. This assumption is justified by the similarity in the physical properties of the Yb ion in Yb$_x$Y$_{1-x}$InCu$_4$ and in Ce$_{1-x}$Yb$_x$CoIn$_5$: the ytterbium valence state is close to Yb$^{3+}$ for $x_{nom} \ll 0.1$ and becomes Yb$^{2.5+}$ for $x_{nom} \sim 0.1$. At the same time, in Yb$_x$Y$_{1-x}$InCu$_4$, for small $x$, the single site Kondo temperature is approximately 2 K [108]. Thus, in our choice of the bare model parameters, we must keep in mind that the condensation temperature for the $a$-bosons is lower than the one for the $b$-bosons, $T_{Yb} < T_{coh}$.

7.2 Coherent Potential Approximation

To analyze the transport properties of the disordered Kondo lattice, we employ the coherent potential approximation (CPA)[109, 110, 111, 112, 107]. The idea of the CPA is to introduce an effective medium potential, which allows for an equivalent description of the disordered system. In particular, the effective potential is considered to be purely dynamical. This approximation is valid when the scattering events on different impurity sites are independent. To formulate the CPA, we introduce the Lagrangian for the disordered Kondo lattice (which is
7.2. Coherent Potential Approximation

related to \( \hat{H}^{(b)}_{mf} \): 

\[
\mathcal{L} = \sum_{k\sigma} \left[ \hat{c}^\dagger_{k\sigma} (\partial_\tau + \epsilon_k) \hat{c}_{k\sigma} + \hat{f}^\dagger_{k\sigma} (\partial_\tau + E_f) \hat{f}_{k\sigma} \right] \\
+ \sum_\sigma \hat{f}^\dagger_{0\sigma} (\partial_\tau + E_f) \hat{f}_{0\sigma} + z N_s \lambda_b (|b|^2 - 1) + \sum_{i\sigma} \xi_i \left( V_f b^* \hat{c}^\dagger_{i\sigma} \hat{f}_{i\sigma} + b \hat{f}^\dagger_{i\sigma} \hat{c}_{i\sigma} \right),
\]

(52)

where, for brevity, we omit the dependence of the fermionic fields on Matsubara time \( \tau \). Note that we have not included the terms that involve \( p \)-fermions. The reason is that the \( p \)-fermions can be formally integrated out, which will lead to the appearance of the self-energy correction \( \Sigma_a(\tau - \tau') \) in the first term of Eq. (52). However, to keep our expressions compact, we will include this term later when we analyze the transport properties. Within the frame of the CPA, we introduce an effective medium Lagrangian for the disordered Kondo lattice system as follows:

\[
\mathcal{L}_{eff} = \beta \int_0^\beta d\tau' \sum_{k\sigma} \hat{\psi}^\dagger_{k\sigma}(\tau) \begin{bmatrix} 
\delta(\tau - \tau') (\partial_\tau + \epsilon_k) + S_{cc}(\tau - \tau', z) & S_{cf}(\tau - \tau', z) \\
S_{fc}(\tau - \tau', z) & \delta(\tau - \tau') (\partial_\tau + E_f) + S_{ff}(\tau - \tau', z) 
\end{bmatrix} \hat{\psi}_{k\sigma}(\tau') \\
+ z N_s \lambda_b (|b|^2 - 1),
\]

(53)

where \( \beta = 1/k_B T \), we introduced the two-component spinor \( \hat{\psi}^\dagger_{k\sigma} = (\hat{c}^\dagger_{k\sigma}, \hat{f}^\dagger_{k\sigma}) \) for brevity, and \( S_{ab}(\tau, z) \) are the components of the coherent potential that we
7.3. Slave Boson Mean-Field Theory for Disordered Kondo Lattice under Hydrostatic Pressure

will have to determine self-consistently. The self-consistency condition for the components of \( S_{ab}(\tau, z) \) is obtained by requiring that the corresponding correlation functions for the effective Lagrangian, Eq. (53), are equal to the disorder-averaged correlators for the disordered Kondo lattice, Eq. (52)[109]. In the “Kondo hole” limit \((E_{0f} \rightarrow \infty)\), it follows:

\[
\hat{S}(i\omega_n, z) = \begin{pmatrix} 0 & bV_f \\ b^*V_f & S_{ff}(i\omega_n, z) \end{pmatrix},
\]

where \(i\omega_n = \pi T(2n + 1)\) is a fermionic Matsubara frequency and

\[
S_{ff}(\omega, x)F_{ff}(\omega) = z - 1,
\]

\[
F_{ff}(\omega)
= \sum_k \frac{\omega - \epsilon_k}{(\omega - \epsilon_k)(\omega - E_f - S_{ff}(\omega, z)) - V_f^2|b|^2}.
\]

These equations allow us to compute the remaining component of the coherent potential (54). \(S_{ff}(i\omega, z)\) is a function of parameters \(E_f\) and \(b\), which will have to be computed self-consistently by minimizing the free energy.

7.3 Slave Boson Mean-Field Theory for Disordered Kondo Lattice under Hydrostatic Pressure

In order to study the effects of pressure in a disordered Kondo lattice, we need to express the change in the total volume of the system with the corresponding changes in the valence states of Ce and Yb ions. For the Ce ions, the change in the \(f\)-shell occupation is positive due to its electronic nature, so that
Figure 32: Pressure $P$ dependence of the slave-boson amplitude and coherence temperature $T_{coh}$ (inset) for various concentrations $z$ of the impurity $f$-sites. The dependence of the coherence temperature $T_{coh}$ on pressure for $z = 0.93$ is shown.
7.3. Slave Boson Mean-Field Theory for Disordered Kondo Lattice under Hydrostatic Pressure

the resonance scattering involves a zero-energy boson, with amplitude \( b \), and an electron: \( f^{n+1}(j, m) = f^n(j, m) + e^- \). In contrast, for the Yb ions, the resonance scattering involves a zero energy boson, with amplitude \( a \), and a hole: \( f^{n-1}(j, m) = f^n(j, m) + e^+ \). Thus, for the total volume of the system within the slave-boson mean-field theory, we write:[107]

\[
\Omega_t = (1 - z)[\Omega_{0Yb} + (1 - a^2)\delta\Omega_{Yb}] \\
+ z[\Omega_{0Ce} + (1 - b^2)\delta\Omega_{Ce}],
\]

(56)

where \( \Omega_{0Yb, Ce} \) are the cell volumes for the singlet (non-magnetic) states on Yb \( f^{14} \) and Ce \( f^0 \) ions, correspondingly. Moreover, \( \delta\Omega_{Yb, Ce} \) account for the difference in cell volumes between two \( f \)-ion configurations. Note that \( \delta\Omega_{Yb} < 0 \) while \( \delta\Omega_{Ce} > 0 \).

To obtain the self-consistency equations for the slave-boson amplitude \( b \) and constraint variable \( \lambda_b \), we define the grand canonical enthalpy for an alloy under pressure \( P \):

\[
K = -k_B T \log Z_{eff}, \\
Z_{eff} = \text{Tr} \left\{ e^{-\frac{\beta}{\hbar} \int_0^\infty L_{eff}(\tau) - P\Omega_t} \right\}.
\]

(57)

Minimizing the enthalpy with respect to \( b \) and \( \lambda_b \), we obtain:

\[
z \left( b^2 - 1 \right) + 2T \sum_{\omega_n} F_{ff}(i\omega_n) = 0, \\
z b(\lambda_b - P\delta\Omega_{Ce}) + 2V fT \sum_{\omega_n} F_{fc}(i\omega_n) = 0.
\]

(58)
7.3. Slave Boson Mean-Field Theory for Disordered Kondo Lattice under Hydrostatic Pressure

where $i\omega_n = i\pi T(2n + 1)$ are Matsubara frequencies and

$$F_{fc}(\omega) = bV_f$$

$$\times \sum_k \frac{1}{(\omega - \epsilon_k)(z - E_f - S_{ff}(\omega, z)) - V_f^2 |b|^2}.$$

In addition, the third equation is the conservation of the total number of particles $N_{tot} = n_c + z n_f$, with

$$n_c = T \sum_{\omega_n} \sum_k e^{i\omega_n t +} G_{cc}(k, i\omega_n),$$

$$G_{cc}(k, \omega) = \frac{\omega - E_f - S_{ff}(\omega, z)}{(\omega - \epsilon_k)(\omega - E_f - S_{ff}(\omega, z)) - V_f^2 |b|^2 - \frac{V^2 a^2}{\omega - \epsilon_f}},$$

which allows us to determine the renormalized position of the chemical potential $\mu_c$. We note that equations that determine the value of $a$ and $\lambda_a$ can be obtained in the same manner as the ones above.

As a result, we find that the slave-boson amplitude $b$ grows linearly with pressure,[107] $b \propto P \delta \Omega_t$, see Fig 32. Also, our analysis of the mean-field equations (58) in the limit $b \to 0$ shows that the Kondo lattice coherence temperature $T_{coh}$ also grows with pressure almost linearly (Fig. 32):

$$T_{coh} \simeq E_f(T_{coh}) \propto P \delta \Omega_t,$$

which is in agreement with our experimental observations [see Fig. Fig1(b)]. In addition, as expected, we find that (i) both slave-boson amplitude and coherence temperature decrease as the concentration of ytterbium atoms increases, and (ii)
the presence of the ytterbium $f$-electrons leads to a small reduction in the value of $b(P)$ relative to the case when $a = 0$.

### 7.4 Transport Properties

In this subsection we discuss the pressure dependence of the residual resistivity of the disordered Kondo lattice described by the Hamiltonian (48). We compute conductivity using the following expression: [113]

$$
\sigma_{\alpha\beta}(i\omega) = \frac{1}{\Omega} \{ \Pi_{\alpha\beta}(i\Omega) - \Pi_{\alpha\beta}(0) \},
$$

(62)

where $\alpha, \beta = x, y$, $s_\alpha = \sin k_\alpha$, $v_F$ is a Fermi velocity of the heavy-quasiparticles, and

$$
\Pi_{\alpha\beta}(i\Omega) = e^2 v_F^2 T \sum_{i\omega_n} \nabla \times \sum_\mathbf{k} s_\alpha G_{\alpha\alpha}(\mathbf{k}, i\omega_n + i\Omega) s_\beta G_{\beta\beta}(\mathbf{k}, i\omega_n).
$$

(63)

To obtain the dependence of conductivity on the real frequency, we will perform the analytic continuation from $\Omega_n = \frac{2\pi k_B T n}{\Omega_n} > 0$ to real frequencies $i\Omega_n \rightarrow \omega$.

The residual resistivity can be computed from $\rho_0 = \sigma^{-1}(\omega \rightarrow 0)$. We present our results on Fig. 33. In agreement with our experimental results, we find that the residual resistivity decreases with pressure. At ambient pressure, the residual resistivity grows linearly with ytterbium concentration, which is again expected given our CPA approximation.

The temperature dependence of resistivity can also be obtained from Eq. (62). Naturally, we find a ‘square-T’ dependence: $\rho(P, T; z) = \rho_0(P, z) + A_{FL}(P, z) T^2$. 

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Figure 33: (Color online) Pressure $P$ dependence of the residual resistivity $\rho_0$ for various alloy concentrations $z$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure33}
\caption{(Color online) Pressure $P$ dependence of the residual resistivity $\rho_0$ for various alloy concentrations $z$.}
\end{figure}
7.5. Summary

Because $A_{FL}(P, z)$ decreases with pressure, as does the coefficient in front of the linear-in-$T$ term, we conclude that the inelastic scattering of heavy-quasiparticles determines the value of $A(P, z)$.

7.5 Summary

Our theoretical analysis of the disordered Kondo lattice model with “magnetic” disorder ions shows that despite the presence of “magnetic” impurities rather than “Kondo holes”, the coherence temperature grows and residual resistivity decreases with pressure as expected for “electron-like” Kondo ions [107]. The growth of the coherence temperature leads to the corresponding growth of the superconducting critical temperature, indicating that superconductivity originates predominantly from the “heavy” Fermi surface.
CHAPTER 8

Summary and Outlook

The motivation behind this dissertation work was to probe the nature of superconducting pairing and to understand the origin of many unconventional properties in Ce$_{1-x}$Yb$_x$CoIn$_5$ family of heavy fermion compounds. The parent material CeCoIn$_5$, of this family, has superconducting transition temperature $T_c = 2.3$ K while the other end member YbCoIn$_5$ is a non magnetic metal. Ytterbium is a rare earth substituent on Ce site but shows many unconventional properties in comparison to any other rare earth substitution.

Ytterbium substitution on Ce site is unique in the sense that Yb appears in a mixed valence state, while any other rare earths are either in the magnetic or non magnetic valence state. Yb is known to exhibit an average valence of +2.3 for doping level $x > 0.20$. For doping levels $0 < x \leq 0.20$, the average Yb valence changes rapidly and approaches a value of +3 with decreasing doping. Among the previously reported unconventional properties Ce$_{1-x}$Yb$_x$CoIn$_5$ system demonstrated a very robust superconducting transition and Kondo coherence as a function of disorder. Additionally, the system exhibited a strange non fermi liquid resistivity throughout the whole doping range.
To address the unconventional behavior observed with Yb substitution, we relied on our electronic resistivity and magnetoresistance measurements as described in Chapter 3. We developed a method based on the magnetoresistance analysis to extract the location of field induced quantum critical point in Ce\(_{1-x}\)Yb\(_x\)CoIn\(_5\) system. Using this method we demonstrated that the QCP is suppressed rapidly on doping with Yb and reaches a value close to 0 T for doping level \(x = 0.20\). At the same time the coherence temperature \(T_{coh}\) and the superconducting transition temperature \(T_c\) are very robust and survive for very high doping levels of Yb.

Based on these observations we were able to discuss that the phenomenon of coherence and superconducting pairing have the same origin and it appears to be different from often proposed spin fluctuation mediated pairing.

In addition, the analysis of resistivity data suggests the presence of two distinct non Fermi liquid contributions to scattering. From our analysis we could explain a linear-in-\(T\) contribution to be coming from the presence of quantum critical fluctuations. This contribution is suppressed with doping and becomes negligible for \(x = 0.20\), the doping level where the QCP is suppressed almost to zero field. On the other hand an additional \(\sqrt{T}\) contribution is also seen which is absent in the parent compound CeCoIn\(_5\) and grows with Yb doping. The relative weight of this contribution reaches a maximum value for \(x = 0.20\) (where the linear-in-\(T\) contribution is minimum) and thereafter stays constant with Yb doping. We attributed this contribution to resistivity to be coming from the scattering of the
quasiparticles from the Yb $f$-electrons.

One other important finding from our analysis was the nature of the QCP scenario. Nature of QCP in heavy fermion materials are being discussed either as a Spin Density Wave (SDW) scenario or a Kondo breakdown scenario [114]. With our magnetoresistance analysis, we were able to extract the Lande’s $g$-factor for electrons above and below the field induced QCP for different doping levels ($x \leq 0.20$) in Ce$_{1-x}$Yb$_x$CoIn$_5$ system. Based on a sharp change in $g$-value across the QCP, we discuss that the nature of the QCP in this material is “Kondo Breakdown” type.

The next important goal for us was to understand the nature of unusually robust Kondo coherent scattering in Ce$_{1-x}$Yb$_x$CoIn$_5$ system even when the Ce-lattice is severely diluted with Yb. Again, using our transport measurements we identified two distinct regimes of coherent scattering; one attributed to the Ce local moments and the other to the Yb $f$-electrons in the intermediate valence state.

For doping levels $x \leq 0.70$, the system is found to be in the Ce local moment regime with predominantly coherent scattering of quasiparticles for low dilutions ($x \leq 0.20$), and predominantly incoherent quasiparticle scattering for $0.40 \leq x \leq 0.70$. Interestingly, signatures of presence of some coherent contribution to scattering in this regime for $0.40 \leq x \leq 0.70$ crystals were observed
in our resistivity data while the magnetoresistance data showed no sign of coherent scattering. This contrasting behavior was resolved by our scaling analysis of magnetoresistance data for the intermediate doping range. We demonstrated that the single impurity Kondo energy scale of this system in the intermediate doping range is modified by the presence of robust coherent scattering. As a result, the dilution of the Ce lattice by Yb in the Ce local moment regime transforms the system from Kondo lattice to Kondo single impurity type, with a higher Kondo temperature $T_K = 14$ K. It is important to note that this robustness of coherence for small Yb concentrations could be a result of proposed Yb impurity correlations [32].

For higher Yb doping $x > 0.70$ start showing the reappearance of prominent coherent scattering contribution by means of a positive contribution to magnetoresistance data. We attribute this new coherence to be developed by participation of Yb $f$-electrons in hybridizing with the conduction electrons. For large Yb concentrations this hybridization becomes significant and results in the coherence effects.

Based on our analysis we conclude that since superconducting transition temperature decreases linearly throughout the whole Yb doping range, superconductivity has purely local origin associated with Cerium. On the other hand coherence effects are decoupled from superconductivity and can be caused by hybridization of conduction electrons with either the Ce local moments or Yb $f$-electrons.
Clearly at higher Yb concentrations, interesting changes in the physics of the system are observed as Yb f-electrons start hybridizing with the conduction electrons. In view of the recent theoretical proposals of a Lifshitz transition of Fermi surface at certain higher Yb doping, we extended our detailed transport study to the higher Yb doping levels. Our findings (reported in Chapter 5) in $x = 0.75$ crystals suggest a low temperature crossover from non Fermi liquid resistivity to a Fermi liquid resistivity. This crossover together with the unconventional temperature dependence of magnetoresistance peak in $x = 0.75$ crystal is suggestive of re-appearance of quantum critical point at higher Yb doping. Using our analysis of transport data we identified a zero field quantum critical point for $x = 0.75$ Yb doping. Although the origin of this quantum criticality is not yet clear to us Yb valence fluctuations or quadrupolar ordering could be the possible mechanism for this high doping QCP. We propose a detailed heat capacity or thermal conductivity measurements to get more details about the nature of this quantum critical point.

As discussed in above paragraphs, the experimental evidence suggest that the spin fluctuations mediated pairing does not seem to be the valid scenario in Ce$_{1-x}$R$_x$CoIn$_5$ system. It has been suggested that the screening of the local moments in a lattice takes place via the exchange of spin with the metallic environment in two distinct symmetry channel. In such a case the moments become
overscreened, forming a condensate of composite pairs. Thus within the framework of composite pairing scenario, both the local moments and the conduction electron pairs are involved in formation of the superconducting condensate. To test the validity of the composite pairing mechanism of superconductivity, we performed mean field theoretical calculations to look for the effect of pressure on transport properties in Ce$_{1-x}$Yb$_x$CoIn$_5$ system. The findings from the theory suggest that within the composite pairing scenario, $T_c$ should decrease while $T_{coh}$ should increase as a function of pressure. Experimental findings, on the other hand show that for small pressure both of these temperatures increase. To reconcile the disagreement, we propose that the quantum valence fluctuations could effectively change the spin exchange coupling to compensate for the change in ionic volume due to the pressure.

Lastly we presented the results of the mean field theoretical calculations focused on effect of pressure on Kondo coherence and residual resistivity in a disordered Kondo lattice. The results suggest that for the system with magnetic impurities, $T_{coh}$ increases with pressure while the residual resistivity decreases. The findings from the experiments [95] are in excellent agreement with the results from this theory and provide strong evidence that both the superconductivity and the antiferromagnetic fluctuations in Ce$_{1-x}$Yb$_x$CoIn$_5$ originate from the “heavy” Fermi surface in this material. This result is significant in terms of suggesting the nature of the Fermi surface which is involved in SC pairing. Till date there are
differing opinions about the nature of Fermi surface responsible for SC in CeCoIn$_5$ and our findings from pressure dependent transport measurements suggest that SC primarily develops at large Fermi surface.

**Note:** A recent, in-depth analysis of Ce$_{1-x}$Yb$_x$CoIn$_5$ crystals reveals that the actual concentration of Yb which goes into the grown crystal differs from the nominal concentration. The relationship between the nominal and actual concentrations obtained in this study are summarized in table in Appendix.A. However, it is worth mentioning that this difference in the nominal and actual doping levels does not alter the physics of this system reported in this dissertation or any other publications related to this material. The effect basically shifts the doping dependent phase diagram to lower $x$-values. For the purpose of present dissertation, only the nominal doping levels are used to avoid confusion.
APPENDIX A

Actual Doping Levels

<table>
<thead>
<tr>
<th>$x_{nominal}$</th>
<th>$x_{actual}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>0.20</td>
<td>0.07</td>
</tr>
<tr>
<td>0.40</td>
<td>0.16</td>
</tr>
<tr>
<td>0.50</td>
<td>0.23</td>
</tr>
<tr>
<td>0.65</td>
<td>0.38</td>
</tr>
<tr>
<td>0.70</td>
<td>0.46</td>
</tr>
<tr>
<td>0.75</td>
<td>0.54</td>
</tr>
<tr>
<td>0.775</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 4: Conversion between nominal and actual Yb concentrations
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