Corneliu Florin Miclea

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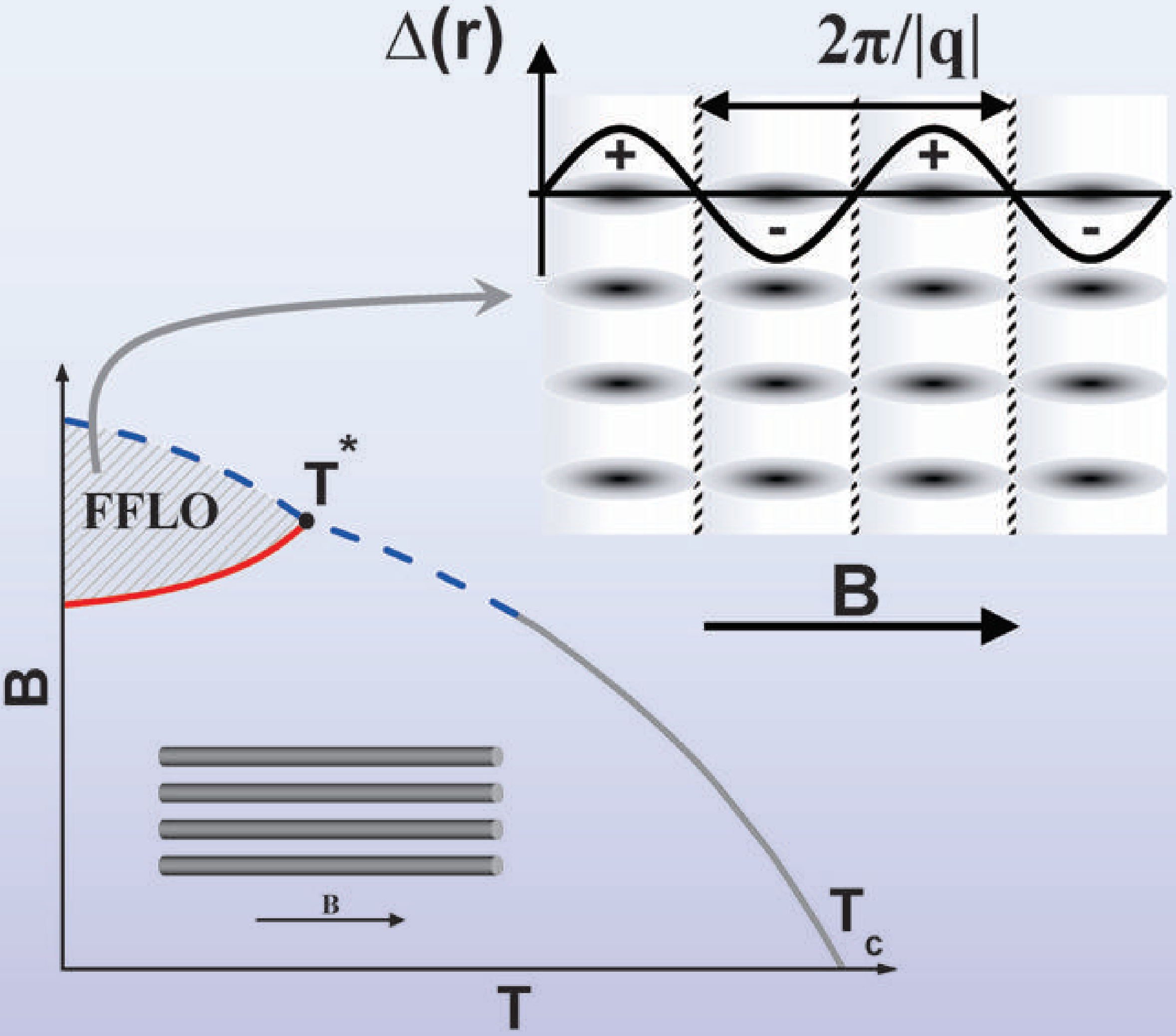

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Investigation of superconducting order parameters in heavy-fermion and low-dimensional metallic systems under pressure

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Corneliu Florin Miclea

geboren am 04. April 1974 in Petrosani, Rumänien

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Contents

Introduction

The understanding of new emerging unconventional ground states is a great challenge for experimental and theoretical solid-state physicists. New ground states are developing, where different energy scales compete, leading to a high sensitivity of the system to external tuning parameters like doping, pressure or magnetic field.

The exploration of superconductivity proved to be a fascinating and challenging scientific undertaking. Discovered by H. Kammerlingh Onnes in 1911, prior to the development of the quantum theory of matter, superconductivity was defying a microscopic theory for more than four decades until the BCS theory was formulated in 1957 by J. Bardeen, L. N. Cooper and J. R. Schrieffer. Superconductivity of most of the simple metals or metallic alloys is well described within the frame of the BCS scenario, however, in the last thirty years numerous new superconducting materials were found to exhibit exotic properties not accounted for by the BCS theory. Among them are included the high-T_c compounds, the heavy-fermion superconductors and as well the organic superconductors. It was the purpose of this work to probe different facets of superconductivity in heavy-fermion and in low-dimensional metallic compounds.

In the class of the heavy-fermion systems the Kondo-effect, leading to a non-magnetic ground state, competes with the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions which favors magnetic order. It is this competition which leads to unusual physical properties in proximity to a quantum critical point, where the magnetic ordering temperature is suppressed to zero. The heavy-fermion compound $CeCoIn_5$ is superconducting at atmospheric pressure having the highest superconducting transition temperature, among all Ce-based heavy-fermion systems [1]. $CeCoIn_5$ is assumed to be situated close to an antiferromagnetic quantum critical point giving rise to non-Fermi liquid behavior in the normal state [2]. Recently, the possible appearance of an inhomogeneous superconducting state in $CeCoIn_5$, called Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state, attracted much attention not only among solid state physicists [3, 4]. The FFLO state, predicted independently by Fulde and Ferrell [5] and by Larkin and Ovchinnikov [6] 40 years ago, is a spatially inhomogeneous superconducting phase, where the order parameter is periodically modulated in real space. It is predicted to appear in type-II superconductors close to the upper critical field if the orbital pair-breaking is negligible relative to the Pauli-limiting effect, in sufficiently clean systems. The theoretical concept of the FFLO state is not only of importance in solid state physics, but also in elementary-particle physics [7]. The FFLO state eluded the experimental confirmation until very recently. $CeCoIn_5$ is the first material where different physical experiments show strong evidence pointing to the realization of the FFLO state at low temperatures close to the upper critical field for superconductivity. However, the presence of strong antiferromagnetic fluctuations in this compound might be responsible for the anomaly taken as signature of the FFLO state.

The central part of the present work is the exploration of the nature of this low temperature phase observed inside the superconducting state in $CeCoIn_5$ at high magnetic fields. Using external pressure to suppress the magnetic fluctuations we were able for the first time to provide evidence that the FFLO state in $CeCoIn_5$ exists away from the influence of the strong magnetic fluctuations present at atmospheric pressure. For this purpose we developed a new type of miniature pressure cell allowing us to conduct heat capacity studies under quasi-hydrostatic pressure conditions at high magnetic fields up to $B = 14$ T and at low temperatures down to $T = 100$ mK, on precisely oriented $CeCoIn_5$ single crystals. We studied the evolution of the magnetic field – temperature phase diagram with pressure. Not only the first-order character of the transition from the normal to the superconducting state at high magnetic fields persists with increasing pressure, but we could also follow the transition from the vortex to the FFLO state for all pressures. Moreover, the FFLO region in the phase diagram is extended at high pressures. This strongly supports the genuine FFLO origin of the anomaly in the superconducting state and makes a magnetic origin very unlikely.

Despite of more than two decades of intensive experimental studies to characterize the heavy-fermion superconductor UBe_{13}, many details behind its physical properties remain undisclosed. Several experiments probing the superconducting state of this material, revealed anomalous features which are regarded as evidence for unconventional superconductivity. The most compelling evidence obtained so far for unconventional superconductivity regards the giant ultrasonic absorption anomaly observed directly below T_c [8, 9] which was ascribed to collective modes or domain-wall damping due to a multi-component order parameter [10]. Theoretical calculations by Sigrist *et al.* [11, 12] predict the behavior of a multi-component order parameter for an anisotropic superconductor under uniaxial stress. Uniaxial stress is lowering the crystal symmetry and the degeneracy in the order parameter representation might be lifted leading to a split of the superconducting transition. We performed high resolution AC specific heat experiments under uniaxial pressure up to $p = 0.55$ GPa. A small feature resembling a superconducting temperature splitting is induced by pressure. However, this feature has to be regarded carefully as, though improbable, pressure anisotropy cannot be completely ruled out as origin.

The interplay between superconductivity and a charge-density wave (CDW) instability remains an interesting experimental and theoretical challenge. The opening of a dielectric gap in the electronic spectrum due to electron-hole pairing, reduces the density of states at the Fermi-level. However, not uncommon are the examples of compounds displaying a CDW instability which at lower temperatures enter a superconducting ground state. In such cases the superconductivity sets in from a normal but gapped state. We thoroughly investigated the quasi-one-dimensional, metallic compound $Tl_xV_6S_8$ employing resistivity, specific heat and susceptibility measurements at ambient pressure for different Tl fillings. Moreover, in resistivity studies, we followed the evolution with pressure of both superconducting and CDW phases in the above mentioned compounds.

This dissertation is divided into six chapters. After this introduction, in Chapter 1 we will outline the basic theoretical concepts later needed for the analysis of the experimental results. In Chapter 2 we briefly introduce the experimental techniques with a special focus on the new pressure cells developed during this thesis and used for the measurements presented in Chapters 3 to 5. In Chapter 3 the possible realization of the inhomogeneous superconducting FFLO state in $CeCoIn_5$ is studied by specific heat measurements under hydrostatic pressure, while in Chapter 4 the results of AC specific heat experiments on UBe_{13} under uniaxial pressure are presented. The ambient pressure properties as well as results obtained by resistivity measurements under hydrostatic pressure on the one-dimensional metallic compounds $Tl_xV_6S_8$ are discussed in Chapter 5. At the end, Chapter 6 summarizes and concludes this thesis.

Chapter 1

Theoretical concepts

This chapter serves to outline some of the basic theoretical concepts which are related to the experimental results to be presented in the following chapters.

1.1 Fulde-Ferrell-Larkin-Ovchinnikov state

1.1.1 Introduction

For a type-II singlet superconductor (SC), in the clean-limit and for which the main pair-breaking mechanism is due to the spin susceptibility (Pauli paramagnetism), an inhomogeneous superconducting phase is predicted to appear at low temperatures and close to the upper critical field (B_{c2}), between the normal and the vortex state [5, 6]. At the core of this phase, called Fulde-Ferrell-Larkin-Ovchinnikov (FFLO), lie competing interactions of basic nature. One is the energy necessary to bind the electrons into Cooper pairs (the condensation energy) and the other is the interaction between the spin of the electrons and the magnetic field. In the normal state, the electrons are free to lower their total energy by preferentially aligning their spins along to the external magnetic field, leading to a temperature-independent Pauli susceptibility. On the other hand, in the superconducting state, the numbers of spin-down and spin-up electrons are equal and since they cannot all be aligned along the magnetic field, the ground state energy is higher than in normal state. In this way, Pauli paramagnetism will always favor the normal state against the spin-singlet superconducting phase. This effect, called Pauli-limiting, is reducing the upper critical field B_{c2} to the characteristic Pauli field B_P, defined in the absence of all other pair-breaking mechanisms. The magnetic field can also suppress superconductivity when the kinetic energy of the supercurrent around the superconducting vortices becomes greater than the superconducting condensation energy; this is the orbital limiting effect and reduces the B_{c2} to the orbital-limiting field B_{c2}^{orb} defined in the absence of Pauli-limiting.

1.1.2 Pauli paramagnetism and superconductivity

The Pauli field for a classical BCS-superconductor was determined by A. M. Clogston [13] and B. S. Chandrasekhar [14]. The stability of the superconducting state compared to the normal state is given by the free-energy balance

$$F_s - F_n = -\frac{B_c^2}{8\pi}, \tag{1.1}$$

where F_n and F_s are the free energies per volume unit in the normal and superconducting state, respectively, and B_c is the thermodynamic critical field. A metal, in the normal state, has a finite paramagnetic susceptibility χ_n caused by the electronic density of states at the Fermi-level. Upon applying magnetic field B the free energy will be lowered, due to the spin polarization, by an amount of $\frac{1}{2}\chi_n B^2$. The same metal, in the superconducting state, will have a susceptibility χ_s which is smaller than in the normal state due to the formation of Cooper pairs. According to the BCS theory, χ_s vanishes as the temperature is lowered to $T = 0$ K. Therefore, the free energy balance between the normal and the superconducting state, at absolute zero temperature, can be written as:

$$F_n - \frac{1}{2}\chi_n B_c^2 = F_s. \tag{1.2}$$

Considering the electronic gyromagnetic factor g and the electronic density of states at $T = 0$ K, $N(0)$, the spin susceptibility becomes:

$$\chi_n = \frac{1}{2}(g\mu_B)^2 N(0), \tag{1.3}$$

where μ_B is the Bohr-Procopiu magneton. The jump in the free energy at the superconducting phase transition can be related to the superconducting energy gap at

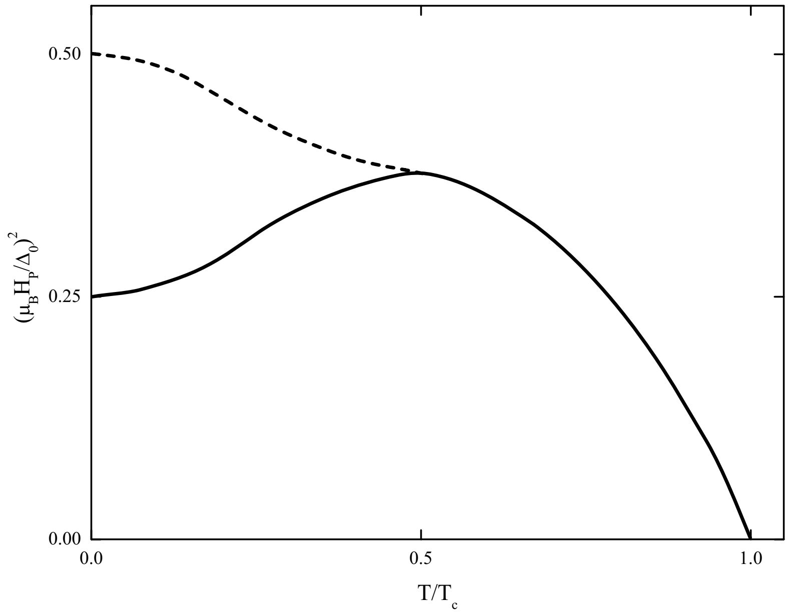

Figure 1.1: Above the critical point $t_0 = T_0/T_c = 0.556$ the solid line is the critical field for the second-order phase transition. Below t_0 the dotted line corresponds to the first-order phase transition and the solid line to the supercooling critical field.

$T = 0$ K, $\Delta(0)$ by:

$$F_n - F_s = \frac{1}{2}N(0)\Delta(0)^2. \tag{1.4}$$

Therefore, the upper limit for the critical field in the absence of any orbital effect (i.e., the Pauli field B_P), for a BCS superconductor, can be written as [13]:

$$B_P = B_{c2}(0) = \frac{\sqrt{2}\Delta(0)}{g\mu_B}. \tag{1.5}$$

The effect of Pauli paramagnetism on the order of the superconducting phase transition was discussed by G. Sarma [15] and K. Maki and T. Tsuneto [16]. They found that for a clean superconductor in which the Pauli paramagnetism is the dominant limiting factor for the upper critical field, the phase transition changes from second- to first-order as the temperature is lowered (Fig. 1.1). Below the critical point $t_0 = T_0/T_c = 0.556$ the phase transition between the normal and the superconducting phase, changes from second- to first-order; in this region, the gap equation has two solutions, one corresponding to the actual gap (dotted line) and the other corresponding to a supercooling critical field. It is important to remark that the lower line, below t_0 is not associated with a phase transition between a classical BCS phase and an inhomogeneous superconducting state.

In the dirty-limit (one would intuitively expect a short mean-free path for superconductors for which the orbital effect can be neglected) the phase transition should remain second-order for the whole temperature range [16].

1.1.3 FFLO state

Fulde and Ferrell [5] and at the same time Larkin and Ovchinnikov [6] have studied the effect of a large exchange field B acting only on the electronic spins, assuming that some of the Cooper pairs are broken in certain regions around the Fermi-surface. Those regions of unpaired electrons are stabilized by field and the corresponding opposite areas of the Fermi-surface are completely depleted of electrons with opposite spin orientation (Fig. 1.2). These regions are blocked for the pair formation process

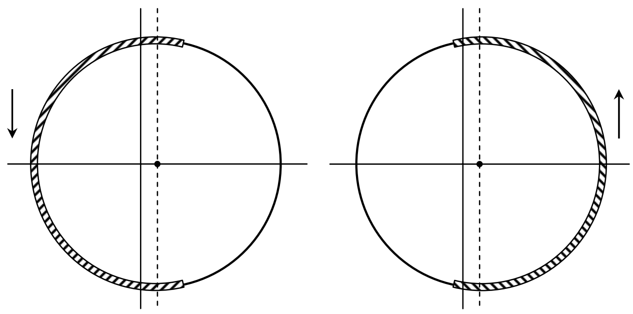

Figure 1.2: Depairing in momentum space produced by field. The Fermi-surface is shifted to the right. The left hashed area is fully occupied by down spin electrons polarized along the field. The right hatched area is completely depleted of spin-up electrons

since the BCS-theory requires that the states with opposite momenta are either both occupied or both empty.

If the BCS energy gap in the absence of any magnetic field is Δ_0 and $2H\Delta_0$ is the splitting of the electron energy due to the exchange field, the Hamiltonian of the system can be written as:

$$\mathcal{H} = \mathcal{H}_0 + H\Delta_0 \sum_i \sigma_i \ , \tag{1.6}$$

where $\mathcal{H}_0$ is the usual BCS Hamiltonian for a superconductor in the absence of an exchange field and σ_i is the operator ± 1 reflecting the spin alignment ("up" or "down") of the i-th electron with respect to the magnetic field. The second term of the Hamiltonian is proportional to the total electronic spin component parallel to the field, which operator commutes with $\mathcal{H}_0$ and therefore has the same set of eigenfunctions and associated eigenvalues with $\mathcal{H}_0$. Thus an approximate eigenfunction of $\mathcal{H}$ is the BCS ground state wave function.

For a field which produces a split of the conduction electrons energy of $\sqrt{2}\Delta_0$, the normal state undergoes already enough spin orientation to acquire a lower free energy than the BCS ground state [17]. Electronic configurations which lower further the energy of the system have even lower symmetry than in Fig 1.2 [5]. Therefore, the unpaired electrons are distributed asymmetrically around the Fermi-surface and this leads to a net current flow. But in the absence of magnetic field acting on the electron orbits, the ground state should not carry any current (Bloch's theorem).

Consequently, it is necessary for the remaining paired electrons to establish a counterflow current exactly canceling out that of the unpaired electrons. This leads to a remarkable result: the Cooper pairs are formed from states $(\mathbf{k}, -\sigma)$ and $(\mathbf{k}' = -\mathbf{k} + \mathbf{q}, \sigma)$ and have a finite momentum $\mathbf{q}$, where $\mathbf{k}$ and σ are the momentum and the spin of the one electron wave function (Fig. 1.3). The choice of $\mathbf{q}$ determines the size of regions with unpaired electrons and the value of the superconducting gap. The pairing wave vector $\mathbf{q}$ is determined as a function of the magnetic field imposing that the depaired current and the supercurrent (which both depend on $\mathbf{q}$) sum up to zero.

This new inhomogeneous superconducting phase yields a highly degenerate ground state characterized by the direction of the pairing momentum. For this phase to qualify as a ground state, the single-particle excitations must all have positive energies. Goldstone's theorem [18, 19], implies that there must exist low-lying collective modes. The mixed state was found to be stable over a finite range of the magnetic field. This range, for weakly coupled electrons is:

$$0.71\,\frac{\Delta_0}{\mu_B} < B < 0.76\,\frac{\Delta_0}{\mu_B} \;\; [5]. \tag{1.7}$$

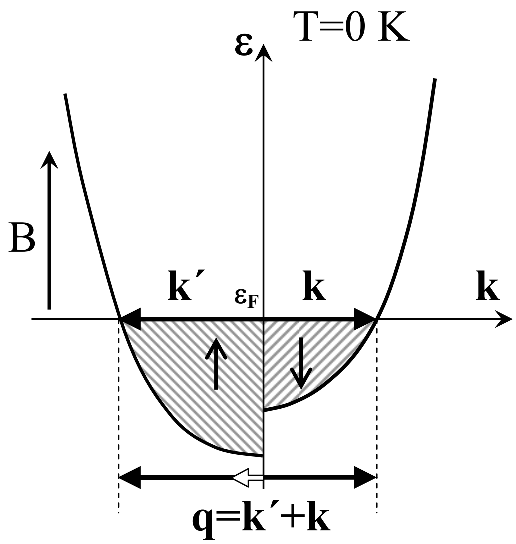

Figure 1.3: The Cooper pairs are formed from $(\mathbf{k}, -\sigma)$ and $(\mathbf{k}', \sigma)$ states, with a finite momentum $\mathbf{q}$. The energy is lowered for the electrons with the spins parallel to the magnetic field B.

An increased coupling strength will decrease the stability of the depaired phase relative to the BCS state, but will decrease the energy of the normal state even more, due to enhanced magnetization. Therefore, the stability range for the strong coupling case is significantly extended to:

$$0.83\,\frac{\Delta_0}{\mu_B} < B < 1.13\,\frac{\Delta_0}{\mu_B}\ \ [5]. \tag{1.8}$$

The BCS superconducting gap has to be integrated taking into account the regions of the Fermi-surface allowed to pairing:

$$\Delta = N(0)V\left(\int_0^{\hbar\omega_0}\frac{\Delta}{E_{\mathbf{k}}}d\varepsilon_{\mathbf{k}} - \int_{blocked}\frac{\Delta}{E_{\mathbf{k}}}d\varepsilon_{\mathbf{k}}\right), \tag{1.9}$$

where the second integral is over all depaired regions, $E_k = \sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta^2}$, $\varepsilon_{\mathbf{k}}$ is the electron energy relative to the Fermi-level ε_F and $\varepsilon_F - \hbar\omega_0 < \varepsilon_{\mathbf{k}} < \varepsilon_F + \hbar\omega_0$, $N(0)$ is the density of states at the Fermi-level and V is the volume. For this phase to be a ground state, all single-particle excitations must have positive energies. The quasiparticle energy associated with the addition of a particle with the wave vector $\mathbf{k}$ and energy $\varepsilon_{\mathbf{k}}$ is given by:

$$\mathcal{E}_{\mathbf{q},B} = E_{\mathbf{k}} + \frac{1}{2}g\mu_B B\sigma + \frac{\hbar}{m}\mathbf{qk} \geq 0\ , \tag{1.10}$$