Doctoral Thesis

On the symmetry of the order parameter in the heavy-electron superconductor UBe$_{13}$

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On the Symmetry of the Order Parameter in the Heavy-Electron Superconductor UBe\textsubscript{13}

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Abstract

The superconducting order parameter or energy gap function of the heavy-electron superconductor UBe$_{13}$ may not be isotropic in k-space as in common BCS-type low temperature superconductors. Up to now, only experiments which probe the absolute value of the order parameter, and which are not sensitive to its phase and can therefore not detect possible sign changes of the order parameter under rotation in k-space, have been reported. In this thesis, we present results of experiments which probe for the first time not only the absolute value of the superconducting order parameter of UBe$_{13}$ but also its phase difference for different directions in k-space. We find clear evidence, that the order parameter changes sign under rotation in k-space and must have an unconventional topology. Furthermore, a scaling of the specific heat of UBe$_{13}$ at low temperatures and high magnetic fields, which provides further evidence for an unconventional topology of the energy gap function, is found.

In a first part, we report on measurements of the differential conductivity $G$ of UBe$_{13}$–Au contacts at temperatures between 0.33 and 1.3 K. We find evidence for low-energy Andreev surface bound states in the heavy-electron superconductor UBe$_{13}$ below $T_c$. Such bound states may only form in superconductors with complicated, non-isotropic orderparameters or energy gap functions, and are identified via huge conductance peaks at zero bias. From the voltage dependence of $G$ at $T < T_c$ we establish a lower limit of the energy gap amplitude and present the first decent data on its temperature dependence. Using the data at the lowest temperatures, the normalized energy gap amplitude was found to be $\frac{2\Delta(0)}{k_B T_c} > 6.7$, much in excess of the weak coupling BCS value of 3.5, and directly indicating strong coupling effects in superconducting UBe$_{13}$.
We performed differential conductivity measurements of the same UBe$_{13}$-Au contact in external magnetic fields up to 7 Tesla and in the same temperature range as in zero field. The huge conductance peaks at zero bias persist up to magnetic fields close to the upper critical field of UBe$_{13}$. Using the same procedure as in zero field, we were able to establish a lower limit of the superconducting energy gap amplitude of UBe$_{13}$ as a function of the applied magnetic field.

Finally, we report on measurements of the low temperature specific heat $C_p(T,B)$ of UBe$_{13}$ at temperatures between 0.08 and 0.37 K and in magnetic fields up to 7 Tesla. At $B \approx 2$ Tesla, a substantial change in the magnetic field dependence of the temperature derivative of the magnetic field induced contribution to the specific heat $C_H(T,B)$, resulting from the flow of supercurrents around the vortices, is observed, suggesting a crossover between two different regions in the superconducting phase diagram of UBe$_{13}$. For fields $B > 2$ Tesla, $C_H(T,B)$ exhibits a scaling behavior with respect to $TB^{-1/2}$, which provides evidence for the existence of point nodes in the quasiparticle excitation spectrum of the superconductor.
Kurzfassung

Der Ordnungsparameter oder die Energie-Lücke des Schwere-Elektronen Supraleiters UBe$_{13}$ ist mit großer Wahrscheinlichkeit nicht isotropisch wie in gewöhnlichen BCS-Typ Tief-Temperatur Supraleitern. Bis anhin wurden nur Experimente durchgeführt, die den Betrag des Ordnungsparameters messen, jedoch keinerlei Informationen über die Phase liefern und somit auch nicht einen möglichen Vorzeichenwechsel des Ordnungsparameters unter Rotation im $k$-Raum feststellen können. In dieser Dissertation werden wir Experimente vorstellen, welche das erste Mal nicht nur den Betrag sondern auch die Differenz in der Phase des Ordnungsparameters für verschiedene Richtungen im $k$-Raum bestimmen können. Wir finden deutliche Hinweise, dass der Ordnungsparameter unter Rotation im $k$-Raum einen Vorzeichenwechsel erfährt, also eine unkonventionelle Topologie aufweist. Im weiteren wurde ein Skalierungsverhalten der spezifischen Wärme von UBe$_{13}$ bei tiefen Temperaturen und hohen Magnetfeldern gefunden, das zusätzliche Hinweise auf eine unkonventionelle Topologie der Energie-Lücke liefert.

In einem ersten Teil werden wir Messungen der differentiellen Leitfähigkeit $G$ von Au–UBe$_{13}$ Kontakten bei Temperaturen zwischen 0.33 und 1.3 K diskutieren. Dabei finden wir Hinweise für gebundene, nieder-energetische Andreev Oberflächen-Zustände im Schwere-Elektronen Supraleiter UBe$_{13}$ unterhalb der kritischen Temperatur $T_c$. Solche gebundenen Zustände können sich nur in Supraleitern mit einem komplizierten, nicht-isotropen Ordnungsparameter oder Energie-Lücke formieren und äußern sich durch eine starke Erhöhung der differentiellen Leitfähigkeit bei Null-Energie. Aus der Spannungsabhängigkeit von $G$ bei $T < T_c$ können wir eine untere Schranke für die Amplitude der Energie-Lücke bestimmen und wir präsentieren in dieser Arbeit die ersten Daten über
Kurzfassung

deren Temperaturabhängigkeit. Unter Verwendung der Daten bei den tiefsten Temperaturen finden wir für die normierte Amplitude der Energie-Lücke $\frac{2\Delta(0)}{k_B T_c} > 6.7$, was den durch die BCS-Theorie unter der Annahme schwacher Kopplung berechneten Wert von 3.5 erheblich übertrifft und damit unmittelbar aufzeigt, dass in supraleitendem UBe$_{13}$ starke Kopplungseffekte involviert sind.

Wir haben Messungen der differentiellen Leitfähigkeit derselben Au–UBe$_{13}$ Kontakte auch bei hohen Magnetfeldern bis zu 7 Tesla und in demselben Temperaturbereich wie im Null-Feld durchgeführt. Die sehr grosse Erhöhung der Leitfähigkeit bei Null-Energie wurde bis zu Magnetfeldern, die sehr nahe des oberen kritischen Feldes von UBe$_{13}$ sind, beobachtet. Unter Anwendung der gleichen Technik wie im Null-Feld konnte ebenso eine untere Limite der Amplitude der Energie-Lücke von UBe$_{13}$ als Funktion des angelegten Feldes bestimmt werden.

Zum Schluss diskutieren wir Messungen der Tief-Temperatur spezifischen Wärme $C_p(T,B)$ von UBe$_{13}$ zwischen 0.08 und 0.37 K in Magnetfeldern bis zu 7 Tesla. Bei $B \approx 2$ Tesla finden wir eine beachtliche Änderung in der Magnetfeld-Abhängigkeit der Ableitung nach der Temperatur der durch das Magnetfeld induzierten spezifischen Wärme $C_H(T,B)$, die durch den Suprastrom um die Wirbel verursacht wird. Dies deutet auf einen Übergang zwischen zwei verschiedenen Regionen im Phasendiagramm von UBe$_{13}$ hin. Für Magnetfelder $B > 2$ Tesla zeigt $C_H(T,B)$ ein Skalierungsverhalten bezüglich $TB^{-1/2}$, das verträglich ist mit der Annahme, dass das Anregungsspektrum des Supraleiters punktförmige Nullstellen aufweist.
1 Introduction

The low temperature electronic properties of some intermetallic compounds where one of the constituents of the formula unit is a lanthanide or actinide atom with a partially filled $f$-electron shell are governed by strong interaction and correlation effects. The effective masses of the conduction electrons in these systems, which are a measure of the strength of the interaction, encountered in these materials are two to three orders of magnitude larger than in ordinary metals. This has lead to the term "heavy-electron" or sometimes "heavy-fermion" systems for this rather special class of materials. The first heavy-electron material, CeAl$_3$, was discovered more than two decades ago and the main characteristic low temperature features, such as a large linear-in-$T$ term of the electronic specific heat and an anomalously large $T^2$ term in the electrical resistivity were found [1].

The subsequent discovery of superconductivity below 0.65 K in the heavy-electron system CeCu$_2$Si$_2$ [2] and later on in UBe$_{13}$ [3] confirmed, by means of the pronounced anomaly of the electronic specific heat at $T_c$, that the unusual low temperature properties of heavy-electron systems are indeed of electronic nature. The occurrence of superconductivity in heavy-electron materials was somewhat unexpected, because it was believed that the local moments on the Ce or U atoms always suppress superconductivity by breaking the Cooper pairs.

Ever since the discovery of superconductivity in UBe$_{13}$, the question of the exact nature and origin of this phenomenon has been subject of interest and research. It has been postulated, that the superconductivity in these materials is not caused primarily by the usual electron-phonon mechanism but rather by some magnetic interaction [4, 5]. The possible involvement of magnetic interaction in the pair formation makes it very likely
that the superconducting state is of unconventional nature, i.e., characterized by a reduced symmetry of the order parameter. Such superconducting ground states automatically lead to the possibility of electronic excitation spectra with gap zeros on certain parts of the Fermi surface, in contrast to the overall non-zero gap in the electronic excitation spectrum of the conventional BCS ground state. Gap zeros, or gap nodes, lead to finite electronic densities of states at low energy even at $T = 0$. This in turn means that many thermal and transport properties of the superconducting state, which are governed by electronic excitations no longer show the well known BCS exponential temperature behaviour, but obey some power law temperature dependencies, dictated by the topology of the gap nodes. Among various other experiments, for UBe$_{13}$ such anomalous behaviour has been observed in the low temperature electronic specific heat well below $T_c$ ($C_p \propto T^3$) [6] or the London penetration depth well below $T_c$ ($\Delta \lambda \propto T^2$) [7].

The electronic density of states at low energies, measured from the Fermi energy $E_F$, is strongly influenced by the presence of a magnetic field, which causes a Doppler shift of the energy scale [8]. This Doppler shift leads to a magnetic field induced additional density of states, depending on the topology of the gap nodes. Measurements of the magnetic field induced contribution to the specific heat directly probe this extra density of states and provide further information on the existence and topology of nodes in the excitation spectrum. In this work, we will discuss the results of such experiments made on the heavy-electron superconductor UBe$_{13}$.

Recently, experiments which directly probed the phase of the superconducting order parameter of the high-temperature superconductor YBa$_2$Cu$_3$O$_7$ successfully demonstrated a sign change of the superconducting order parameter between the (100) and the (010) direction in $k$-space, using the magnetic flux modulation of the critical current of YBa$_2$Cu$_3$O$_7$—conventional superconductor dSQUIDs [9, 10] or using the concept of flux quantization in superconducting YBa$_2$Cu$_3$O$_7$ rings with multiple $\pi$-type Josephson junctions$^a$ at artificially grown grain boundaries on specially designed substrates [11]. So far, no experiments probing directly the phase of the order parameter in UBe$_{13}$ have been made. In this work, we investigate the behaviour of the superconducting order parameter

$^a$ A Josephson Junction is called $\pi$-junction if the Cooper pairs acquire a phase shift $\pi$ in the Josephson tunneling process between two linked superconductors, which corresponds to a negative critical current of the junction.
of UBe$_{13}$ under rotation in k-space by probing the properties of the quasi particle transfer through a normal metal–superconductor interface, realized via UBe$_{13}$–Au contacts. The quasiparticles may experience different phases (different signs) of the order parameter, depending on the direction of their momenta, which would affect the differential conductivity of the contact in a very particular way.

The organization of this work is as follows. A short overview of the heavy-electron state which occurs in UBe$_{13}$, including the onset of superconductivity below 1 K, is given in chapter 2. Also some aspects of unconventional superconductivity are included in this chapter. In chapter 3, a description of the experimental setups for the investigations discussed in this work, is given. Chapter 4 deals with the differential conductivity measurements of UBe$_{13}$–Au contacts in zero-field, and in chapter 5 similar measurements, but in non-zero fields, are discussed. The investigation of the electronic specific heat of UBe$_{13}$ in magnetic fields is discussed in chapter 6.
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2 UBe$_{13}$: An Unconventional Heavy-Electron Actinide Superconductor

2.1 Heavy-Electron Phenomena in UBe$_{13}$

Heavy-electron materials are intermetallic compounds containing elements of the actinide or rare-earth series with partially filled $f$-electron shells. At elevated temperatures, these materials behave as if these $f$-electrons were localized and only weakly interacting among themselves, as indicated by the Curie-Weiss-type temperature dependence of the magnetic susceptibility $\chi$. On cooling, an ordinary $f$-electron system usually undergoes a magnetic phase transition with ordered moments, predominantly antiferromagnetically. In heavy-electron systems, however, the situation is rather different. At low temperatures, some of these $f$-electrons seem to become itinerant, forming a metallic state with electronic properties consistent with those of an ordinary metal, but whose Fermi energy $E_F$ is situated inside a narrow band. This is experimentally indicated by an almost temperature independent magnetic susceptibility and a linear-in-$T$ electronic specific heat. The absolute values of these quantities, however, are two to three orders of magnitude enhanced compared to those of ordinary metals. Both quantities are proportional to $D_F$, the density of states at the Fermi energy, which is, in the framework of the concept of effective masses, proportional to the effective mass $m^*$ of the charge carriers. This yields effective masses which are as big as $1000 \times m_0$, with $m_0$ the mass of the free electron, justifying the term "heavy-electrons". The high temperature properties of heavy-electron metals are well described by models involving weakly interacting magnetic impurities in a metal.
It is remarkable, however, that the low-temperature properties are in agreement with the ideas of the Fermi liquid theory and resembles those of simple metals but with strongly renormalized parameters, e.g., with very large effective masses $m^*$. Several review articles describe the experimental [12-15] and theoretical [16-18] aspects of heavy-electron materials in great detail.

$\text{UBe}_{13}$ was the first actinide material, where extreme heavy-electron behaviour was recognized [3]. The normal state properties of $\text{UBe}_{13}$ clearly reveal the attributes of a heavy-electron metal. The specific heat $C_p$ at $T > 10$ K can fairly well be described by the usual expression for the specific heat of an ordinary metal, $C_p(T) = \gamma T + \beta T^3$, where the first term describes the electronic part of the specific heat and the latter the lattice contribution at $T \ll \Theta_D$, with $\Theta_D$ the Debye temperature, which is more than 600 K in this material [19,20]. The electronic specific heat in the normal state shows a broad maximum at around 3 K. This maximum has been discussed in connection with low-lying energy levels in $\text{UBe}_{13}$ and attributed to a Schottky-type anomaly with a level splitting of about 7 K [21]. If the electronic specific heat divided by the temperature, $C_{el}/T$, is considered in the normal state at low temperatures, it is strongly $T$-dependent below 7 K and, with decreasing temperatures, increases its value by more than a factor of 4 down to 1 K. This upturn of $C_{el}/T$ with decreasing temperatures is a general feature of heavy-electron metals (see e.g. Ref. 12). At very low temperatures, the increase of $C_{el}/T$ changes into a saturation of $C_{el}/T$. Furthermore, it was demonstrated that the behaviour of the electronic specific heat at low temperatures is strongly influenced by the interatomic distance by doping $\text{UBe}_{13}$ with Th or Lu. While the onset of the characteristic upturn of $C_{el}/T$ was shifted to lower temperatures and the saturation value increased for Th doping, just the opposite is true for Lu doping [22]. The former dopant has a tetravalent configuration and expands the lattice whereas the latter’s configuration is trivalent and contracts the lattice. The magnetic susceptibility $\chi$ of $\text{UBe}_{13}$ at elevated temperatures shows a Curie-Weiss-type behaviour with an effective moment $\mu_{\text{eff}}$ of 3.08 $\mu_B$/ion, where $\mu_B$ is the Bohr magneton, and a negative Curie paramagnetic temperature $\Theta_p$ of $-53$ K [19]. This indicates the existence of fairly well localized moments due to the partially filled $5f$-electron.

---

$^a$ The electronic specific heat of $\text{UBe}_{13}$ was determined by subtracting off the lattice contribution, which is almost negligible at $T < 10$ K, from the total measured specific heat. The justification of this procedure becomes obvious when concerning the specific heat at the superconducting transition, where the large specific heat in the normal state at $T_c$ is removed, as expected because of the gap formation in the electronic excitation spectrum due to the occurrence of superconductivity.
2.2 The Occurrence of Superconductivity in UBe$_{13}$

Superconductivity below 0.9 K in the heavy-electron material UBe$_{13}$ was discovered by Ott et al. in 1983 [3]. Measurements of the specific heat around the superconducting phase transition clearly demonstrated that the same electrons, those with predominant $f$-symmetry and large effective masses, which in other compounds are responsible for magnetic ordering phenomena, were now involved in the formation of a superconducting state. The superconductivity in UBe$_{13}$ was found to be of extreme type II, with a coherence length $\xi_0$ of about 50 Å and a field penetration depth $\lambda(0)$ of the order of 8000 Å, revealing a Ginzburg-Landau (GL) parameter $\kappa \approx 10^2$. Shortly after the discovery of this new state, ideas suggesting that the attractive electron-electron interaction might be different from the usual phonon-mediated interaction in conventional superconductors were discussed. It was claimed by Varma [4] and Anderson [5] that some kind of magnetic interaction might be involved. This would automatically make it very likely that the superconducting ground state cannot be described by a simple BCS state, which is isotropic in $\mathbf{k}$-space and exhibits an overall non-zero gap in the electronic excitation spectrum. States with more complicated symmetries, which involve gap nodes on certain parts of the Fermi
surface, had to be considered. The non-vanishing low-energy electronic density of states even at $T \to 0$ leads to non-exponential temperature dependencies of several thermal and transport properties which are governed by electronic excitations of the heavy-electron superconductors well below $T_c$ (for a review, see e.g. Ref. 27).

Measurements of the specific heat of UBe$_{13}$ below $T_c$ clearly revealed deviations from the BCS-type behaviour. The discontinuity $\frac{C_s(T_c) - C_n(T_c)}{C_n(T_c)}$ of the specific heat at $T_c$, where $C_{s,n}$ denotes the specific heat in the superconducting and in the normal state, respectively, is approximately 2.5, which is large compared to the BCS value of 1.43 and indicates the rather strong coupling effects involved in superconducting UBe$_{13}$ [6]. It has further been demonstrated that the specific heat in the superconducting state of UBe$_{13}$ is fairly well described if a state, which corresponds to the ABM (Anderson-Brinkman-Morel) state of the anisotropic A-phase of superfluid $^3$He and which is characterized by points of zeros of the energy gap, is assumed [6]. Anderson noted, that the analogy between the superfluid state in $^3$He and the superconducting state in the heavy-electron metal UBe$_{13}$ should not be stressed too far, because crystal field effects due to the crystal symmetry and strong spin-orbit coupling, which are to be expected in UBe$_{13}$, are absent in superfluid $^3$He [28]. A more detailed discussion of the similarities and differences of heavy-electron materials to $^3$He is given in Ref. 29. The specific heat data at temperatures well below the superconducting transition are fitted rather well using an expression of the form $C_p(T) = \gamma_c T + \beta_c T^3$. The cubic-in-$T$ term provided substantial evidence for the existence of point nodes in the electronic excitation spectrum and it was demonstrated that the apparent linear term to $C_p$ arises from resonant impurity scattering. The low temperature data of the specific heat are in rather well agreement with calculations taking into account the effect of resonant impurity scattering on the low energy excitation spectrum and assuming an ABM state [30].

Another property which shows a clear deviation from the conventional BCS-type exponential temperature dependence, is the penetration depth of a magnetic field into a superconductor, the so-called London penetration depth $\lambda_L$ [7, 31]. At temperatures well below $T_c$, the data showed a nice quadratic-in-$T$ behaviour, which has been demonstrated to be compatible with expectations assuming a superconducting state with point nodes in the electronic excitation spectrum. The influence of Fermi-liquid corrections on the behaviour of $\lambda_L$ was analyzed in Ref. 32 and a different superconducting state, a polar
state, which is characterized by lines of nodes in the energy gap, instead of an axial state was claimed to be realized in UBe$_{13}$.

Similar strong deviations from the exponential temperature dependence predicted by the BCS theory was observed in NMR spin-lattice relaxation rate measurements, where $T_1^{-1} \propto T^3$ just below $T_c$ and the absence of a coherence peak was reported [33]. Measurements of the absorption of ultrasound in UBe$_{13}$ revealed a quadratic temperature dependence for $T \to 0$. Just below the superconducting transition, the observation of a pronounced peak was reported. The peak shifts to lower temperatures as magnetic field is applied, in accordance with the reduction of $T_c$ [34]. The thermal conductivity of UBe$_{13}$ in the [001] direction was measured and found to vary as $T^2$, which was interpreted as evidence for a polar state [35,36].

The temperature dependence of the upper critical magnetic field $H_{c2}$ is also rather unusual [25,37]. At $T_c$, the slope $\frac{\partial H_{c2}}{\partial T}$ is at least of the order of several hundred kOe/K, and might be even much larger. The zero temperature value of $H_{c2}$ is around 140 kOe, extremely large for a superconductor with a $T_c$ of less than 1 K. The lower critical field $H_{c1}$ was reported to be around 42 Oe at $T = 0$ and to decrease quadratic-in-$T$ as $T$ increases [38]. These values of the zero temperature critical fields are in rough agreement with the GL-parameter $\kappa$ discussed above.

While in ordinary superconductors, distinct pair-breaking effects arise from magnetic impurities, non-magnetic impurities do not drastically alter the superconducting state [39]. The situation observed in UBe$_{13}$ is rather different. A substantial suppression of superconductivity occurs even when small amounts of non-magnetic impurities are introduced [22]. The effects of non-magnetic impurities on triplet states were first considered in the Born approximation by Ueda and Rice [40] and by Gor'kov and Kalugin [41]. They found that in an axial state, a non-zero (critical) concentration of impurities is required to have a non-zero density of states at $E_F$ at $T = 0$, whereas in the polar state even an arbitrarily small concentration of impurities leads to a non-vanishing $D_F$ at $T = 0$. Subsequent investigations of possible corrections to the Born approximation revealed that the critical concentration in the axial state is sensitive to the scattering phase shift vanishing in the limit that the impurities have a resonance centered at $E_F$ [42–45].
A rather special and unexpected situation is obtained when substituting a small fraction of the U atoms with Th. Not only is $T_c$ a nonmonotonic function of the doping value $x$, but for $1.9 < x < 4.5\%$ a second phase transition at $T_{c2} < T_c$ occurs [46]. It was argued that the transition at $T = T_{c2}$ is also a superconducting transition. On the other hand, $\mu$SR measurements [47] pointed to the appearance of a magnetic moment below $T_{c2}$ which was taken as evidence that a SDW state occurs below $T_{c2}$, coexisting with the superconducting state. Since the anomaly of $T_c(x)$ at $x \approx 1.9\%$ is very sharp, it has been proposed that it is due to a crossing of transition temperatures belonging to superconducting states of different symmetries. A phase diagram which is consistent with the experimental findings and which predicts a time-reversal breaking state for $1.9 < x < 4.5\%$ below $T_{c2}$ has been proposed by Sigrist and Rice [48]. A review of the situation in $U_{1-x}Th_xBe_{13}$ is given, e.g., in Ref. 27. When doping $UBe_{13}$ with $3\%$ B at the Be site, the discontinuity of the specific heat is drastically enhanced, whereas the superconducting transition temperature is not altered significantly. A similar situation is obtained for $U_{1-x}Th_xBe_{13-y}B_y$ for $x < 1.9\%$, whereas for $x > 4.5\%$ $T_c$ is suppressed and the anomaly in the specific heat at the superconducting transition is reduced. For intermediate $x$ values, the two subsequent transitions are still observed, but when doping with the same concentration of Cu instead of B, both transitions are wiped out.

The behaviour of a multidimensional order parameter in a cubic system when exposed to uniaxial stress to lower its symmetry has been studied theoretically in Refs. 49 and 50. They found that in certain cases the superconducting phase transition may split into two or more transitions. A recent experimental study of the influence of uniaxial pressure in the [110] direction on the superconducting transition of $UBe_{13}$, however, did not reveal any splitting [51].

Above, a large variety of examples of the properties of the superconducting state of $UBe_{13}$, which show very unusual behaviour and in most cases strong deviations from the exponential temperature dependence predicted by the BCS theory, were discussed. The conclusions drawn from these experiments concerning the symmetry of the superconducting order parameter are somewhat contradicting, but nevertheless, as a whole they certainly provided enormous evidence that the superconductivity in $UBe_{13}$ is of unconventional nature and may not be viewed as a simple BCS ground state. However, all these experiments which revealed distinct power-law dependencies of various physical properties only probed the absolute value of the superconducting order parameter, which is
2.3 Unconventional Superconductivity

a complex quantity in general (see also section 2.3) and may have a $k$ dependent phase. Thus, the definitive identification of the proper symmetry of the superconducting order parameter is still not complete, and phase-sensitive investigations are certainly indispensable on the course towards a more complete understanding of the superconductivity in UBe$_{13}$.

Triggered by the success of the phase-sensitive experiments probing the superconducting order parameter in high-temperature superconductors based on Josephson effects [9–11], several attempts were made to establish Josephson currents between UBe$_{13}$ and either UBe$_{13}$ or a $s$-wave superconductor. Two types of experiment involving Josephson currents between Nb and UBe$_{13}$ have been reported. The observation of Shapiro-step like features when rf irradiating the Nb–UBe$_{13}$ contact at temperatures even well above $T_c$ of UBe$_{13}$ was taken as evidence for negative $s$-wave proximity effect in UBe$_{13}$ [52]. Recently, periodic oscillations of the Josephson supercurrent when varying the applied magnetic field through a Nb–UBe$_{13}$ contact have been demonstrated [53].

Only very recently it was suggested to take advantage of the fact that the phase shift which is experienced by the wave function of electrons or holes which are Andreev reflected at the surface of a superconductor is a function of the (possibly) $k$ dependent phase of the superconducting order parameter [54]. Subsequently, it has been shown that at the interface of a normal metal–superconductor contact a bound state may form at a certain quasiparticle energy and affect the differential conductivity of the contact in a very particular way. The bound state energy is related to the phase structure of the superconducting order parameter, thus providing a tool to probe the phase of the order parameter. In this work, this technique has been applied to UBe$_{13}$ by means of investigating the properties of Au–UBe$_{13}$ contacts and therefore providing, for the first time, phase-sensitive investigations of the superconducting order parameter in UBe$_{13}$.

2.3 Unconventional Superconductivity

Common low temperature $s$-wave superconductors such as Al or Sn are well described by the theory of Bardeen, Cooper and Schrieffer (BCS) [55]. They demonstrated that in the presence of an arbitrarily small phonon mediated attractive electron-electron interaction,
Cooper pairs in an angular momentum \( l = 0 \) spin singlet state (s-wave state), are formed. It was argued, using the picture of the BCS theory, that heavy-electron superconductors, where the quasiparticles, which form narrow bands with predominantly \( f \)-character, are responsible for the superconductivity, would have difficulties to form ordinary isotropic s-wave Cooper pairs, because of the strong Coulomb repulsion. To avoid large overlap of the wave functions of the paired quasiparticles, the system would rather choose an unconventional, anisotropic channel with an angular momentum \( l > 0 \), such as a \( p \)-wave or \( d \)-wave state.

It has been shown that for a phonon-mediated electron-electron interaction, other attractive channels than the isotropic channel are only possible for a very anisotropic electron-phonon interaction, which is not very likely in metals [56]. However, other interactions could favor anisotropic pairing, which might be realized in heavy-electron systems. In this work, we will rather use the term “unconventional superconductor” instead of “anisotropic superconductor” to describe paring states, different from the BCS ground state, which are due an anisotropic attractive electron-electron interaction. An equivalent classification of the pairing state may be obtained using symmetry arguments. In the superconducting state, one or more symmetries of the system in its normal conducting state are broken, i.e., \( g \Delta (g^{-1}k) \neq \Delta (k) \), where \( g \) denotes an element of the full symmetry group \( G \) of the normal state, which is given by \( G = \mathcal{G} \times \text{SU}(2) \times \mathcal{K} \times \Phi \). \( G \) is the point group of the crystal lattice symmetry, which is \( O_h \) (cubic) for UBe\(_{13}\), \( \text{SU}(2) \) the spin rotation symmetry group, \( \mathcal{K} \) the symmetry group of time-reversal and \( \Phi \) the \( \text{U}(1) \) gauge symmetry group. In conventional BCS superconductors, the symmetry at the phase transition is lowered by breaking the \( \text{U}(1) \) gauge symmetry. In superconductors, which are unconventional in the sense discussed above, the gauge symmetry \( \text{U}(1) \) is no longer the only broken symmetry. The best understood unconventional superconductivity up to now is the superfluidity in \( ^3\text{He} \), where the attractive interaction is mediated by spin-fluctuations and the pairing state is a \( p \)-wave, spin triplet state. The theoretical aspects of this kind of superconductivity are reviewed in Ref. 57 and a review of the experimental properties of \( ^3\text{He} \) is given in Ref. 58.

\(^b\) We note that the superfluidity in \( ^3\text{He} \) is caused by a pairing of neutral atoms, whereas in superconductors the pairing of charged electrons leads to superconductivity. Nevertheless, in both systems, a pairing of fermions occurs.
A more general theory of superconductivity than BCS, which includes all kinds of pairing interactions, has been discussed in the context of spin triplet superconductivity by Anderson and Morel [59] and by Balian and Werthammer [60]. They used a generalized BCS theory, where the Hamiltonian of the many-body problem was treated using a mean-field approach. The resulting mean-field Hamiltonian is given by

\[ \mathcal{H} = \sum_{k,s} \epsilon(k) a_{ks}^{\dagger} a_{ks} + \frac{1}{2} \sum_{k,s_1,s_2} \left( \Delta_{s_1 s_2}(k) a_{ks_1}^{\dagger} a_{-ks_2}^{\dagger} - \Delta_{s_1 s_2}^{*}(-k) a_{-ks_1} a_{ks_2} \right), \]  

(2.1)

where \( \epsilon(k) \) is the band energy measured from the chemical potential \( \mu \), \( a_{ks}^{(\dagger)} \) are the destruction (creation) operators of a quasiparticle with momentum \( k \) and spin \( \sigma \), and \( \Delta \) the mean-field of interactions. The mean-field is defined in the usual way [55] from the attractive effective electron-electron interaction \( \tilde{V} \) and is often called a pair potential. It turns out that this mean-field \( \Delta \) can be identified with the superconducting energy gap [55] and in the context of the Landau theory for second order phase transitions [61] as the superconducting order parameter. Furthermore, it may be seen from Eq. (2.1), that the mean-field \( \Delta \) and the pair wavefunction \( a_{ks_1}^{\dagger} a_{-ks_2}^{\dagger} \) in \( k \)-space (eigenfunction) must have the same symmetry. The microscopic mechanism of the superconductivity of the heavy-electron superconductors is still obscure and a specific form of the pairing potential \( \tilde{V} \) is not available. However, using the symmetry properties of the Hamiltonian and the system in connection with group theoretical arguments, possible energy gap functions can be deduced. This has been discussed in the framework of a phenomenological theory of unconventional superconductivity in great detail in the review article of Sigrist and Ueda [27]. In order to classify possible pairing states of the heavy-electron superconductor UBe\(_{13}\), we will give a brief overview on unconventional superconductivity using symmetry arguments below.

In the absence of spin-orbit coupling, and neglecting the presence of the crystal field, the possible eigenvalues of the system may be characterized using the center-of-mass angular momentum \( L \) and the spin \( S \) of the pairs. In this simplified system, the eigenfunctions may then be expressed by the spherical harmonics for the orbit part and the spin functions \( \chi(S, s_z) \) for the spin part.  

For \( S = 1 \), the spin function \( \chi(1, s_z) \) may be transformed into another basis \( \hat{x}, \hat{y}, \hat{z} \), by using the relations \( \hat{x} = \frac{1}{2} (\chi(1, -1) - \chi(1, +1)) \),
\[ \psi = \frac{1}{\sqrt{2}} (\chi(1,-1) + \chi(1,+1)) \] and \[ \zeta = \frac{1}{\sqrt{2}} \chi(1,0). \] We recall here that the eigenfunction spaces for every single eigenvalue form a basis of an irreducible representation of the symmetry group of the Hamiltonian.

In the presence of a spin-orbit interaction, which is particularly strong in heavy-electron superconductors, the spin and the orbit space are coupled and \( S \) has to be treated as a pseudo spin [27]. In the presence of a crystal electric field, the symmetry of the system is lowered from the continuous rotation group to a discrete point group with only few representations. In the case of the cubic point group \( O_h \), which is the point group of \( UBe_{13} \), only 10 classes of different eigenfunction spaces exist, corresponding to the four one-dimensional representations \( \Gamma_1^\pm, \Gamma_2^\pm \), the two two-dimensional representations \( \Gamma_3^\pm \) and the four three-dimensional representations \( \Gamma_4^\pm, \Gamma_5^\pm \). The \( \pm \) sign denote the behaviour under parity. Each representation has its own \( T_c(\Gamma) \), but for the following discussion it is assumed that the highest \( T_c \) is much larger than all other \( T_c(\Gamma) \) and a (possible) mixing of components belonging to different representations may be neglected. The order parameter of each representation for singlet states is given by

\[
\Delta_{\Gamma,m}(\mathbf{k}) = \begin{pmatrix} 0 & \Psi_{\Gamma,m}(\mathbf{k}) \\ -\Psi_{\Gamma,m}(\mathbf{k}) & 0 \end{pmatrix}
\]

and for triplet states by

\[
\Delta_{\Gamma,m}(\mathbf{k}) = \begin{pmatrix} -d^{x}_{\Gamma,m}(\mathbf{k}) + id^{y}_{\Gamma,m}(\mathbf{k}) & d^{z}_{\Gamma,m}(\mathbf{k}) \\ d^{x}_{\Gamma,m}(\mathbf{k}) & d^{y}_{\Gamma,m}(\mathbf{k}) + id^{z}_{\Gamma,m}(\mathbf{k}) \end{pmatrix}
\]

where the scalar functions \( \Psi_{\Gamma,m}(\mathbf{k}) \) and the vector functions \( \mathbf{d}_{\Gamma,m}(\mathbf{k}) \) with the components \( d^{x,y,z}_{\Gamma,m}(\mathbf{k}) \) for all representations \( \Gamma_7^\pm \) of the cubic symmetry group may be found in Refs. 62 and 63. The gap-function to a certain eigenvalue is now given by a linear combination of the basis-functions of the corresponding irreducible representation \( \Gamma \), by \( \Delta_\Gamma(\mathbf{k}) = \)

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\( ^c \) The total pair wavefunction must respect the Pauli principle and its symmetry properties are constrained. Therefore, pairs in the spin singlet state can only have even \( L \)-quantum numbers \( l \) and pairs in the spin triplet state only odd \( L \)-quantum numbers \( l \).
2.3 Unconventional Superconductivity

$\Sigma_m \eta_{\Gamma,m} \Delta_{\Gamma,m}(k)$, where $\Delta_{\Gamma,m}(k)$ is the $m^{th}$ basis function of the $n$ dimensional representation $\Gamma$, and $\eta_{\Gamma,m}$ complex numbers. The set $\{\eta_{\Gamma,m}\}$ may be used to describe the superconducting state.

It is a property of superconductivity induced by anisotropic pairing that the order parameter and therefore the energy gap in the quasiparticle excitation spectrum may have points or lines of zeros. These yield an electronic excitation spectrum, which gives rise to power-law temperature dependencies of various properties at low temperatures instead of the well known exponential behaviour found in conventional superconductors. This will be illustrated on the example of the ABM-like spin triplet state which has been discussed in the previous section in connection with the specific heat of UBe$_{13}$ at $T \ll T_c$. In the above notation, the order parameter is given by

$$\Delta(k) = \begin{pmatrix} k_x + ik_y & 0 \\ 0 & k_x + ik_y \end{pmatrix}.$$  

The size of the gap may now be calculated by $|\Delta(k)| = \sqrt{\frac{1}{2} \text{tr}(\Delta(\mathbf{k})\Delta(\mathbf{k})^\dagger)}$ and leads to $|\Delta(k)| = 0$ for $\mathbf{k} = (0,0,\pm k_z)$, i.e., to point nodes in the excitation spectrum. As a consequence, the specific heat at $T \ll T_c$ should vary as $T^3$, which has been demonstrated for UBe$_{13}$ by Ott et al. [6].

From symmetry arguments alone, it is only possible to classify the gap function as given in Eq. (2.2) and (2.3). To gain further insight of the superconducting state, the system may be described by the phenomenological Ginsburg-Landau (GL) theory [64], which applies, strictly speaking, only in the vicinity of the phase transition, using the concept of the Landau theory for second order phase transitions. The breakdown of a certain symmetry at the phase transition is described by introducing an order parameter, which is only non-zero below $T_c$ and which can be identified with the mean-field $\Delta$ in Eq. (2.1). The GL free energy $F$ may be written as an expansion in the order parameter near $T_c$ by taking into account that $F$ has to be scalar under all symmetry operations. Keeping only terms up to forth order, $F$ will be of the form [27]

$$F(T) = F_0(T) + V \left( A_T(T) \sum_m \eta_{\Gamma,m} \eta_{\Gamma,m}^* + \sum_{ijkl} \beta_{ijkl} \eta_{\Gamma,i} \eta_{\Gamma,j} \eta_{\Gamma,k} \eta_{\Gamma,l}^* \right), \quad (2.4)$$
where $F_0(T)$ denotes the normal state free energy and $V$ the volume of the system. The coefficient of the second order term, $A_T(T)$, is proportional to $\left( \frac{T}{T_c} - 1 \right)$. The last term in Eq. (2.4) represents all the forth-order contributions, where the material-dependent parameters $\beta_{\tau,ijkl}$ include all the microscopic effects of the system. To find the equilibrium order parameter of a certain irreducible representation $\Gamma$, the free energy $\mathcal{F}_\Gamma$ has to be minimized with respect to the coefficients $\eta_{\Gamma,m}$. Depending on the choice of the parameters $\beta_{\tau,ijkl}$, different superconducting phases are found. The resulting functions $\Psi_{\Gamma}(\mathbf{k})$ or $\mathbf{d}_{\Gamma}(\mathbf{k})$ for different choices of the parameters $\beta_{\tau,ijkl}$ are given in Table VI(a) of Ref. 27.
3 Experimental

3.1 Introduction

In this chapter, we first describe the experimental setup for the differential conductivity measurements of UBe\textsubscript{13}–Au contacts, including a detailed discussion of the used $^3$He cryostat and the measurement cell which were, as part of this work, specially designed to perform these differential conductivity experiments at low temperatures and high magnetic fields. In the second part, the setup used to measure the specific heat of UBe\textsubscript{13} in high magnetic fields in a dilution refrigerator is discussed.

3.2 Differential Conductivity Measurements

3.2.1 Measurement Cell

A schematic view of the measurement cell is shown in Fig. 3.1. To form the UBe\textsubscript{13}–Au contact, the sharp Au tip (see below for more details) was moved vertically towards the crystal, until the sharp tip touched the cleaned UBe\textsubscript{13} surface with only tiny pressure. The tip is mounted on a rather strong plate-spring, which itself is fixed into a copper frame. The same copper frame serves as a host for the UBe\textsubscript{13} crystal, such that the tip and the crystal build a rigid unit together. The vertical displacement of the tip was achieved by means of a micrometer screw which is coupled by a soft (compared to the plate-spring) spiral-spring to the plate-spring. The micrometer screw with a pitch of 0.2 mm per turn was operated by a screwdriver (see below for detail). This construction was chosen to
protect the contact from vibrational noise which only affects either the sample or the tip. Once a contact is formed, any motion of the tip relative to the crystal may cause a substantial change of the properties of the contact, whereas small simultaneous motions of tip and crystal together are less harmful. Since the coupling between the tip and the mechanical turning device is made with the rather soft spiral-spring, which absorbs the unwanted external vibrations quite effectively, the contacts could be kept stable for several days.

3.2.2 \textsuperscript{3}He Cryostat

We have performed the differential conductivity experiments described in this work in a home-built, closed-cycle \textsuperscript{3}He cryostat. A careful description of the principles of \textsuperscript{3}He
refrigerators can be found in the literature [65]. We only briefly discuss the main features of the used cryostat. A schematic view of the refrigerator is shown in Fig. 3.2. The cryostat itself is surrounded by liquid $^4\text{He}$ to keep the superconducting magnet and the vacuum can at 4.2 K. It is a closed-cycle cryostat, i.e., gaseous $^3\text{He}$ enters the cryostat continuously and is liquified in the condenser, which is cooled by the $^4\text{He}$ precooling stage (1 K-pot). This allows measuring times of the order of weeks, which is important to take data-points in a large area of the $H-T$ phase diagram. In this continuous mode, temperatures down to 0.31 K have been achieved.
A special feature of the used cryostat was the mechanical screwdriver which could be operated from outside the cryostat while working at the lowest temperatures. This screwdriver is operated by a 20:1 gear, whereby an angular resolution of less than 5° could be achieved. The screwdriver is fed into the vacuum can at room temperature and is thermally anchored at 4.2, 1 and 0.3 K by flexible copper-clamps. To avoid large heat-flow into the cryostat and especially into the measurement cell, the screwdriver was made of stainless steel tubes of 2 x 1 mm (outer x inner diameter) between 4.2 K and room temperature, and of 1 x 0.8 mm between 4.2 and 0.3 K. At 0.3 K, the screwdriver is coupled to the micrometer screw.

### 3.2.3 Experimental Setup

![Experimental Setup Diagram](image)

Figure 3.3: Schematic view of the experimental setup.

The differential conductivity measurements of the UBe$_{13}$-Au contacts were performed by using a standard a.c. modulation technique. In Fig. 3.3, we show a schematic drawing of the experimental setup. The UBe$_{13}$-Au contact was shielded from external rf noise by means of a passive low-pass filter. This filter consisted of small hollow ferrite elements, through which the current and voltage lines were fed before they entered
3.2 Differential Conductivity Measurements

The excitation current through the contact was supplied by a home-made current source. The current source was controlled by the built-in a.c. generator of the analog lock-in amplifier (LIA), such that a small a.c. current was applied to the contact. The a.c. voltage over the contact was then measured differentially by the LIA. The signal of the LIA was measured using the analog signal output of the LIA in connection with the data acquisition card of the computer. This allowed measurements of \( \frac{dV}{dt} \) at zero-bias. To perform measurements at different excitation currents, a d.c. voltage, which was changed only very slowly compared to all typical time constants of the setup, was superimposed to the small a.c. voltage from the LIA by means of a ramp generator. The level of this quasi-d.c. excitation current was determined by measuring the voltage drop over a shunt resistor with the DAQ. The quasi-d.c. voltage over the contact was amplified by a battery powered low noise amplifier and also measured with the DAQ. Therefore, the excitation current \( I \) could be swept very slowly from \(-I_{\text{max}}\) to \(+I_{\text{max}}\), while measuring simultaneously the excitation current \( I \), the voltage over the contact \( V \) and the differential conductivity \( G = \left( \frac{dV}{dt} \right)^{-1} \). This setup allowed for measurements of the differential conductivity of the contact as a function of a very slowly varying quasi-d.c. current. The experiments were performed inside a Faraday-cage to ensure very low influence of external noise and the computer was carefully electrically insulated from the experiment by an opto-coupler, in order to avoid rf-noise from the computer or the DAQ to interfere with the experiment.

3.2.4 Sample Preparation

The process of sample growth of high quality UBe\(_{13}\) material is discussed in detail elsewhere [3].

It turned out to be of great importance, that the surface of the UBe\(_{13}\) crystal was cleaned rather well to be able to form a reasonable contact. To remove all the unwanted surface layers, the sample was lightly etched in a diluted acid (5 vol % HCl in HNO\(_{3}\),

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\*a The current source used was a bipolar-type E.F. #4.2.


\*c National Instruments NB-MIO-16X.
diluted in water) for a few minutes, which caused the surface to become metallically shiny. The sample was then mounted into the measurement cell and brought into vacuum within one hour to avoid heavy oxidation.

The Au-tips were electro-etched from high purity, 1mm thick Au-wire. During the etching process, this wire also served as the cathode, and another gold-wire on the ground of the vessel which contained the solution, as the anode. As a solution, we used 1-molar Mg(ClO_4)_2 in methanol. Only small currents of the order of 10 mA were used in order to get a smooth surface and to avoid fast etching. During the etching process, the Au-wire was pulled out very slowly of the solvent, such that a very sharp tip was formed. As soon as the tip was completely pulled out of the solvent, the etching current was immediately turned to zero to avoid any further etching. This process was repeated several times, until a typical tip-radius of 10 to 50μm was reached. Subsequently, the tips were cleaned in acetone and glued with a two-component conducting epoxy (EpoTek H20E) into a support, which could be mounted on the plate-spring of the measurement cell as described in section 3.2.1.

3.3 Specific Heat Measurements

3.3.1 Relaxation Technique

The relaxation technique is a widely used method to measure the specific heat C_p of mg-sized samples, which allows very accurate measurements of the absolute value of C_p at very low temperatures. If energy is added to an arbitrary system, e.g., by an electrical heater, the specific heat C_p is given by

\[ C_p = \frac{P_{el} - \kappa(T_s - T_b)}{T_s}, \]

where C_p denotes the specific heat of the system at constant pressure, P_{el} the power, which is applied to the system by the heater, T_s the temperature of the sample, \dot{T}_s its derivative with respect to the time t, T_b the temperature of the environment, which also serves as a thermal reservoir and \kappa the thermal conductivity of the heat-link between the system and the environment.
In Fig. 3.4, a schematic view of the calorimeter used for the relaxation measurements is shown. The sample is located on a tiny sapphire plate, which is thermally connected via a weak link to the rest of the cell, which consists of a massive copper block and serves as a thermal reservoir. On the bottom of the sapphire plate, a small 1 k\(\Omega\) RuO\(_2\) chip-resistor\(^d\) was mounted, which was used as a thermometer to control the temperature of the sample platform \(T_h\). A small electrical heater is evaporated directly onto the sapphire plate. The thermal link between the sample platform and the thermal reservoir is realized by the few wires, which are needed to operate the heater and the thermometer. In the following discussion, we will always identify the temperature of the sample platform \(T_h\) with the temperature of the sample \(T_s\). This is justified by the fact that in the present study, the thermal contact between the sample platform and the thermal reservoir is weak in the entire investigated temperature range compared to all other involved thermal contacts. Therefore, sample and sample platform form a single unit with an overall well defined temperature \(T_h = T_s\).

In Fig. 3.5, we show the time evolution of the relevant quantities during the measurement. Starting at the time \(t = 0\), a power \(P_{el} = I^2 R_{el}\) is applied by the heater to the sample and sample platform, where \(R_{el}\) is the resistance of the heater and \(I\) the electrical current through it. Its time-evolution is shown in Fig. 3.5. The sample (and the sample platform)

\(^d\) RCWP-575, Vishay Dale Electronics, Yankton, SD, USA.

The size of the 1 k\(\Omega\) chip resistor was reduced by a laser cutter in all dimensions in order to reduce its specific heat by one order of magnitude. The resistance of the reduced chip at room temperature was 4.2 k\(\Omega\).
are in thermal equilibrium at $t < 0$ and the sample temperature $T_s$ is equal to $T_0$. For $t > 0$, $T_s$ changes according to Eq. (3.1) and its evolution is shown in Fig 3.5. At $t \gg \tau$, where $\tau$ is the average relaxation time at $T_{av} = \frac{T_1 - T_0}{2}$, and $T_1$ the new equilibrium temperature, the sample (and the sample platform) have reached a new thermal equilibrium. The thermal conductivity $\kappa$ of the thermal link at $T_{av}$ may be determined by taking into account that $P_{el} = P_1 = \kappa (T_s - T_h)$, where $P_1$ denotes the power which is released through the thermal link $\kappa$. Its time dependence is shown in Fig. 3.5. The total energy input into the sample, $\Delta E$, is given by the difference of the total energy input into sample and sample platform $\Delta E_{tot}$ and the energy absorbed by the sample platform $\Delta E_h$ by

$$\Delta E = \Delta E_{tot} - \Delta E_h,$$

where

$$\Delta E_{tot} = \int_0^\infty dt \left( P_{el}(t) - P_1(t) \right)$$

and

$$\Delta E_h = \int_0^\infty dt P_h(t) = \int_{T_0}^{T_1} dT C_h(T),$$

(3.2)
where $P_h$ denotes the power which is absorbed by the sample platform. These contributions may be calculated numerically and are shown by the shaded areas in Fig. 3.5. According to Eq. (3.1), the specific heat is then given by

$$C_s = \frac{\Delta E}{T_1 - T_0},$$

(3.3)

where $T_1 - T_0 = \int_0^\infty dtT_s$.

### 3.3.2 Experimental Setup

The measurements of the specific heat $C_p$ at low temperatures and high magnetic fields were made in a dilution refrigerator. The calorimeter, which is shown schematically in Fig. 3.4, was mounted in the center of a superconducting solenoid in order to perform measurements in external magnetic fields up to 7 Tesla. The sample temperatures $T_s$ and the heater power $P_{he}$ were measured using a fast data-acquisition card (DAQ). The specific heats of the sample platform and the grease (Apiezon N), which was used to glue the sample onto the platform and to ensure good thermal contact between sample and sample platform, were measured in a separate experiment. These two contributions were only a few ppm of the total measured specific heat at all temperatures and all fields in this work.

Special care was taken to calibrate the RuO$_2$ sample thermometer attached to the sapphire plate. For this purpose, a calibrated temperature sensor was mounted outside the core of the magnet solenoid and inside a multilayered superconducting magnetic shield [66]. The calibrated sensor was thermally shortcut to the calorimeter to ensure thermal equilibrium between the calorimeter and the calibrated sensor. The magnetic shield was able to shield external fields of the order of 2 Tesla [66], which was, even at fields of 7 Tesla in the center of the superconducting solenoid, enough to keep the calibrated sensor always at zero field. To check the reliability of the shield, a Hall-sensor was mounted inside the shield and close to the calibrated temperature sensor, but no field could be detected even at the highest applied fields.

This experimental setup allows for $C_p$-measurement scans either parallel to the magnetic field $H$ in the $H - T$ phase diagram by varying the temperature in a fixed magnetic field or vice versa, thus providing a good sensitivity to thermodynamic features in any direction of the $H - T$ phase diagram.
3.3.3 Sample

The sample which was used in the specific heat experiments has been cut from a piece of material used in a previous investigation of the specific heat [6]. The specific heat in the superconducting state in zero field is well described by $C_p = \gamma_0 T + \beta_{el} T^3$. Earlier measurements of the specific heat of UBe$_{13}$ had indicated that $C_p$ is sample dependent such that the apparent linear term $\gamma_0 T$ arises from resonant scattering at impurities, imperfections, etc. [22, 30, 40, 45, 67]. The fit parameters $\gamma_0$ and $\beta_{el}$ of the zero-field data presented here are consistent with those obtained in earlier measurements [30].
4 Differential Conductivity of UBe$_{13}$–Au Contacts

4.1 Introduction

In recent years, quasiparticle tunneling from a normal metal to an unconventional superconductor has been the object of many theoretical investigations [68–70]. It has been shown that in unconventional superconductors, low energy Andreev surface bound states, which consist of an electron which is converted into a hole and vice versa by multiple Andreev reflections, may exist at the interface of a normal metal–unconventional superconductor contact. Such bound states are expected to drastically enhance the differential conductivity through the contact at zero bias and thus to cause a rather sharp zero-bias conductance peak (ZBCP) in the conductivity curve of a normal metal–unconventional superconductor contact. The observation of such ZBCPs may therefore be used to identify an unconventional gap-function of a superconductor. The observation of ZBCPs at the normal metal–unconventional superconductor interface has previously been reported for the high-temperature superconductor YBCO [71–77].

In this chapter, we report on measurements of the voltage dependence of the differential conductivity $G(V,T)$ of a normal metal–superconductor (NS) contact at temperatures between 0.33 and 1.3 K, where the superconductor is the heavy-electron superconductor UBe$_{13}$, in polycrystalline form, and the normal metal electrode is pure Au. The observation of very pronounced ZBCPs provides strong evidence for an unconventional energy-gap function in the cubic heavy-electron superconductor UBe$_{13}$.
4.2 Andreev Reflections in NS Contacts

A quasiparticle scattering process which occurs at normal metal–superconductor interfaces (NS contacts) and which is central to the understanding of tunneling phenomena in NS structures is known as Andreev or electron-hole reflection [78]. In earlier work, Blonder, Tinkham and Klapwijk (BTK) [79] investigated in detail the process of Andreev reflections at the NS interface, where the involved superconductor was assumed to be of conventional $s$-wave type. They used the Bogoliubov equations and employed a generalized semiconductor model to treat the reflection and transmission process of quasiparticles at the interface. In the high transparency limit, an excess conductivity, generated by Andreev reflection, was found and calculated to be twice as large as in the normal state of the NS contact. The analogous problem, but for $S$ being an unconventional superconductor, has first been investigated by Bruder [80]. More recent theoretical work has shown that in unconventional superconductors, low energy Andreev bound states may exist at the NS interface [68–70, 81], leading to a strongly enhanced conductivity at zero bias. In this section, we briefly review the properties of the quasiparticle tunneling at the normal metal–unconventional superconductor interface, following closely the work of Honerkamp and Sigrist [68].

In Fig. 4.1, the different reflection and transmission processes at the NS interface of a quasiparticle, approaching the interface from the normal metal side, are sketched. The barrier potential is located at $x = 0$ and assumed to be of the form $H \delta(x)$, whereas the gap function is given by a step function, $\Delta(k, x) = \Theta(x) \Delta(k)$, where $\delta$ is Dirac’s $\delta$-function and $\Theta$ the Heavyside function. Two types of reflection processes have to be considered for the electron, injected from the normal side (N) with energy $E$. The normal reflection (with amplitude $b$), where the incoming electron is reflected as an electron, or the Andreev reflection (amplitude $a$) [78], where the incoming electron is reflected as a hole-like particle, are shown in Fig. 4.1 as $\psi_b$ and $\psi_a$, respectively. Therefore, the wave function on the normal side (N) is given by the sum of the wave functions of the injected

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*a We use the term “normal state” for the contact when the quasiparticle energy is bigger than the energy gap of the superconductor ($eV > \Delta(T)$).
4.2 Andreev Reflections in NS Contacts

Figure 4.1: Schematic illustration of transmission and reflection processes in NS contacts. The solid lines represent the momenta and the dashed lines the group velocities of the different particles.

The wave function on the superconducting side is therefore given by

\[ \psi_S = c\psi_c + d\psi_d. \]  

(4.2)

Since the system is translationally invariant for the direction parallel to the interface, the momenta parallel to the surface are conserved. In this overview, all the trajectories given
in Fig. 4.1 are assumed to be in the xy-plane and the out-of-plane momenta become zero. In the usual two-component notation, which is commonly used to describe the state of a superconductor, with the upper component for the electron and the lower for the missing electron, the x-dependent parts of bulk solutions of the Bogoliubov-de Gennes equations are given by

\[
\Psi_{inc} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ik_x x} \\
\Psi_a = \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{ik_x x} \quad \quad \Psi_b = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-ik_x x} \\
\Psi_c = \begin{pmatrix} u(\phi) \\ \eta^*(\phi) v(\phi) \end{pmatrix} e^{ik_x x} \quad \Psi_d = \begin{pmatrix} (\eta(\pi-\phi) v(\pi-\phi) \\ u(\pi-\phi) \end{pmatrix} e^{-ik_x x},
\]

where the functions \( u \) and \( v \), which depend on the angle of incidence \( \phi \) and the energy \( E \), are given by

\[
u(E, \phi) = \sqrt{\frac{1}{2} \left( 1 + \frac{\sqrt{E^2 - |\Delta(\phi)|^2}}{E} \right)}
\]

\[
u(E, \phi) = \sqrt{\frac{1}{2} \left( 1 - \frac{\sqrt{E^2 - |\Delta(\phi)|^2}}{E} \right)}.
\]

The quantity \( \eta(\phi) = \Delta(\phi)/|\Delta(\phi)| \) denotes the gap phase, which is different for different states and spin channels and only determined up to an angle-independent constant. Matching the bulk solutions given in Eq. (4.3) at the interface with the usual boundary conditions, one finds for the reflection coefficients

\[
a(E, \phi) = \frac{\eta^*(\phi) v(E, \phi) u(E, \pi - \phi)}{u(E, \phi) u(E, \pi - \phi) + Z^2(\phi) h(E, \phi)}
\]

\[
b(E, \phi) = \frac{(Z^2 + iZ) h(E, \phi)}{u(E, \phi) u(E, \pi - \phi) + Z^2(\phi) h(E, \phi)}
\]

with

\[
h(E, \phi) = u(E, \phi) u(E, \pi - \phi) - \eta^*(\phi) \eta(\pi - \phi) v(E, \phi) v(E, \pi - \phi)
\]
4.2 Andreev Reflections in NS Contacts

and \( Z(\phi) = H/(v_F \cos(\phi)) \), which measures the direction dependent strength of the barrier. Eq. (4.6) vanishes for

\[
\eta^*(\phi) \eta(\pi - \phi) = \frac{u(E, \phi)u(E, \pi - \phi)}{v(E, \phi)v(E, \pi - \phi)},
\]  

(4.7)

in which case the effect of the boundary barrier in the reflection amplitudes (Eq. (4.5)) is eliminated, leading to \(|a(E, \phi)|^2 = 1\). This corresponds to a resonance and leads to a bound state at the NS interface in the low transparency limit. The occurrence of this bound state can be understood by a simple model. We consider a one-dimensional NS contact, where the incoming electron-like quasiparticle is Andreev reflected as a hole-like quasiparticle at the superconductor and subsequently normal reflected at the normal metal. The hole-like quasiparticle, which travels in the same direction as the incoming quasiparticle, is Andreev reflected at S as an electron-like quasiparticle and then normal reflected at N, which restores the original situation. Since we are only interested in the Andreev reflections, this corresponds to the situation of a superconductor-normal metal-superconductor (SNS) structure, where the isotropic pairing potentials on the left and the right side are given by \( \Delta_l = \Delta_0 \eta(0) \) and \( \Delta_r = \Delta_0 \eta(\pi) \), respectively, to take the opposite signs of the momenta of the electron- and hole-like quasiparticle into account. \( \Delta_0 \) denotes the gap amplitude, which shall be equal on both sides. The energy of the considered quasiparticle shall be less than the amplitude of the pairing potential on both sides, such that the quasiparticle is confined between the superconductors. Since the Andreev reflection probabilities \(|a|^2 = 1\), the confined quasiparticle travels along a closed path by repeating Andreev reflections at the SN interface on the left side and the NS interface on the right side of the SNS structure. The quasiparticle experiences an energy dependent phase shift at each Andreev reflection process. A bound state is formed, if the accumulated phase on one round trip is an integer multiple of \( 2\pi \). This condition resembles the resonance condition in Eq. (4.7) in the limit \( d_n \to 0 \), where \( d_n \) is the thickness of the normal layer.

According to Eq. (4.7), the energy of possible surface bound states depends strongly on the phase-factor between the incoming and reflected quasiparticle, \( \eta^*(\phi) \eta(\pi - \phi) = e^{i\Delta \phi} \), where \( \Delta \phi \) denotes the phase-difference, which is determined by the gap-function of S. In unconventional superconductors the quasiparticles might feel different signs of the pairing potential depending on the direction of their momenta. For the triplet states, considered in Refs. 68 and 69, the bound state energy for sufficiently small angles of
incidence was calculated to be at $E \approx 0$. In conventional $s$-wave superconductors, the resonance or bound state condition (Eq. (4.7)) can only be satisfied by a quasiparticle with the energy $E = \Delta$.

According to the BTK-model [79], the conductance of the contact may now be calculated from the probability amplitudes (Eq. (4.5)) as

$$g^s(E, \phi) = 1 + |a^s(E, \phi)|^2 - |b^s(E, \phi)|^2. \quad (4.8)$$

The superscript $s$ denotes the spin-channel. In order to get the total conductance of the NS contact, we have to average over a distribution of directions of incoming electrons and to sum over all possible spin-channels $s$. Since in unconventional superconductors low-energy bound states at the NS interface may exist, the conductance of the NS contact may be strongly peaked around zero bias, whereas in conventional superconductors, where the resonance energy is equal to the energy gap amplitude, the conductance may be peaked at $E = \Delta$.

### 4.3 Kondo-Type Exchange Scattering in NN Contacts

Anomalous behaviour of the current–voltage (IV) characteristics of various normal metal–normal metal (NN) contacts centered at zero-bias has been observed in the past. An enhancement of the differential conductivity $G$ around zero-bias in Al–Ta contacts was reported by Wyatt [82]. The anomalies found by Wyatt were peaks in the conductance with logarithmic temperature and voltage dependences. The zero-bias anomalies persisted, and in fact changed very little, when the superconductivity in both materials was either quenched by a magnetic field or the temperature of the contact was above the critical temperature of the superconductor involved. Enhancements of the differential conductivity around zero-bias, similar to those found in NN contacts, have been reported at the same time by Logan and Rowell for semiconductor $pn$ junctions [83]. A number of theoretical attempts have been made to explain the formation of such anomalies. An explanation based on spin-flip scattering from localized impurities at the interface has been suggested by Suhl [84]. Independent of this work, a more complete treatment of the problem, also
based on the existence of localized spins at the interface has been put forward by Anderson [85] and by Appelbaum [86, 87]. In addition to the spin-flip scattering, their model also involves interference terms depending on the spin-flip reflection. With their model, they were able to reproduce the main features of the anomalies found in the NN contacts by Wyatt [82]. In this section, we will briefly review their approach.

An idealized contact, metal A–interface area–metal B, is considered. The interface hosts localized, paramagnetic states with a concentration $N$ per unit area. It is assumed that the conduction electrons are exchange coupled to these localized magnetic states at the interface. Some of the current across the junction is affected by exchange scattering off these localized magnetic states. The Hamiltonian of this system may be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1,$$

where $\mathcal{H}_0$ describes the single-particle conduction-electron energies on both sides of the contact, and $\mathcal{H}_1$ the different transfer contributions from A to B, which will be treated by perturbation theory. There are several possible paths an electron can take from A to B. The electron can travel without any interaction with the localized spins at the interface, which leads to a tunneling matrix element $T$, or can scatter from the localized states without spin exchange (matrix element $T_a$). This leads to 1st order terms in the conductivity, $G^{(1)}$, which are neither voltage nor magnetic field dependent. The scattering process involving spin exchange between the electron and the localized state at the interface ($T_{h_a}$), only contributes to 2nd or higher order terms for the conductivity and leads to a magnetic field dependent term in the 2nd order contribution to the conductivity, $G^{(2)}$, which is, in zero field, still independent on the energy of the electron. The terms in the conductivity, which may cause a zero-bias anomaly in zero field, i.e., which depend on the voltage, only contribute to the 3rd order terms in the conductivity $G^{(3)}$. This anomalous contribution originates from an interference between the transmitted electron ($T_{h_a}$) and the electron, which is backscattered by the exchange interaction $J_a$. It has been derived in detail by Appelbaum in Ref. 87, with the result that

$$G^{(3)} = -cT_a^2 J_a \rho^A \rho^B S(S+1) F(eV),$$

where $\rho^A$ and $\rho^B$ are the electron densities of states in A and B, respectively, $S$ is the spin of the localized state, and $F(eV)$ is a function of the Fermi energy $eV$.
where $S$ is the spin of the localized states, $c$ a positive constant and $\rho^{A,B}$ the electronic densities of states on side $A$ and $B$, respectively. The function $F(x)$ is given by

$$
F(x) = -\int_{-\infty}^{\infty} d\varepsilon \frac{\partial f}{\partial \varepsilon} \int_{E_0}^{E_F} d\varepsilon' \rho^A(\varepsilon') f(\varepsilon') \frac{1}{\varepsilon' - \varepsilon},
$$

where $f$ is the Fermi-Dirac distribution function, $E_F$ the Fermi-energy and $E_0$ a cutoff energy. We note, that the function $F(x)$ depends implicitly on the temperature via $f$. In the limit of $eV \gg k_BT$, $F(x)$ may be approximated by [87]

$$
F(x) \approx \rho^A(E_F) \ln \left(\frac{|x| + k_BT}{E_0}\right).
$$

The term $G^{(3)}$ (Eq. (4.10)) leads to an unusual temperature and voltage dependence of the differential conductivity $G$. It has been shown by Appelbaum [86, 87] that the zero-bias contribution to $G^{(3)}$, $G^{(3)}(0,T)$, varies logarithmically with $T$ as

$$
G^{(3)}(0,T) \sim -\ln(T).
$$

It is useful for further discussions to consider the difference between $G$ at non-zero bias and $G$ at zero bias at a given temperature $T$ and normalize it by the $T$-independent contribution to $G$ at zero-bias, $G_0(0)$, as follows

$$
G_n(V,T) = \frac{G^{(3)}(V,T) - G^{(3)}(0,T)}{G_0(0)}.
$$

In general, the $T$-independent contribution $G_0$ to $G$ may be voltage dependent [82], but in our case, which will be discussed below, $G_0$ does not depend on the voltage and is directly determined by $G(V,T)$ at temperatures, where $G(V,T)$ is constant. According to Eqs. (4.10) and (4.12), the normalized differential conductivity $G_n$ is, in the limit of $\frac{eV}{k_BT} \gg 1$, given by a universal function $G^*$ of the parameter $\frac{eV}{k_BT}$ as

$$
G_n(V,T) = G^* \left(\frac{eV}{k_BT}\right) \sim \ln \left(\frac{eV}{k_BT}\right).
$$
In the following discussion we will use this universality not only for $eV/k_BT \gg 1$, which may be justified numerically. Using Eq. (4.11) and (4.14), we have numerically evaluated $G_n(V,T)$ for various temperatures and voltages. The results of these calculations are shown in Fig. 4.2, from which it may immediately be seen, that the universality (Eq. (4.15)) holds not only at $eV/k_BT \gg 1$, but over an extended range of $eV/k_BT$. It is important to note that the universal function $G^* \left( \frac{eV}{k_BT} \right)$ does not depend on the cutoff energy $E_0$.

![Figure 4.2: Numerical evaluation of $G_n$ for various temperatures of interest in this work using Eq. (4.11).](image)

**4.4 Differential Conductivity Measurements**

The UBe$_{13}$ polycrystal and the sharp Au tip were prepared as described in section 3.2.4. By means of the mechanical feedthrough, the sharp Au-tip was moved towards the crystal...
until it touched, with only tiny pressure, the cleaned surface of the UBe$_{13}$ sample. Neither the sample surface nor the Au-tip was deformed during the experiment, ruling out the possibility of strong pressure effects being involved [88]. The tip-radii of the Au-tips were typically of the order of 10-50 μm, much larger than the average grain-size of the polycrystal. Several different contacts with different normal-state conductances and at various places on our sample, as well as on other UBe$_{13}$ specimens were formed and investigated. All the results were qualitatively similar and therefore, only one set of measurements is presented and discussed here. A detailed description of the procedure to measure the differential conductivity $G$ is given in section 3.2 on page 21ff.

In Fig. 4.3 we show the measured zero-field differential conductivity $G(V,T) = \frac{dI}{dV}(V,T)$ of a UBe$_{13}$–Au contact at various temperatures between 0.33 and 1.3 K as a function of the energy $E = eV$. In the inset, the differential conductivity at zero bias $G(0,T)$ is plotted as a function of temperature. The distinct change of slope $\partial G(0,T)/\partial T$ at $T = 0.905$ K provides an accurate measurement of the transition temperature $T_c$ into the superconducting state of UBe$_{13}$.

At the lowest temperatures, we note very pronounced ZBCPs in $G(E,T)$. The height of this peak decreases with increasing temperature up to $T = T_c$, where it vanishes. Therefore, we conclude that the ZBCP, which is only observed for $T < T_c$, must be related to the superconductivity of the heavy-electron compound UBe$_{13}$. At temperatures above $T_c$, the conductivity at zero bias is still enhanced if compared with the conductivity at large energies, but this broad anomaly is much less pronounced than the anomaly at temperatures below $T_c$. The zero-bias anomaly at $T > T_c$ is, as will be shown below, of different origin than the ZBCP below $T_c$, and is not directly related with the superconductivity of UBe$_{13}$.

4.4.1 $G(E,T)$ for $T > T_c$

We first focus on the “high temperature” part of the $G(E,T)$ measurements. At temperatures above $T_c$, the measured differential conductivity $G(V,T)$ may be separated into a
Figure 4.3: A representative set of measured differential conductivities of a UBe$_{13}$–Au contact vs. energy $E = eV$ at various temperatures. The curves are vertically shifted for clarity. For energies $|E| > 0.6$ meV, the data are identical within experimental errors at all temperatures. The inset shows the measured differential conductivity at zero energy vs. $T$. Its sharp rise was used to identify the superconducting transition temperature as $T_c = 0.905$ K.

$T$-independent term $G_0(V)^b$ and a temperature dependent term $\Delta G(V,T)$:

---

$^b$ The $T$-independent term $G_0$ does not depend on the voltage and is directly determined by $G(V,T)$ either at high temperatures or large voltages, where $G(V,T)$ is constant.
\[ \Delta G(V,T) = G(V,T) - G_0(V). \] (4.16)

\( \Delta G(V,T) \) is enhanced around zero-bias and therefore responsible for the observed, broad zero-bias anomaly at \( T > T_c \). As already discussed in section 4.3, such zero-bias anomalies were first reported for NN contacts [82] and were interpreted as being due to a Kondo-type exchange scattering at the interface [85–87]. Below, we will demonstrate that \( \Delta G(V,T) \) is rather well described by this exchange scattering model.

\[ \begin{align*}
E / T \text{ (eV/K)} & \\
\ln T \text{ (K)} & \\
G_n & \\
\end{align*} \]

Figure 4.4: The normalized conductivity \( G_n \) (see text) vs. \( E / T \), where \( E = eV \), at \( T = 0.96, 0.99, 1.03, 1.06, 1.10 \) and \( 1.12 \text{ K starting from below} \). The inset shows the differential conductivity at zero energy, \( G(0) \) vs. \( \ln(T) \) at \( T > T_c \). The solid line is a linear fit to the data.

It has been argued that the differential zero-bias conductivity due to this effect, \( G^{(3)}(0,T) \), should vary logarithmically with temperature as \(-\ln(T)\) (Eq. (4.13)). Thus, we have plotted the measured \( G(0,T) \) data vs. \( \ln(T) \) in the inset of Fig. 4.4. The solid line in this graph represents a linear fit to the data. As discussed above, the normalized Kondo-term \( G_n(V,T) \) (Eq. (4.14)) is given by the universal function \( G^\ast(eV/k_BT) \) (see Fig. 4.2).
In order to test this scaling prediction, we have calculated the normalized Kondo-term $G_n$ using Eq. (4.14) and assuming $G^{(3)} = \Delta G$. The result of this calculation is shown as a function of $eV/T$ for various temperatures $T > T_c$ in Fig. 4.4. It may be seen that for a certain range of $E/T$ the curves indeed collapse onto a single common curve, as expected for Kondo-type scattering at the interface of a NN contact.

![Graph showing universal curve of the normalized Kondo-term $G_n$ of a UBe$_{13}$-Au contact derived from differential conductivity measurements at $T > T_c$ on linear scale (crosses). The solid line was calculated using Eq. (4.11). The inset shows the same curves on a logarithmic $E/T$-axes, demonstrating the logarithmic behaviour of $G_n$ at $eV/k_B T \gg 1$, which corresponds in our case to $E/T \gg 8.6 \times 10^{-5}$ eV/K. The dashed line is a logarithmic fit to the data in the range $2.2 \times 10^{-4} < E/T < 5 \times 10^{-4}$ eV/K.]

Figure 4.5: Universal curve of the normalized Kondo-term $G_n$ of a UBe$_{13}$-Au contact derived from differential conductivity measurements at $T > T_c$ on linear scale (crosses). The solid line was calculated using Eq. (4.11). The inset shows the same curves on a logarithmic $E/T$-axes, demonstrating the logarithmic behaviour of $G_n$ at $eV/k_B T \gg 1$, which corresponds in our case to $E/T \gg 8.6 \times 10^{-5}$ eV/K. The dashed line is a logarithmic fit to the data in the range $2.2 \times 10^{-4} < E/T < 5 \times 10^{-4}$ eV/K.

In order to compare the experimentally established universal curve with the theoretical predictions of Appelbaum [87] discussed in section 4.3, we show in Fig. 4.5 the universal curve derived from our data vs. $E/T$ together with the numerically evaluated function $G_n$, using Eq. (4.11). We recall that the only free parameter in fitting the calculated curve to the experimental data is a proportionality factor. The agreement
between the measured data and the calculation is excellent. In the limit $eV/k_B T \gg 1$, i.e., $E/T \gg 8.6 \cdot 10^{-5} eV/K$ in our case, this universal function $G^*(x)$ can be approximated by $-\ln(x) [85-87]$. This is demonstrated by the inset of Fig. 4.5, where the measured and the calculated $G_n$ data are shown vs. $E/T$ on logarithmic scale. The logarithmic behaviour is indicated by the dashed line, which represents a linear-in-$\ln(E/T)$ fit to the data at large values of $E/T$. Above a certain limit of $E/T$, this universality fails [82].

The observed agreement between the $G_n$ data, calculated on the basis $G^{(3)} = \Delta G$ for $T > T_c$ and the theoretical predictions for the Kondo-like exchange scattering model, thus suggests that the zero-bias anomaly in $G(V,T)$ observed in our experiments at temperatures $T > T_c$ is of similar origin as the one previously described in Ref. 82.

4.4.2 $G(E,T)$ for $T < T_c$

The situation for temperatures $T < T_c$ is more complicated. Of course, the Kondo-type scattering observed for $T > T_c$ may also contribute to the differential conductivity at $T < T_c$. To estimate a possible contribution to $G(V,T)$ due to Kondo-type scattering at the interface at $T < T_c$, we assume that the normalized Kondo-term $G_n$ at $T < T_c$ is, as for $T > T_c$, still given by the universal curve $G^*(E/T)$ (see Fig. 4.5), thus using Eq. (4.14) we find for the Kondo contribution

$$G_K(V,T) = \left( G^* \left( \frac{eV}{k_B T} \right) G_0(0) \right) + G_K(0,T) - G_0(0) + G_0(V). \quad (4.17)$$

The background contribution $G_0$ does not depend on the temperature and is therefore the same above and below $T_c$. The Kondo-related differential conductivity at zero bias $G_K(0,T)$ was evaluated by extrapolating the $\ln T$-behaviour found at $T > T_c$ (see inset of Fig. 4.4 and Eq. (4.13)) down to lower temperatures. In Fig. 4.6, we show the measured data of $G(V,T)$ at the lowest temperature reached in this study. The solid line indicates the calculated estimate of the Kondo-type exchange scattering term $G_K(V,T)$, extrapolated from the data above $T_c$ as explained above. The zero-bias anomaly due to this term is much smaller than the observed ZBCP, and its height as well as its shape differs substantially from the measured data. Although it is not a priori clear, how the Kondo-type exchange scattering term influences $G(V,T)$ in the superconducting state, where the large
4.4 Differential Conductivity Measurements

Figure 4.6: Differential conductivity of a UBe$_{13}$-Au contact at $T = 330$ mK. The solid line shows the estimated Kondo-contribution $G_K(E = eV, T)$ as discussed in the text. The vertical arrows indicate the onset of the sharp drop of $G(E)$, which is used to identify a lower limit of the energy gap.

enhancement of the differential conductivity around zero bias is observed, we nevertheless argue that a possible influence would be small and would not significantly influence the results of our discussion below.

In conventional $s$-wave superconductors, Andreev reflections at the interface between a conventional superconductor and a normal metal may also lead to an enhancement of the conductivity at zero bias, compared to the normal-state conductivity of the contact. The conductivity at zero bias can, however, never be larger than twice the normal-state conductivity and is only realized in a highly transparent junction at $T \ll T_c$ [79]. The ZBCP observed in our experiment (Fig. 4.6) is, with $G(0)/G(E \gg \Delta) \approx 10$, clearly much more pronounced. We are not aware that enhancements of the differential conductivity at zero bias of comparable size have been observed in any NS contact before.
This very pronounced ZBCP is certainly related with the superconductivity in the heavy-electron superconductor UBe$_{13}$, because it is only present below $T_c$, which is seen by observing its height vs. temperature in the inset of Fig. 4.3. Unfortunately, no theoretical calculations of the differential conductivity in cubic systems have been reported, but considering previous theoretical calculations for various types of order parameters belonging to different irreducible representations of other crystal symmetries [68–70], this very pronounced ZBCP clearly indicates the existence of low-energy bound states at the surface, forming only, if the symmetry of the energy gap function is non-trivial, i.e., such that the quasiparticles feel different signs of the pairing potential depending on the direction of their motion.

Another feature indicating the unconventional nature of superconductivity in UBe$_{13}$ is the sharp drop of $G(V,T)$ at an energy $E_{\text{drop}}$, marked by vertical arrows in Fig. 4.6. The occurrence of this sharp feature does not depend on the measuring conditions, ruling out the possibility of local heating effects being involved [89]. Again, a sharp drop followed by a steep increase of $G(V,T)$ towards small energies cannot be explained by assuming conventional superconductivity [79]. Our experimental results are reminiscent of the results of calculations for several unconventional pairing states [68–70], but a more detailed analysis requires additional numerical work.

### 4.5 Energy Gap of UBe$_{13}$

Depending on the exact symmetry of the gap function and the current directions, the sharp drop of $G(E,T)$ is expected to occur at different energies, but $E_{\text{drop}}/|\Delta(T)| \leq 1$ in all cases [68–70], where $|\Delta(T)|$ denotes the gap amplitude which will be abbreviated by $\Delta(T)$ in the following discussion. Hence, we may use the observed sharp drop of $G(E,T)$ for establishing a lower limit for the energy gap amplitude $\Delta(T)$ of UBe$_{13}$. In Fig. 4.7, we show the calculated ratio $\frac{2\Delta(T)}{k_BT_c}$ vs. $T$ as closed circles. We are not aware of any other measurements providing data of similar quality on the amplitude and temperature dependence of the energy gap in the heavy-electron superconductor UBe$_{13}$. In the BCS weak coupling limit, which applies for a large variety of conventional superconductors, the value of the ratio at $T = 0$ has been calculated to be $\frac{2\Delta(0)}{k_BT_c} \approx 3.5$. Using a generalized BCS theory for more complex pairing states than $s$-wave states, it can be shown that
4.5 Energy Gap of UBe$_{13}$

\[ \frac{2\Delta(0)}{k_B T_c} < 3.5 \] [57]. In spite of the lack of data for $T < 0.33$ K, we may compare the BCS ratio at $T = 0$ with the value obtained for UBe$_{13}$ at $T = 0.33$ K.

From $\Delta(T = 0.33\text{K})$ we conclude that $\frac{2\Delta(0)}{k_B T_c} > 6.7$ for UBe$_{13}$, much in excess to the BCS weak-coupling limit. Since this ratio is a measure for the strength of the coupling in the pair formation, we argue that our observation gives convincing additional support for unusual strong coupling effects in UBe$_{13}$. This has already been concluded from specific heat measurements [6], where an unusual large value of the discontinuity $\Delta C$ at $T_c$ was observed and, more recently, from measurements of the pressure dependence of $H_{c2}$ [37].

To compare the temperature dependence of our results of the lower limit of the energy gap amplitude with the BCS gap function, we calculated $\frac{2\Delta_{BCS}(T)}{k_B T_c}$, following Ref. 90. The result of this calculation is shown as open triangles in Fig. 4.7. We note that $\Delta_{BCS}(T)$

---

**Figure 4.7:** The circles show the normalized superconducting energy gap amplitude of the heavy-electron superconductor UBe$_{13}$ (see text) and the triangles indicate the BCS weak coupling expectation for $\Delta(T)$. 

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<thead>
<tr>
<th>$T$ (K)</th>
<th>$2\Delta(T)/k_B T_c$</th>
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does not match our experimentally established \( \Delta(T) \) for UBe\(_{13}\). Despite of the fact that the BCS-approach, which has been used above, is only valid in the weak-coupling limit, we scaled up \( \Delta_{\text{BCS}}(T) \), such that \( \Delta_{\text{BCS}}(T = 0.33 \, K) = \Delta_{\text{UBe}_{13}}(T = 0.33 \, K) \). This is shown by the solid line in Fig. 4.7, again demonstrating the different behaviour of the energy gap of UBe\(_{13}\) compared with the BCS-solution. While the BCS gap at \( T < T_c/3 \) is almost constant, the measured gap-values of UBe\(_{13}\) still increase with decreasing temperature in this range.

### 4.6 Conclusions

We have measured the differential conductivity \( G(E,T) \) of a UBe\(_{13}\)–Au contact at temperatures below and above the superconducting transition temperature \( T_c \) of the heavy-electron superconductor UBe\(_{13}\). At \( T > T_c \), a broad zero-bias anomaly was observed. This enhancement of \( G(E,T) \) around zero-bias is very reminiscent of previous observation that have been traced back to a Kondo-like exchange scattering process which may happen at a NN interface with localized spins at the interface. At \( T < T_c \), our experiments, which provide the first phase-sensitive test of the superconducting order parameter of UBe\(_{13}\), clearly indicates the existence of low-energy Andreev surface bound states in UBe\(_{13}\), manifest by the huge ZBCP observed in the \( G(V,T) \) measurements. The ZBCPs are much larger and different in shape than a possible enhancement of the differential conductivity around zero bias due to the Kondo-like exchange scattering process. Such bound states are a clear and new indication of a non-s-wave symmetry of the gap function.

The evaluation of a lower limit for the superconducting energy gap amplitude leads to the conclusion that the superconducting state in the heavy-electron superconductor UBe\(_{13}\) is related with substantial strong coupling effects. Finally, our experiments provide the first decent data on the amplitude and temperature dependence of the energy gap in superconducting UBe\(_{13}\).
5 Differential Conductivity of UBe$_{13}$–Au Contacts in External Magnetic Fields

5.1 Introduction

In this chapter we report on measurements of the differential conductivity $G(E,T,B)$ of UBe$_{13}$–Au contacts in external magnetic fields up to 7 Tesla and at temperatures between 0.334 and 1.37 K. In the following discussion we will describe the applied external magnetic field by $B$ rather than $H$, using the relation $B = \mu_0 H$. The results are compared with the different models, which were introduced and discussed for the zero-field situation in chapter 4. The field dependence of the very pronounced ZBCP is discussed and the existence of low-energy Andreev surface bound states at $T < T_c$ is confirmed.

The UBe$_{13}$–Au contacts were similar to those described in the previous chapter. For the thermometry in high magnetic fields, a multilayered magnetic shield [66] was used in the same way as discussed in section 3.3.

5.2 Differential Conductivity Measurements

5.2.1 $G(E,T,B)$ for $T > T_c$

We first focus on the temperature region $T > T_c$, in which the observation of a broad zero-bias anomaly in the zero-field differential conductivity $G(E,T)$ of a UBe$_{13}$–Au contact
was reported (see section 4.4). This zero-bias anomaly was interpreted to be due to a Kondo-like exchange scattering at the NN interface. In Fig. 5.1, we show the measured $G(E,T,B)$ data at $T = 1.37$ K for various external fields. The height of the anomaly increases with increasing field and is rather pronounced at the largest fields in this experiment. Below, we compare our experimental results of the differential conductivity measurements, $G(E,T,B)$, in external magnetic fields with the predictions of the Kondo-like exchange model.

![Graph](image-url)

Figure 5.1: A representative set of measured differential conductivities of a UBe$_{13}$-Au contact vs. energy at constant temperature $T = 1.37$ K and at various magnetic fields ($B = 0, 1, 2, 3, 4, 5, 6, 7$ Tesla from the top to the bottom). The curves are vertically shifted for clarity.
5.2 Differential Conductivity Measurements

In section 4.3, the anomalous contribution to \( G \) (Eq. (4.10)) has been discussed in zero-field. In finite magnetic fields, the second-order contribution to the conductivity, \( G^{(2)} \), resulting from scattering processes involving spin exchange \( \langle T_{2v} \rangle \), depends on the energy. Its magnetic field dependent part is given by [87]

\[
G^{(2)} = cT_0^2 \langle M \rangle \frac{1}{2} \left( \tanh \left( \frac{\Delta Z + eV}{2k_BT} \right) + \tanh \left( \frac{\Delta Z - eV}{2k_BT} \right) \right),
\]

where \( \langle M \rangle \) denotes the average magnetisation of the localized spins, \( \Delta Z = g\mu_B H \) is the Zeeman splitting of the localized spin energies and \( \mu_B \) is the Bohr magneton. This contribution is reduced at \( |E| < \Delta Z \) by a factor of \( \frac{5}{5+1} \) compared to the values at large energies. The third order term, \( G^{(3)} \), which is given in zero field by Eq. (4.10), is also strongly influenced by the magnetic field. This term has been calculated by Appelbaum [87] and is given by

\[
G^{(3)} = C \left( (2 - 2a + b_+ + b_-) F(eV) + (1 + a + b_+) F(\Delta Z + eV) + (1 + a + b_-) F(\Delta Z - eV) \right),
\]

where \( C = -cT_0^2 I_0 \rho^a \rho^b S(S+1) \), \( a = \frac{\langle M^2 \rangle}{S(S+1)} \) and \( b_{\pm} = \frac{\langle M \rangle}{S(S+1)} \tanh \left( \frac{\Delta Z \pm eV}{2k_BT} \right) \). The first term causes a decrease of the conductivity at zero bias compared to the zero-field value, whereas the latter terms cause peaks at \( E = \pm \Delta Z \). Taking the energy dependent terms of the second (Eq. (5.1)) and third order contributions (Eq. (5.2)), the anomalous contribution to the conductivity changes from a single peak at zero bias in zero field to a double-peak structure in finite fields.

The differences between the predictions and the measured data (Fig. 5.1) are obvious. The single peak structure in zero field is not transformed into a double-peak structure by applying a magnetic field. On the contrary, the single peak becomes much more pronounced with increasing field and, even at the highest applied fields, no signs of peaks at \( E = \pm \Delta Z \) are observed. Due to the lack of a detailed understanding of the interface layer between the heavy-electron metal UBe_{13} and the ordinary metal Au, it is not possible to establish a numerical value for \( g \) and therefore for \( \Delta Z \), and for that reason, we cannot
exclude that the side peaks might be at $|E| > 2$ meV. This would be rather surprising, because the curves in Fig. 5.1 seem to have reached the energy independent regime already at $|E| \gtrsim 1$ meV.

![Figure 5.2: Zero bias differential conductivity at $T = 1.37$ K vs. magnetic field.](image)

The discrepancy between experiment and the above mentioned model is even more apparent, if the zero-bias conductivity $G(0, T, B)$ at constant $T$ is considered. According to Eq. (5.1) and (5.2), the zero-bias conductivity should decrease significantly with increasing field. In Fig. 5.2, the measured data of $G(0, T, B)$ are shown at a constant temperature $T = 1.37$ K as a function of applied magnetic fields. This clearly demonstrates that, in contradiction to the model calculation, $G(0, T, B)$ increases with increasing field.

These discrepancies between the measured data in Fig. 5.1 and the predictions indicate that the differential conductivity in external magnetic fields may not be explained by
5.2 Differential Conductivity Measurements

using Appelbaum's exchange model in the present form. Nevertheless, we note that the predictions of Appelbaum's exchange scattering model in external magnetic fields were, at least qualitatively, verified in Ta-Al contacts [91]. When calculating the anomalous contributions to the differential conductivity of a NN contact, Appelbaum used several simplifications, which are well justified in ordinary metals, but may be questionable in rather unusual heavy-electron metals such as UBe$_{13}$. The most important point is probably the fact that Appelbaum assumed the electronic density of states to be constant in the vicinity of $E_F$. This may not be true for UBe$_{13}$, where the heavy electrons form a very narrow band at $E_F$ [92,93]. Also, UBe$_{13}$ has a rather large spin susceptibility, which is of the order of $10^2$ times larger than in ordinary metals and leads to a rather strong influence on the electronic density of states in external magnetic fields. Some other problems, such as the large difference of the effective mass between UBe$_{13}$ and Au, or the very different Fermi velocities $v_F$ on either side of the contact, may also require corrections in the model.

Concerning these uncertainties in the applicability of the assumptions made by Appelbaum to the system discussed here, we cannot draw any final conclusions. For a more definitive answer, additional theoretical work going beyond the assumptions, which are questionable in this context, and taking into account the rather different properties of a heavy-electron material on one side and an ordinary metal on the other side of the contact, is required.

5.2.2 $G(E,T,B)$ for $T < T_c$

In Fig. 5.3 and 5.4, the results of differential conductivity measurements of the UBe$_{13}$-Au contact at constant temperatures $T = 334$ and $458$ mK are shown for various magnetic fields up to 7 Tesla. We first focus on the $T = 334$ mK data. At zero field, the very pronounced ZBCP which has been discussed in the previous chapter in the context of the differential conductivity measurements in zero field, is reproduced. With increasing magnetic field, the ZBCP becomes less pronounced and its height decreases. At the largest field of these experiments ($B = 7$ Tesla), the ZBPC cannot be resolved anymore, because it is either masked by another contribution, which becomes dominant above a certain field, or the superconductivity of UBe$_{13}$, which is responsible for the ZBCP, is suppressed.
Figure 5.3: A representative set of measured differential conductivities of a UBe$_{13}$–Au contact vs. energy at constant temperature $T = 0.334$ K and at various magnetic fields ($B = 0, 1, 2, 3, 4, 5, 6, 7$ Tesla from the top to the bottom). The curves are vertically shifted for clarity.

by the large magnetic field. If the height and the width of the ZBCP are traced, it may be seen that the peak ought indeed to be rather small around $7$ Tesla, but still present, and is probably masked by the increasing, broad contribution. From the behaviour of the height and the width of the ZBCP with increasing magnetic field, we can estimate that at this temperature the critical field above which the ZBCP is completely suppressed is $B_{c2} = 7.5 \pm 1$ Tesla. This value is in fair agreement with the literature value of the
upper critical field $B_{c2}$ of UBe$_{13}$ at $T = 334$ mK of approximately 8.5 Tesla [37]. This agreement provides further evidence, that the ZBCP observed in the UBe$_{13}$–Au contacts must be related to the superconductivity in UBe$_{13}$. Finally, the existence of the ZBCP in magnetic fields even close to the critical field $B_{c2}$, provides some evidence that the unconventional superconducting state with a non-isotropic order parameter, which causes
the low energy Andreev surface bound states, is also stable in large external magnetic fields.

The broad anomaly around zero bias, which gives the main contribution at large fields, has also been observed at \( T > T_c \) and was discussed in section 5.2.1. At the lowest fields, where the superconductivity of UBe\(_{13}\) is still rather stable, the differential conductivity seems not to be influenced by this broad zero-bias anomaly, which is compatible with the assumption that this anomalous contribution is due to an exchange scattering at the NN interface.

The same characteristics are observed for the measurements at \( T = 458 \text{ mK} \) (see Fig. 5.4). The ZBCP is less pronounced than at lower temperatures, and it is completely masked already around 4 Tesla. Tracing the height and the width of the ZBCP with increasing field, the critical field at this temperature can be estimated to be \( 5 \pm 1 \text{ Tesla} \). This is also in rough agreement with the upper critical field of UBe\(_{13}\) reported in the literature [37].

### 5.3 Energy Gap of UBe\(_{13}\) in Finite Magnetic Fields

It has already been discussed in connection with the zero field measurements in chapter 4 that the sharp drop, which is observed in the \( G(E, T, B) \) measurements, may be used to establish a lower limit for the energy gap amplitude \( \Delta(T, B) \) of UBe\(_{13}\). In Fig. 5.5, we show the energies at which the sharp drop of \( G(E, T, B) \) occurs, and which we identify with the energy gap amplitude \( \Delta(T, B) \), at the constant temperature \( T = 334 \text{ mK} \) vs. applied magnetic field. Data are only available from 0 to 6.5 Tesla, but if the overall tendency is used to extrapolate the data to higher fields, it may be seen, that the energy gap amplitude \( \Delta(T, B) \) vanishes at around 7.5 to 8 Tesla, which is in rather good agreement with the \( B_{c2} \) value given in the literature [37]. At about 3 Tesla, we note a kink-like feature in the \( \Delta(B) \) curve. At present, the origin of this kink is not clear.

The same procedure has been applied to the differential conductivity measurements at higher temperatures. With increasing temperatures it becomes more difficult to extract
Figure 5.5: The lower limit of the superconducting energy gap amplitude of the heavy-electron superconductor UBe$_{13}$ at a constant temperature $T = 334$ mK vs. applied magnetic field.

decent values of the superconducting energy gap amplitude, and since there are no characteristic differences compared to the behaviour at the lowest temperatures, no plots are shown here.

5.4 Summary

We have measured the differential conductivity $G(E,T,B)$ of UBe$_{13}$-Au contacts in external magnetic fields up to 7 Tesla at temperatures between 0.334 and 1.37 K. At $T > T_c$, a broad anomaly in $G(E,T,B)$ is observed which increases with increasing magnetic field. Although this anomaly is in excellent agreement with a Kondo-like exchange scattering model in zero field, it does not match the model's predictions for finite fields. However,
these predictions are based on simplifications which might not apply in the present case, where one of the involved metals is a heavy-electron system. At $T < T_c$, the differential conductivity data clearly reveals the existence of low energy Andreev surface bound states via the huge ZBCP. The ZBCP persists up to fields close to the upper critical field of the heavy-electron superconductor UBe$_{13}$, which demonstrates that the non-isotropic order parameter, which causes the low-energy bound states, is stable even in very large fields. Finally, we have established a lower limit of the superconducting energy gap amplitude of UBe$_{13}$ as a function of the applied magnetic field at constant temperatures.
6 Properties of the Magnetic Field Induced Specific Heat of UBe$_{13}$

6.1 Introduction

The magnetic field induced contribution to the specific heat $C_p(T, B)$ of a superconductor with gap nodes strongly depends on the topology of these nodes. Measurements of the specific heat in external magnetic fields may therefore directly serve as a tool for investigating the topology of the gap nodes [8]. In several recent specific heat studies of the high-$T_c$ superconductor YBCO [94–97], the magnetic field induced contribution to the specific heat has been investigated and found to match the predictions for a $d$-wave superconductor with line nodes in the quasiparticle excitation spectrum. Similar experiments were made on the heavy-electron superconductor UPt$_3$ and some evidence for line nodes of the gap was found [98]. In order to test the predictions in connection with the unconventional and strongly type-II heavy-electron superconductor UBe$_{13}$, the specific heat $C_p(T, B)$ of a small piece of polycrystalline UBe$_{13}$ ($\sim 50$ mg) has been measured in various temperature ranges between 0.08 and 0.38 K and in external magnetic fields between 0 and 7 Tesla. In the following discussion we will describe the applied external magnetic field by $B$ rather than $H$, using the relation $B = \mu_0 H$. In this chapter, we demonstrate the existence of a crossover at $B \approx 2$ Tesla between two different regions in the phase diagram of UBe$_{13}$ and we further demonstrate that for $B > 2$ Tesla, the behaviour of $C_H(T, B)$ of the heavy-electron superconductor UBe$_{13}$ as a function of $T$ and $B$ leads to the conclusion that its superconducting energy gap exhibits point-nodes.
6.2 Electronic Density of States in Magnetic Fields

Unconventional superconductors may condense into a superconducting state where the energy-gap is not isotropic and may be zero at some points in k-space. Such gap nodes (points, lines or even areas where the energy gap is zero) strongly influence the electron density of states (EDOS) at low energies. Whereas at $T \to 0$ the EDOS is zero at $E < \Delta$ in fully gapped superconductors, the existence of gap nodes leads to a power-law dependence of the EDOS on the energy $E$ at low energies, i.e., $E \ll \Delta$ [99]:

$$D(E) \sim D_F \left( \frac{E}{k_B T_c} \right)^{2-D}, \quad (6.1)$$

where $D_F$ denotes the EDOS at the Fermi energy $E_F$ in the normal state and $D$ the dimension of the nodes, i.e., $D = 0$ for point-nodes and $D = 1$ for line-nodes. In the mixed state of a type-II superconductor, i.e., in the presence of a magnetic field $B > B_{c1}$, the supercurrent circulating around the vortices leads to a Doppler-shift $\Delta E_D$ of the energy scale, $E \to E + \Delta E_D = E + v_s(r) \cdot p$, where $v_s(r)$ is the local velocity of the supercurrent and $p$ the momentum of the quasiparticle. For small gap-values, i.e., at and close to the gap-nodes, this Doppler-shift has a dramatic effect on the EDOS at small energies, and leads to a finite EDOS at zero energy even at $T = 0$, depending on the topology of the gap-nodes. In the limit $k_B T \ll \Delta E_D$ and $B \ll B_{c2}$, the EDOS at zero energy is given by

$$D(0) \sim D_F \left( \frac{p_F v_s}{k_B T_c} \right)^{2-D}, \quad (6.2)$$

where $p_F$ denotes the Fermi-momentum and $v_s$ the characteristic value of $v_s(r)$ in the vortex array. It may be shown that $p_F v_s / k_B T_c \sim \sqrt{B / B_{c2}}$ [100], which then leads to

$$D(0) \sim D_F \left( \frac{B}{B_{c2}} \right)^{1-D/2}. \quad (6.3)$$

This expression is valid for line nodes ($D = 1$), but for point-nodes ($D = 0$) only, if the field is exactly parallel to the direction of the nodes. If the field orientation is in an arbitrary
6.3 Specific Heat of UBe$_{13}$ in Magnetic Fields

The magnetic field induced extra-contribution to the EDOS (Eqs. (6.3) and (6.4)) at small energies leads to an additional term to the specific heat at low temperatures, which depends on the applied magnetic field as well as on the topology of the gap-nodes. According to Eqs. (6.3) and (6.4), the extra-EDOS due to the applied magnetic field does not depend on the temperature, and therefore, the magnetic field induced contribution to the specific heat at low temperatures, $C_H(T, B)$, will be linear-in-$T$ and is given by [8]

$$
\frac{C_H(T, B)}{T} \sim \frac{D(0)}{D_F}.
$$

In Fig. 6.1, we show a representative set of the low temperature specific heat of UBe$_{13}$, measured for $0.08 \leq T \leq 0.20$ K and $0 \leq B \leq 7$ Tesla, as a function of temperature measured at constant magnetic fields. A detailed description of the measurement procedure is given in section 3.3 on page 26ff. The slight upturn at low $T$ and high $B$ is due to the nuclear Zeeman contribution of the Be atoms.

We also measured the specific heat at constant temperatures vs. magnetic field. A representative set of these results is shown in Fig. 6.2. We note that $C_p(B)$ at constant $T$ shows a broad shoulder-like feature centered around $B \approx 3$ Tesla. In a recent study [102] of the specific heat of UBe$_{13}$ in external magnetic fields at somewhat higher temperatures, similar features of $C_p(T, B)$ at $B \approx 2$ Tesla have been reported and were interpreted as an indication for the occurrence of a second phase in superconducting UBe$_{13}$. In Ref. 103, the results of thermal expansion and specific heat measurements have been combined to show the existence of an additional feature in the phase diagram of UBe$_{13}$. Below, we find further evidence for the existence of an additional feature in the phase diagram of UBe$_{13}$, which might be related to the shoulder-like feature, but which appears at slightly different $B$. 

$$
\frac{D(0)}{D_F} \sim \ln \left( \frac{B_c^2}{B} \right).
$$

6.3 Specific Heat of UBe$_{13}$ in Magnetic Fields

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In this work, we are mainly interested in the magnetic field induced electronic contribution to the specific heat, \( C_H(T, B) \). The Be nuclei carry a nuclear spin, causing a magnetic field dependent and, especially at high fields and low temperatures, non-negligible contribution to the specific heat, \( C_N(T, B) \), which is proportional to \( B^2 T^{-2} \) and is discussed in great detail in Ref. 104. Aiming only at the magnetic field induced electronic contribution, we consider

\[
C_H(T, B) = C_p(T, B) - C_p(T, 0) - C_N(T, B),
\]

where \( C_p(T, B) \) is the measured specific heat in an applied magnetic field \( B \), \( C_N(T, B) \) the evaluated nuclear contribution and \( C_p(T, 0) \) the measured specific heat in zero field.

This procedure for obtaining the magnetic field induced electronic contribution \( C_H(T, B) \)
6.3 Specific Heat of UBe$_{13}$ in Magnetic Fields

Figure 6.2: Representative data of the as-measured total specific heat of UBe$_{13}$ vs. magnetic field measured at constant temperatures.

to be discussed below, does not depend on any fit parameters or unknown background contributions and, therefore, leads to reliable results of $C_H(T, B)$.

According to Eq. (6.5), in the limit of $T \ll T_c$ and $B \ll B_{c2}$, a possible contribution to the specific heat in the mixed state of a superconductor due to the supercurrent circulating around the vortices should vary linearly with $T$. Thus, we have plotted the magnetic field induced electronic contribution to the specific heat divided by the temperature, $C_H(T)/T$, at constant fields vs. $T$ in Fig. 6.3. The discrepancy between the theoretical predictions and the experimental data is obvious. The model leading to Eq. (6.5) is expected to be valid only in the limit where $k_B T \ll \Delta E_D$, i.e., $x = \frac{T}{T_c} \sqrt{\frac{B^2}{B_c^2}} \ll 1$ [100]. Setting the magnetic field to $B = B_{c2}/5$, which is already at the upper limit of the valid regime, the condition $x \leq \frac{1}{2}$ can only be fulfilled if $T/T_c \leq 0.09$. The critical temperature of the present material is $T_c = 0.91$ K. Thus, for the model to be applicable, the temperature has to be below 0.08 K, the lower limit of the temperature range covered in these experiments.
Figure 6.3: Magnetic field induced electronic contribution to the specific heat $C_H$ in constant magnetic fields divided by $T$ vs. temperature for various fields. According to Eq. (6.5) this quantity should be constant.

This upper limit of the temperature decreases further with decreasing magnetic field and, therefore, in this model's context and using these data, no conclusions concerning the topology of possible gap nodes can be drawn.

### 6.4 Scaling Properties of the Specific Heat in Magnetic Fields

A more general way to analyze the magnetic field induced specific heat has been promoted by Volovik [100] and by Simon and Lee [105]. They showed that the magnetic field induced contribution $C_H(T,B)$ obeys a scaling behavior with respect to the scaling
6.4 Scaling Properties of the Specific Heat in Magnetic Fields

Parameter $x \sim \frac{T}{T_c} \sqrt{\frac{B_{c2}}{B}}$ of the form

$$C_H(T, B) \sim B^{\frac{2-D}{2}} f(x). \quad (6.7)$$

This scaling may be rewritten as

$$\frac{C_H(T, B)}{T^{2-D}B^{1/2}} \sim F(x), \quad (6.8)$$

where $D$ denotes the dimension of the nodes, i.e., $D = 0$ for point nodes and $D = 1$ for line nodes. $F(x)$ is a universal scaling function [100, 105]. According to Eq. (6.5), its asymptotic behavior for $x \ll 1$ is of the form $F(x) \sim x^{D-2}$. This scaling law provides a more general approach to analyze the topology of possible gap-nodes and is independent of considerations concerning the regime of $x$. According to Eq. (6.8), $C_H(T, B)/(T^{2-D}B^{1/2})$ should be proportional to a universal function of the parameter $x \sim \frac{T}{T_c} \sqrt{\frac{B_{c2}}{B}}$. In order to test these scaling predictions, we have plotted our $C_H(T, B)$ data from both sets of measurements ($C_H(T)$ at constant field and $C_H(B)$ at constant $T$) in the form $C_H(T, B)/(T^{2-D}B^{1/2})$ versus $y = T/\sqrt{B}$, setting $D = 0$ and $D = 1$, respectively, for the entire investigated magnetic field range, although this scaling relation may be valid for $T \ll T_c$ and $B \ll B_{c2}$ only.

The result for $D = 0$ is shown in Fig. 6.4. While the open symbols represent the magnetic field scans at constant $T$, the full symbols correspond to the temperature scans at constant field. We may separate the investigated field regime into a low field part ($B < B^* \approx 2$ Tesla) and a high field part. By inspecting Fig. 6.4 it turns out that all the data collapse onto a single common curve, except for those obtained at $B < B^*$, where the scaling behaviour according to Eq. (6.8) is not obeyed at all. We note here, that the difference in field between two plotted curves around the crossover field $B^*$ is the same in the low as well as in the high field regime. The same behaviour is observed for the field-scan data (open symbols in Fig. 6.4). In the high-field regime of the field scan data (i.e., at small $y$-values), the curves for all temperatures collapse onto the previously experimentally established scaling curve, whereas for $B < B^*$, the data deviate from scaling behaviour. We note that in Fig. 6.4 also data for fields up to $B \approx B_{c2}/2$ are shown, but even for the highest fields, the data reveal the scaling behaviour.
6. Properties of the Magnetic Field Induced Specific Heat of UBe$_{13}$

This scaling with respect to the scaling variable $\frac{T}{\sqrt{B}}$ is rather unique and implies the occurrence of nodes in the superconducting energy gap. Since this scaling is appropriate for $D = 0$, we conclude that for $B > B^*$ the energy-gap function of superconducting UBe$_{13}$ exhibits point nodes. It thus appears that the scaling prediction of Eq. (6.8) is more robust than previously expected and might even apply up to $B \approx B_{c2}/2$. In the region in the $B-T$ phase diagram of UBe$_{13}$, at low magnetic fields ($B < B^*$), where no scaling behavior of $C_H(T, B)$ has been established, we cannot make any claims about the topology of possible gap-nodes. We might speculate that some type of crossover between the regions for $B < B^*$ and $B > B^*$ takes place at $B^* \approx 2$ Tesla. This is also apparent, if we consider the derivative of $C_H(T, B)$ with respect to the temperature, which is displayed in Fig. 6.5 as $\frac{\partial C_H}{\partial T} |_{T=\text{const}}$ vs. $B$. At $B < B^*$, the data are rather well described by a power law
as indicated by the solid line in Fig. 6.5, whereas for $B > B^*$, the behaviour is distinctly different. At present, the origin of this crossover at 2 Tesla remains unclear.

Figure 6.5: Derivative of the magnetic field induced specific heat $C_H$ with respect to the temperature at $T = 0.15$ K vs. magnetic field. The solid lines is a power law fit to the data below 2 Tesla, revealing an exponent of $5/3$. A remarkable change may be seen at $B \approx 2$ Tesla, which corresponds to the change of behaviour observed in the scaling-plot (Fig. 6.4).

As a test, the same scaling procedure, but setting $D = 1$, has been applied to both sets of data, and the result is shown in Fig. 6.6. It is immediately seen, that no evidence for a scaling behaviour in the whole investigated magnetic field and temperature range can be established.

We note here that in the mixed state of a superconductor, another contribution to the specific heat might arise from the low lying excitations localized near the core of the vortex. This problem has been discussed for s-wave superconductors by Caroli et al. [106] and by Bardeen et al. [107]. According to that work, the lowest excitation level is expected at $E_0 \approx \frac{\Delta}{E_F}$, where $\Delta$ denotes the energy gap amplitude far away from the vortex. It is well
Figure 6.6: Scaling plot of the magnetic field induced contribution to the specific heat for line-nodes (see text). The open symbols are measurements at constant temperatures ($T = 0.107, 0.147, 0.2$ K from the left to the right) as a function of magnetic field and the full symbols are measurements in constant magnetic fields as a function of temperature ($B = 1.5, 1.7, 2, 2.2, 3, 5, 7$ Tesla, from the bottom to the top).

established that UBe$_{13}$ is a strong coupling superconductor (see section 4.5 of this work or Refs. 6 and 37), which implies an energy-gap amplitude substantially larger than the BCS weak-coupling approximation of $\Delta \approx 1.76 \, k_B \, T_c$. The Fermi temperature of UBe$_{13}$, given by $T_F = \frac{E_F}{k_B}$, is of the order of 10 K [6]. Using these values and the predictions for $s$-wave superconductors, we find the lowest level of the low-energy excitations in the vortex core to be at significantly higher energies than the typical thermal energies $k_B T$ of this experiment. Furthermore, the observed scaling behaviour with respect to $TB^{-1/2}$ is, as discussed above, rather unique, and cannot be associated with the mentioned vortex-core contribution [108].
6.5 Conclusions

In conclusion we note that for magnetic fields $B > 2$ Tesla the magnetic field induced contribution to the specific heat exhibits a scaling behavior with respect to the scaling parameter $T/\sqrt{B}$ which, according to Eq. (6.8) for $D = 0$, suggests the existence of point-like nodes in the superconducting energy gap of UBe$_{13}$. No scaling could be established for the superconducting state of UBe$_{13}$ at low temperatures and $B < 2$ Tesla. Further evidence for some type of crossover at $B \approx 2$ Tesla into another superconducting state was provided by the magnetic field dependence of the temperature derivative of the magnetic field induced specific heat, where a drastic change of behaviour was observed at 2 Tesla. The same data set gives no similarly convincing evidence for the existence of nodes with $D > 0$, in any regime of the $B - T$ phase diagram.
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Bibliography


Bibliography


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