Magnetic Quantum Oscillations in the Organic Antiferromagnetic Superconductor $\kappa$-(BETS)$_2$FeBr$_4$

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Abgabetermin: 25.4.2016
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1 Introduction

In 1911 Heike Kamerlingh Onnes \cite{1} discovered superconductivity by measuring the resistance of mercury down to 4.2 K. With time more and more materials showing superconductivity were discovered, and in 1958 Bardeen, Cooper and Shrieffer developed the microscopic theory for superconductors (SC). They explained superconductivity by pairs of electrons, which are called Cooper pairs, forming a bosonic state and are held together by an attractive exchange interaction. They showed that phonons mediate this positive exchange interaction in conventional superconductors. Today many unconventional superconductors like cuprat, heavy fermion and iron pnictides are known, where the pairing mechanism is not yet understood. In 1964 W. A. Little \cite{2} proposed possible superconductivity in organic superconductors, where a long organic aromatic main chain with polarisable side chains forms a superconductor. The oscillation in the side chains could generate an attractive interaction between the electrons in the main molecule, and provide the attractive interaction giving rise to SC pairing at high critical temperatures. However Little’s theory could so far not be realized, but lead to the discovery of organic superconductors. These superconductors known today are quasi 1D or quasi 2D organic charge transfer salts consisting of an inorganic anion and an organic aromatic molecule, for examples see \cite{3}.

In this thesis we will focus on $\kappa$-(BETS)$_2$FeBr$_4$. $\kappa$-(BETS)$_2$FeBr$_4$ is part of the family of (BETS)$_2$FeX$_4$ where X stands for Cl or Br and the greek letter labels the packing modification of the BETS molecules in the salt. The salts of this family are alternating layers of BETS and FeX$_4$, where the $\pi$ orbitals of the BETS molecules overlap and form conducting bands. The layered structure results in strongly quasi 2D conduction bands. The interest to this family started when superconductivity induced by magnetic field was discovered in $\lambda$-(BETS)$_2$FeCl$_4$ \cite{4,5}. A strong interaction between the $\pi$ electrons and the 3d spins of the Fe ions in $\lambda$-(BETS)$_2$FeCl$_4$ leads to an antiferromagnetic (AFM) type of ordering of the 3d spins and the $\pi$ electrons at low temperatures \cite{6} and even to an insulating ground state. As this insulating ground state is broken by magnetic field $\lambda$-(BETS)$_2$FeCl$_4$ shows an insulator-metal-superconductor transition at low temperatures with rising magnetic field. The main focus in this thesis is on the role of $\pi$-d interactions on the conducting layers more precisely on the effect of internal magnetic fields on the Shubnikov-de Haas quantum oscillations as well as the impact of the AFM ordering on the Fermi surfaces. To investigate these questions we measured Shubnikov-de Haas oscillations in the antiferromagnetic state as well as in the paramagnetic state of the salt, as the salt transfers to a paramagnetic state when the antiferromagnetic ordering is broken by magnetic field. In the AFM state, a slow oscillation has been reported and which has been interpreted as a result of a superstructure due to the AFM ordering. Since only one low frequency Shubnikov-de Haas oscillation has been detected, more experimental evidence is desirable to support this theory and to further...
1 Introduction

clarify the structure of the Fermi surface in the AFM state. Another issue addressed in this thesis is related to the effect of AFM ordering on the different spin subbands of the $\pi$-electron conduction layers. By theory it was proposed that there is no Zeeman splitting for the carriers in antiferromagnetic conductors with small carrier pockets \[7, 8\]. In the paramagnetic state all 3d iron spins are ordered and form an internal field, so we expect Zeeman splitting for the energy levels of the carrier bands in the conducting layers. We investigated the influence of Zeeman splitting on the Shubnikov-de Haas oscillations, and compared it to the behavior predicted by theory.
2 The organic metal \(\kappa-(\text{BETS})_2\text{FeBr}_4\)

2.1 Sample preparation

The single crystals of \(\kappa-(\text{BETS})_2\text{FeBr}_4\), where BETS stands for the organic molecule Bis(ethylenedithio)tetraselenafulvalene, were prepared electrochemically as described in [9]. Therefore, the sections about the crystal structure and band structure, follows closely [9]. BETS and tetraethylammonium iron(III) tetrabromide were dissolved in a 10% ethanol/chlorobenzene solution and for 2-4 weeks a constant current of 0.7\(\mu\)A was applied between the electrodes at room temperature or at 40\(^{\circ}\)C. The grown crystals were thin black plates with typical dimensions of 0.7x0.7x0.05 mm\(^3\). The \(\kappa-(\text{BETS})_2\text{FeBr}_4\) samples used in this experiment were provided by H.Fujiwara.

2.2 Crystal structure

The \(\kappa-(\text{BETS})_2\text{FeBr}_4\) crystals consist of conducting and insulating layers arranged alternating along the \(b\)-axis. The crystal has an orthorombic structure, with the unit cell parameters \(a = 11.5\) Å, \(b = 36.4\) Å and \(c = 8.5\) Å. The unit cell is large along \(b\) direction, as it contains two BETS and anion layers. The isolating layers consist of \(\text{FeBr}_4^-\) anions that carry a magnetic moment and act as an acceptor, while the BETS molecules, which form the conducting layers, act as donor cations. Due to this transfer we call \(\kappa-(\text{BETS})_2\text{FeBr}_4\) a charge transfer salt. Fig. 2.1 shows the BETS molecule and the \(\text{FeBr}_4^-\) anion as well as atom labeling, and Fig. 2.2 shows the crystal structure. Fig. 2.2 a) shows the layered structure of the compound and in Fig 2.2 we see the structure of the BETS layers which are aliened in the typical way of \(\kappa\)-structure, where the BETS molecules are strongly dimerised. Compared to the \(\lambda-(\text{BETS})_2\text{FeCl}_4\) salt, the interaction between the \(\pi\)-conducting electrons of the BETS layer and the \(\text{Fe}^{3+}\) 3d localized spins are weaker in the \(\kappa-(\text{BETS})_2\text{FeBr}_4\) salt. In the conducting layer short S-S and Se-S contacts provide the inter molecular overlap that forms the metallic bands.

![Figure 2.1: Labeling of the atoms in the BETS and FeBr$_4^-$; (taken from [9]).](image-url)
Figure 2.2: (a) Structure of the crystal and (b) orientation of the BETS molecules within the layers in the $\kappa$ configuration (taken from [9]).
2.3 Band structure and electronic properties

![Energy band diagram](image)

Figure 2.3: Band structure of $\kappa$-(BETS)$_2$FeBr$_4$ and Fermi surface in the metallic state; (taken from [9]).

The band dispersion and Fermi surface calculated by Fujiwara et al. [9] from the crystal structure at room temperature, based on the extended Hückel approximation, are shown in Fig. 2.3.

![Fermi surface diagrams](image)

Figure 2.4: 2D representation of the Fermi surface of $\kappa$-(BETS)$_2$FeBr$_4$ (a) in the metallic state above the antiferromagnetic (AFM) transition and (b) in the AFM state (taken from [10]).

There is a significant mid-gap energy in $\kappa$-(BETS)$_2$FeBr$_4$ of 0.68 eV due to the dimerisation and the bandwidth is 1.44 eV. This leads to two effectively half-filled bands resulting in a metallic behavior. The Fermi surface in the metallic state shows a closed circle in the $k_a$-$k_c$ plane. Along the $b$-axis the Fermi surface is a slightly warped cylinder.
2 The organic metal \( \kappa-(\text{BETS})_2\text{FeBr}_4 \)

If we also take into account the other Brillouin zones, we get a closed \( \alpha \) orbit, and open sheets, shown in Fig. 2.4(a), as the neighboring Fermi surfaces have a little gap between them. Under high fields, the electrons can tunnel through this gap, and we get a new orbit called \( \beta \). This effect is called magnetic breakdown (MB). The \( \alpha \) orbit, has an area of 20% of the first Brillouin zone, while the bigger \( \beta \) orbit has an area equal to the first Brillouin zone.

An elegant way to study quasi 2D metals is observing Shubnikov-de Haas oscillations. As we see later in the theory chapter, the amplitude and the observed frequencies reveal a lot of information about the structure of the Fermi surface.

Yet there are two separated \( \beta \) oscillations observed, differing only in about 1% \( \text{[12]} \text{[13, 14, 15]} \) suggested that the two \( \beta \) frequencies are due to an internal magnetic field and, therefore, a result of the spin splitting of the energy levels of the Fermi surface, which we discuss later in the theory section. \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) shows an AFM ordering below a Néel temperature of 2.5K, that coexists with the superconducting (SC) phase. Fig. 2.5 shows the phase diagram for the field and the temperature.

![Phase diagram](image)

**Figure 2.5:** Phase diagram for magnetic field in the \( bc \) plane. Here CAF stands for canted AFM and FISC is field induced superconductivity (taken from [16]).

In the AFM state we have to take the spins into account. By theory \( \text{[16]} \) there are two types of spin arrangement: the horizontal type that doubles the size of the primitive cell and that is more stable than the AFM type which orders vertically and leaves the primitive cell unchanged. In the AFM state the crystal lattice unit cell carries spins shown in Fig. 2.6 where the metallic state unit cell is indicated as solid line. The horizontal type of ordering seen in Fig. 2.6(c) has opposite spins at each boundary of the unit cell in the \( c \)-direction, but the same spins at each end in \( a \)-direction. As the unit cell has a translation symmetry in \( a \) and \( c \) directions we need to modify the original unit cell for the horizontal ordering type and double it in \( c \) direction. Now we have the same spin at each boundary of the unit cell. In the vertical type of ordering Fig. 2.6(b) we already have the same spin at each end of the unit cell. Therefore it stays unchanged.

Assuming the horizontal ordering, the primitive cell in the AFM state, consists of
two metallic-state-primitive-cells. Doubling the volume of the primitive cells leads to half the volume of the first Brillouin zone, and a corresponding folding of the original Fermi surface. This leads to a reconstructed multiple-connected Fermi surface as shown in Fig. 2.4(b). Until today, only the little grey circles shown in Fig. 2.4(b), have been revealed by SdH oscillations. The question is whether they really come from the proposed reconstructed Fermi surface or simply reveal a violation of the metallic Fermi surface from the predicted calculated one. In the former case one would expect more SdH frequencies caused by various orbits on the reconstructed Fermi surface. Assuming the vertical type of ordering, the Fermi surface stays the same as in the paramagnetic metallic state seen in Fig. 2.4(a).

Figure 2.6: The two possibilities of the AFM ordering in \( \kappa \)-(BETS)\(_2\)FeX\(_4\) (taken from [10]).
3 Theoretical background

3.1 Electrodynamics in a magnetic field

We want to give a brief introduction to the model of electron motion in a magnetic field and Shubnikov de-Haas (SdH) oscillations following [11], for a more detailed theory see e.g. [17]. We consider electrons in the vicinity of the Fermi level \( \epsilon_F \), which are responsible for the conducting properties. We further assume that scattering processes can be approximated, simply by introducing a constant relaxation time \( \tau \), which we say is independent of the electron’s momentum and magnetic field. This \( \tau \)-approximation is not always justified as we see later, when we consider the scattering probability with the states an electron can be scattered in. As we will see the number of states an electron can be scattered in varies with magnetic field.

When a magnetic field \( B \) is applied to a metal, the conduction electrons are subject to the Lorentz force

\[ \mathbf{F}_L = \frac{d\mathbf{p}}{dt} = e\mathbf{v} \times \mathbf{B}, \]  

where \( \mathbf{p} \) is the electrons momentum, \( \mathbf{v} \) the velocity and \( e \) the charge. From Eq. \((3.1)\) it follows that the Lorentz force affects the momentum perpendicular to the field, while the component of the momentum parallel to the field \( \mathbf{p}_B \) is constant. As the force is always perpendicular to the velocity, the energy does not change. Therefore the motion of the electron in the momentum space is in the intersection of contours of constant energy and paths of constant \( \mathbf{p}_B \). For low fields the change of the momentum during the scattering time can be neglected, as the trajectory of the electron is only slightly curved. The characteristic radius of curvature (Larmor radius), \( r_L = \mathbf{p}_F/(eB) \), where \( \mathbf{p}_F \) is the Fermi momentum, is much larger than the mean free path \( \ell \). With all this it can be shown that, for a current perpendicular to the field, the relative change in the resistivity is

\[ \frac{\Delta \rho(B)}{\rho(0)} \propto \left( \frac{\ell}{r_L} \right)^2 \propto B^2. \]  

(3.2)

Now we want to look at higher fields where \( r_L \leq \ell \). From eq. \((3.2)\), the momentum of each electron will change within the time \( \tau \). This results in a varying electron velocity \( \mathbf{v}(\mathbf{p}) = \partial \epsilon(p) / \partial \mathbf{p} \). Now the velocity depends on the momentum, and is always perpendicular to the Fermi surface. Using this, we solve the kinetic Boltzmann equation in the presence of both, electric and magnetic field. For our semiclassical \( \tau \)-approximation the solution is the conductivity tensor \( \sigma_{\alpha\beta} \) in the form

\[ \sigma_{\alpha\beta} = -\frac{2e^2\tau}{(2\pi\hbar)^3} \int \frac{df_0}{d\epsilon} v_\alpha(\mathbf{p})v_\beta(\mathbf{p})d\mathbf{p}. \]  

(3.3)
where $\alpha$ and $\beta$ stand for the directions in space, $df_0/d\epsilon$ is the energy derivative of the equilibrium Fermi distribution function and $\overline{v}_\beta(p)$ is the velocity averaged over the scattering time $\tau$:

$$\overline{v}_\beta(p) = \frac{1}{\tau} \int_{-\infty}^{0} v_\beta(p,t)e^{t/\tau} dt.$$ (3.4)

Eqs. (3.3) and (3.4) show us, that the conductivity is determined by the average velocity, which depends on the magnetic field through eq. (3.1) and $v(p) = \partial\epsilon(p)/\partial p$. Equations (3.1), (3.3) and (3.4) allow us to calculate the conductivity numerically and therefore the resistivity provided the dispersion law $\epsilon(p)$ and the velocity $v(p)$ are known. Lifshitz and co-workers have shown that the asymptotic behavior of the conductivity in high magnetic fields is qualitatively determined by the topology of electron orbits on the Fermi surface. Using this, important information about the Fermi surface geometry can be derived from the conductivity.

The electron motion along a closed orbit in $p$-space can be characterized by a cyclotron frequency:

$$\omega_c = \frac{2\pi eB}{(\partial S/\partial \epsilon)p_B} = \frac{eB}{m_c},$$ (3.5)

where $S$ is the orbit area and

$$m_c = \frac{(\partial S/\partial \epsilon)p_B}{2\pi}$$ (3.6)

is the cyclotron mass. Looking at the high-field limit $\omega_c\tau \gg 1$, the electron completes many turns in its orbit around the Fermi surface before being scattered.

The allowed states for electrons in a magnetic field follow the Landau subbands or Landau levels and their energy becomes quantised in the direction perpendicular to the field as

$$\epsilon(n,p_B) = (n + \frac{1}{2})\hbar\omega_c + \frac{p_B^2}{2m_e},$$ (3.7)

where $m_e$ is the free electron mass, $n$ an integer number of the level and $p_B$ the momentum parallel to the field $B$. The electronorbits in the magnetic field follow the intersections of Fermi surface and the Landau subbands.

### 3.2 Shubnikov-de Haas oscillations

The theory of Shubnikov de-Haas (SdH) oscillations is very complex, as one should, in principle, consider a detailed problem of scattering processes modified by a quantizing magnetic field. Fortunately, in our case we can obtain a satisfactory description by following Pippard’s idea that the scattering probability, and hence the conductivity is proportional to the density of states around the Fermi level $D(\zeta)$, the states an electron can scatter into. The density of states oscillates in quantizing magnetic field. It is possible to show (see e.g. [17, 18]) that the $D(\zeta)$ is proportional to the field derivative of the magnetization.

$$\tilde{D}(\zeta) \propto \left(\frac{m_e B}{S_{extr}}\right)^2 \frac{\partial \tilde{M}}{\partial B},$$ (3.8)
3.2 Shubnikov-de Haas oscillations

where $S_{\text{extr}}$ is the Fermi surface with the biggest or smallest area. Using this, the oscillatory part of the conductivity can be expressed in the form

$$\frac{\tilde{\sigma}}{\sigma_0} \propto \frac{1}{r_{1/2}^1} \sum_{r=1}^{\infty} \left( \frac{m_c B^1}{(\partial^2 S/\partial p_B^2)_{\text{extr}}} \right)^{1/2} \cos \left[ 2\pi r \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right] R_T(r) R_D(r) R_S(r), \quad (3.9)$$

where $\sigma_0$ is the background conductivity and

$$F = \frac{S_{\text{extr}} \hbar}{2\pi e} \quad (3.10)$$

the fundamental frequency. Eq. (3.9) will be hereafter referred to as the Lifschitz-Kosevich formula. $R_T(r), R_D(r)$ and $R_S(r)$ are damping factors we want to discuss below.

### 3.2.1 Temperature damping $R_T$

The first damping factor originates from smearing of the Fermi distribution with rising temperature. Roughly speaking, the Fermi distribution for finite temperatures is like the Fermi distribution for $T = 0$ K, but with a few unoccupied states below the Fermi energy and a few states occupied above the Fermi energy in a range that broadens with temperature. The possible orbits and, hence, the electron oscillation frequencies $F = \frac{S_{\text{extr}} \hbar}{2\pi e}$ then slightly differ from each other. This leads to a smearing in the phase, and, hence, to a destructive interference, which decreases the amplitude. The exact expression for $R_T$ is

$$R_T(r) = \frac{K r \mu B}{\sinh(K r \mu T / B)}, \quad (3.11)$$

where

$$\mu = \frac{m_c}{m_e} \quad (3.12)$$

is the cyclotron mass normalized to the free electron mass and

$$K = \frac{2\pi^2 k_B m_e}{\hbar^2} \approx 14.7 \frac{T}{K} \quad (3.13)$$

As eq. (3.11) contains the effective cyclotron mass, while all other parameters are known, it can be used to obtain the effective cyclotron mass, by measuring the amplitude of the oscillations at different temperatures.

### 3.2.2 Impurity damping $R_D$

In a perfect crystal, the free path $\ell$ is infinite or $\frac{1}{\tau} = 0$. A finite relaxation time widens these Landau subbands. This broadening is usually described by the Lorentz distribution function with the half-width $\Gamma = \frac{\hbar}{2\tau}$. The effect on the conductivity can be expressed in the so-called Dingle temperature and the Dingle damping factor for the oscillation amplitude

$$R_D(r) = \exp \left( - \frac{\pi \tau}{w_c \tau} \right) = \exp \left( - \frac{K r \mu T_D}{B} \right) \quad (3.14)$$
with the Dingle temperature

\[ T_D = \frac{\hbar}{2\pi k_B \tau}. \]  

(3.15)

Knowing the effective mass \( \mu \) from the temperature fit, we can obtain the relaxation time \( \tau \) from the field dependent amplitude. One should note that \( \tau \) is not necessarily the same as the usual transport relaxation time, as internal stains and dislocations also contribute.

### 3.2.3 Spin damping \( R_S \)

As we need it very often later, we will have a deeper look at the spin damping factor, as it is described in [18]. In magnetic fields \( B \), an electron with spin parallel to the field has a lower energy, and an electron with a spin antiparallel to the field has a higher energy compared to the case without field. Each energy level without field is split into two new energy levels

\[ \epsilon \pm \frac{1}{2} \Delta \epsilon, \]  

(3.16)

where

\[ \Delta \epsilon = \frac{1}{2} g \beta_0 B \]  

(3.17)

and

\[ \beta_0 = \frac{e \hbar}{m_e} \]  

(3.18)

\( \beta_0 \) is twice the Bohr magneton and \( g \) the Landé factor. As this splitting of the Landau level, can be seen as two Landau levels, close to each other, we can formulate the energy difference as a phase difference

\[ \phi = \frac{2r\pi \Delta \epsilon}{\beta B}. \]  

(3.19)

between the oscillations coming from spin-up and spin-down electrons. Here \( \beta = \mu \beta_0 \) and we multiply the phase difference with \( r \) for the \( r \)-th harmonic. Two successive Landau levels that are \( \beta B = \hbar \omega_c \) apart, pass through a Fermi surface having a phase difference of \( 2\pi \). The phase difference between two cylinders coming from the spin splitting is the fraction \( \frac{\Delta \epsilon}{\beta B} \) of the full phase difference between two Landau tubes. In a case where the phase difference is \( \pi \) we speak of spin zeros. The superposition of the spin-up and spin-down oscillations is, therefore, an interference that leads to a damping factor in the original amplitude

\[ R_S(r) = \cos \left( \frac{1}{2} r \phi \right) = \cos \left( \frac{r \pi \Delta \epsilon}{\beta B} \right) = \cos \left( \frac{1}{2} r \pi g \mu \right). \]  

(3.20)

We consider \( \kappa-(\text{BETS})_2\text{FeBr}_4 \) in this thesis. As our material contains magnetic Fe ions, we have to take into account interaction of conducting electrons with magnetic moments, which is spin-dependent and the new field dependent \( \phi \) can be written as

\[ \phi = 2\pi \left[ \frac{g \mu}{2} \left( 1 - \frac{B_{ex}}{B} \right) \right]. \]  

(3.21)
In the quasi 2D (q2D) materials, the area of the Fermi surface cross section perpendicular to the field $B$, rises with higher angles as $1/\cos(\theta)$, and by definition leads to an increasing cyclotron mass $\mu(\theta) = \mu(0)/\cos(\theta)$. Inserting this and our new phase difference into eq. (3.20) we get a modified spin damping factor

$$R_S(r) = \cos \left[ \frac{r \pi g \mu}{2 \cos \theta} \left( 1 - \frac{B_{ex}}{B} \right) \right].$$

Later on, we will focus on the first harmonic $r = 1$, for all damping factors, since the second and higher harmonics are hard to observe, only for the strong $\alpha$ oscillations we could see a tiny second harmonic.
4 Experimental setup

4.1 Sample preparation and sample holder

The samples where contacted with annealed 10 μm platin wires that were glued onto the sample with graphite paste, in an ac four-point measurement arrangement, shown in Fig. 4.1. With this arrangement we can measure the sample resistance, without the wire and contact resistances. We wanted to measure the SdH oscillations in the AFM state. The transition from the AFM to the normal metallic state, is the lowest for magnetic field parallel $a$. Therefore in this experiment the samples were rotated in the $bc$-plane. For that orientation the transition field was as high as possible, which was important to see as many SdH oscillations in the AFM state as possible. Sample resistance at low temperatures was below 0.6 Ohm, and the contact resistances were 50 Ω so we needed to take currents lower or equal to 100 μA, as we did not want to overheat...
4 Experimental setup

the sample. We measured with a lock-in amplifier, with an ac current with a frequency between 50 Hz and 250 Hz. The lock-in measurement filters all frequencies but the measurement frequency, all other frequencies vanish, effectively eliminating most noise.

4.2 $^3$He-system

To measure the SdH oscillations at low field with reasonable amplitudes, it is necessary to cool the sample below 1 K, as we have very high effective cyclotron masses that damp our oscillation amplitude strongly with rising temperatures. For that a $^3$He setup was used. $^3$He was condensed and then pumped, to use the cooling power of the vaporizing liquid $^3$He. By decreasing the pressure in the $^3$He space, due to the vapor pressure curve, the temperature of the $^3$He and the temperature of the sample then decreased. The lowest $T$ achieved by pumping $^3$He was 0.4 K.

4.3 Superconducting magnet

To apply magnetic fields to the sample, we used a superconducting magnet from Cryogenics, that could produce magnetic fields up to $B = 14$ T at a current of 101 A when cooled to $T = 4.2$ K and up to 16 T at 115 A when cooled to 2.2 K. The magnet consists of an outer coil, made from NbTi, and an inner coil made of Nb$_3$Sn. The magnet is equipped with a shunt connected to a heater. The shunt is in parallel with the coils and forms a closed SC electric circuit. If heated, the shunt has a finite ohmic resistance, and the closed SC circuit is opened, so the magnetic field in the coil can be changed and an electric current can be applied. If the heater is switched off and the shunt becomes superconducting the current stays in the coil and the magnetic field in the coil is conserved. This is used to keep a constant magnetic field.
5 Results and discussion

5.1 Temperature and field dependent resistance

5.1.1 Superconducting transition

![Graph](image)

Figure 5.1: The temperature-dependent resistance below 3.0K

In Fig. 5.1 we see the temperature dependent resistance. We see the AFM transition at 2.45K, and the SC transition starting from 1.4K. In our salt only the BETS layers become superconducting, so the electrons have to tunnel the insulating FeBr$_4$ layers, as we measure the resistance perpendicular to the planes.

5.1.2 Magnetoresistance

In Fig. 5.2 we see the magnetoresistance from 0 to 14 T. At low angles the SC transition is at low fields, starting almost at zero field and the SC state is fully broken at 0.25 T. The lower boundary, where the SC state is broken, is moving to higher fields for increasing angles up to 2.5 T for field parallel to the $c$-axis[20]. Above the SC transition we see the AFM state and SdH oscillations. In the AFM state there is a clear hysteresis between up and down sweep, seen in the inset of Fig. 5.2 between up and down sweep. The AFM state is broken at 5.5 T, indicated by the end of the hysteresis. Above the AFM state the paramagnetic state begins, showing also SdH oscillations we are going to discuss later.
5 Results and discussion

5.2 The antiferromagnetic state: Shubnikov-de Haas oscillations

Figure 5.2: Magnetoresistance from 0 to 14 T, for 0.43 K and $\theta = 2.5^\circ$ with an inset from 0 to 6 T.

Figure 5.3: Fast Fourier transformation (FFT) spectrum of the SdH oscillations in the AFM state in the field window 3-5 T. The $\delta$-oscillation has a frequency of 62 T while the new frequency $F_\eta = 178 T$.

In the AFM state, we see two frequencies in the SdH oscillations, one the $\delta$-frequency.
5.2 The antiferromagnetic state: Shubnikov-de Haas oscillations

with 62 T that has already been reported by Konoike\cite{10}, and a new frequency with 178 T, which has not been reported yet.

5.2.1 $\delta$ frequency orbit

We want to further analyze the $\delta$ oscillations, which is the dominating frequency in the SdH spectrum in the AFM state.

Cyclotron mass

$$|A_{osc}| = a m_c^2 T \sinh(Km_c T/B_m)$$

where $a$ is a fitting factor, $m_c$ the cyclotron mass of the $\delta$-oscillations later for analyzing their angular dependence, we measured the amplitude of the oscillations at different temperatures and $\theta = 0^\circ$ and fitted the data with the temperature-dependent part of the Lifschitz-Kosevich formula

$$|A| = a \frac{T}{\sinh \left( \frac{K\mu T}{\tilde{B}} \right)},$$

where $\tilde{B}$ the inverse average of the used field window $\tilde{B} = \left( \frac{1}{B_{\text{start}}} + \frac{1}{B_{\text{end}}} \right)^{-1}$. We get $\mu = 1.3$. This differs from the value of other publications$[10, 19] m_c = 1.1 m_e$. A reason for this might be that we analyzed only a small temperature window, as we got the data, as a byproduct from measuring the cyclotron mass of the $\eta$ oscillations.
5 Results and discussion

Angle dependence

We know the frequency of the oscillations is proportional to the area of the Fermi surface projection perpendicular to the field. As our Fermi surfaces are cylinders, we get a simple dependence of the frequency on the angle

\[ F(\theta) = \frac{F_0}{\cos(\theta)}. \]  

(5.2)

This formula we fit to our measured frequencies shown in Fig. 5.5 on the left. We get a Frequency \( F_0 = 62.1 \pm 0.2 \) T at \( \theta = 0 \). The frequency is consistent with other publications [10]. Initially we used the angel dependent \( F(\theta) \) to determine the exact sample orientation.

![Figure 5.5: Left: The frequency of the oscillations plotted against the polar angle.](image)

Oscillations amplitude

Our main aim when measuring the angle dependence of \( \delta \)-oscillations was measuring spin zeros. The reason was a theory [8] that predicts the absence of spin zeros. By fitting the Lifshitz-Kosevich Formula to the data

\[
|A_{osc}| = a \cdot \frac{K \mu T}{B^{1/2}} \left[ 1 - \exp \left( -\frac{B_{MB}}{B_{\perp}} \right) \right]^2 \exp \left( -\frac{K \mu T}{B_{\perp}} \right) \cdot \frac{\pi \mu g}{2 \cos \theta} \cdot \cos \left( \frac{\pi \mu g}{2 \cos \theta} \right) \tag{5.3}
\]

where \( B_{MB} \) the magnetic breakdown field, \( B_{\perp} = B \cos \theta \) the field component perpendicular to the \( ac \)-plane, \( T_D \) the Dingle temperature, \( a \) a prefactor and \( \theta \) the angle.
5.2 The antiferromagnetic state: Shubnikov-de Haas oscillations

We take $T_D$ and $a$ as fitting parameters and set $B_{MB} = 20 \, \text{T}$, $\mu = 1.3$, $K = 14.7 \, \text{T/K}$ and an averaged $B_\perp = \left( \frac{1}{B_{\text{start}}} + \frac{1}{B_{\text{end}}} \right)^{-1} \cos \theta$, with $B_{\text{start}} = 3 \, \text{T}$ and $B_{\text{end}} = 5 \, \text{T}$, as well as $g = 0$ (solid line), $g = 0.6$ (blue line) and $g = 1.4$ (broken line) in Fig. 5.6. The measured data points fit well to the fit curves for $g = 0$. To ensure that there is no $g$ factor other than $g \leq 0.25$ possible, we fitted the data with all reasonable $g$ factors. Where the fits for $g \neq 0$ differ from the fit for $g = 0$, we have two or more points close to the $g = 0$ fit, and far away from the $g \neq 0$ fit. Only for $g$ factors smaller than 0.25, the spin zeros would be at such high angles that we have no data for those angles. A spin splitting factor $g \leq 0.25$ is unrealistic. Therefore, we can say that there are no spin zeros.

5.2.2 $\eta$ frequency orbit

We found new oscillations and a new peak in the FFT of the SdH oscillations. We name the frequency $F_\eta = 178 \, \text{T}$. The third harmonic of $\delta$ would have a frequency of $F_{3\delta} = 186 \, \text{T}$. This is close to our new frequency, so one could think that we found $F_{3\delta}$ instead. But we can determine the oscillation frequency to 1.5 T accuracy, so we clearly found a new frequency.
5 Results and discussion

![Graph showing FFT Amplitude vs Temperature][1]

**Effective Mass**

To determine the cyclotron mass we proceeded as for the $\delta$ oscillations. By fitting we determined the cyclotron mass to be $m_c = 2.75 m_e$ as shown in Figure 5.7.

**Comparison with Fermi surface reconstruction model**

Looking at the Fermi surface Fig. 5.8 there are three different pockets: the little $\delta$ circles, almost rectangular grey-dyed "bone" in the middle of the Brillouin zone and the star-like areas around the $\delta$-circle. We neglect the gap in the Brillouin zone. By defining the $\delta$ area as the intersections of two $\alpha$ ellipses, we can calculate the area of the bone. To do so, we split up the areas in the Fermi surface, as the upper area $A_{up}$, consisting of the $\alpha$ area, the $\delta$ areas and the star areas, the middle area $A_{mid}$ containing the bone, and the lower area $A_{down} = A_{up}$, being the same as the upper area. The upper area in the first Brillouin zone of the normal metallic state, is:

$$A_{up} = \frac{\alpha}{4} + \frac{\alpha}{2} - \frac{\delta}{2} + \frac{\alpha}{4} - \frac{\delta}{2} = \alpha - \delta = A_{down}$$  \hspace{1cm} (5.4)

Here we denote $A_{\delta}$ by $\delta$ and the same for the others. The area in the middle is

$$A_{mid} = b + 2 \left[ \frac{\beta}{2} - 2 \left( \frac{\alpha}{2} + \left( \frac{s}{4} - \frac{\delta}{4} \right) \right) \right],$$  \hspace{1cm} (5.5)

where $b$ is the bone area and $s$ is the complete star area. $A_{mid}$, $A_{down}$ and $A_{up}$ together are equal to the area of the metallic state first Brillouin zone and the latter is equal to $\beta$.
5.3 The normal metallic state

5.3.1 Field induced superconductivity

We measured the magnetoresistance for $T = 0.42\,\text{K}$ and $\theta = 90^\circ$ for $B$ parallel to the $c$-axis in the full field window, as shown in Figure 5.9. At roughly 1.8 T we see the SC transition, to normal conductivity. We see a feature between 11 and 14 T. This feature is due to FISC. We subtract the monotonic magnetoresistance, assuming it to be linear in $B$, with the result shown in Figure 5.9(b) $B_{\text{ex}}$ is the middle of the feature, we get after

$$
\beta = A_{\text{mid}} + A_{\text{down}} + A_{\text{up}} = 2(\alpha - \delta) + b + 2\left[\frac{\beta}{2} - 2\left(\frac{\alpha}{2} + \frac{s}{4} - \frac{\delta}{4}\right)\right] \\
= 2\alpha - 2\delta + \beta - 2\alpha - s + \delta + b \\
0 = -\delta - s + b \\
b = \delta + s
$$

We see that the area of the bone is equal to the area of the star plus the $\delta$ area. This is consistent with a theorem of Luttinger [21], as the bone is hole like, and the star and the $\delta$ are electron like. As the bone has a bigger surface and is therefore harder to observe we assume that the new found frequency is the star shaped surface. Thus observation of the new SdH with corresponding cyclotron mass appears to be consistent with model of the Fermi surface reconstruction, thus supports the prediction of the horizontal AFM order [16]. For an unambiguous assignment as well as to verify the Fermi surface more experimental data is necessary.
Results and discussion

Figure 5.9: Field induced superconductivity (FISC) at around 12.6 T, for field perfectly parallel to conducting layers. (a) Resistance against magnetic field, (b) The same data in the field window 10 to 15 T, after subtracting the monotonic background. The resistance minimum reveals the effective field of the π-d exchange interaction.

subtracting the monotonic magnetoresistance. We get $B_{\text{ex}} = 12.6$ T, which is consistent with earlier measurements [20].

There are two mechanisms that break SC, in a magnetic field. One is the Zeeman effect that breaks apart Cooper pairs, if they are in a spin singlet. This happens when the energy gain from arranging the spin parallel to the field is higher than the energy gain from forming a Cooper pair. The other effect is the orbital effect, where the SC current necessary to shield the vortices in the SC layer becomes over critical. For q2D SC the orbital effect is suppressed, if the magnetic field is applied parallel to the SC layers. In this case only the Zeeman effect destroys SC.

In our materials we have a magnetic ordering of the iron 3d spins in the metallic state, that creates an internal effective field acting on the conduction π-electrons in BETS layers. This internal field then breaks the cooper pairs by the Zeeman effect. This happens in the paramagnetic state above 4.4 T in Fig. 5.9 If this internal field is compensated by an external field, the paramagnetic pair breaking effect does not any longer destroy SC and we see FISC. The exchange field we measure is 12.6 T, consistent with other measurements [20]. This effect we measure is also called Jaccarino-Peter compensation effect[14].

Uji et al. found in 2001 FISC in λ-(BETS)$_2$FeCl$_4$ [4], while FISC was proposed for κ-(BETS)$_2$FeBr$_4$ by Cépas et al.[14], and found experimentally by Fujiwara et al. [22] and Konoike et al.[20]. As the magnetic field we have to compensate is around 12.6 T, and therefore in our field range and the suppression of the orbital pair breaking effect is very sensitive to orientation of the sample relative to the field, we used it to measure the real zero degree angle position of the sample on the rotator.
5.3 The normal metallic state

Figure 5.10: The inverse FFT of the oscillation for the $\beta$ frequency, conserving the amplitude and arranging them by the angles. Different curves for different angles are vertically shifted, different measurements for the same angle colored differently, but shifted to the same position.
5 Results and discussion

5.3.2 β Shubnikov-de Haas oscillations

In 5.10 we see the inverse FFT of the β oscillations. The inverse FFT for the angles were shifted to different positions to compare the inverse FFT of different angles. For some angles we measured the oscillations several times, so all the measurements were put on the same position, but colored differently. We see that the inverse FFT are zero or show a minimum for some $B$. These points we call nodes or beats.

From theory we would predict that the nodes are shifting towards a constant $B_{\text{ex}}$ with rising angle by the formula

$$\left| A_{\text{osc}} \right| = \left| A \cos \left( \frac{\pi \mu g}{2 \cos \theta} \left( \frac{B_{\text{ex}}}{B} - 1 \right) \right) \right|$$  \hspace{1cm} (5.7)

Where $A$ is the angle- and field-dependent amplitude, and the cos function the modulation due to the spin up and downs. $\mu$ is the cyclotron mass of $\beta$. We fit, as shown in Fig.5.11. We fit only the nodes with Eq. (5.7) as other factors of the oscillation amplitude also depend on the magnetic field, and only the nodes depend solely on our equation (5.7).

![Figure 5.11: Fit of the nodes, with (5.7) using $B_{\text{ex}}$ and $g$ as fitting parameters, shown as an example for $\theta=9^\circ$.](image)

From FISC we know the $B_{\text{ex}} = 12.6\ T$. From Fig.5.12 we see that the exchange field is only for $\theta = 0^\circ$ equal to the exchange field we know from field FISC. In between $\theta = 0^\circ$ and $20^\circ$, $B_{\text{ex}}$ and $g$ differ from their $\theta = 0^\circ$ values and show a strange behavior as seen in Fig.5.12 and Fig.5.13. Above $20^\circ$, the behavior of $B_{\text{ex}}$ and $g$ stabilizes at $B_{\text{ex}} = 12.95\ T$ and $g = 2.05$. For high angles around $45^\circ$ we see some instabilities in $B_{\text{ex}}$ and $g$. This might come from errors in the $\frac{1}{\cos \theta}$ term, as this term gets very sensitive to errors in the angle for high angles. It seems as in the range $\theta = 0^\circ$ to $20^\circ$ that another mechanism than spin-splitting is involved.
5.3 The normal metallic state

Figure 5.12: The exchange field as obtained by the fit. Clearly visible, the $B_{ex}$ is not constant. The error bars show the errors estimated by the fitting algorithm.

Figure 5.13: The $g$ factor obtained from the fit. The error bars show the errors estimated by the fitting algorithm.
5 Results and discussion

5.3.3 Α Shubnikov-de Haas oscillations

In Fig. 5.14 we see the evolution of the SdH oscillations corresponding to the α-orbit. Below 20° there are no beats visible. Above 20°, we see beats appearing, becoming more pronounced at increasing angles. The angle range above 20° is the same angle range where the beats in β more or less behave as predicted by theory, showing almost constant $B_{ex}$ and $g$. As there are not enough visible beats to fit in α, to obtain $B_{ex}$ and $g$, we try to compare the beats we would expect, using the $B_{ex}$ and $g$ from the β oscillations, to the beats we find in the α oscillations, shown in Fig. 5.15.

We see that below the exchange field, the theory nodes are where we expect them. But we also see that from theory we would expect also nodes where in the measurement we see a clear maximum. Above the exchange field, the nodes in theory do not fit at all with the nodes we measure, as we see nodes in theory where we do not see nodes in the measurement and nodes in the measurement where we do not see nodes in the theory. Further investigation is necessary, to find if the absence of nodes below 20° in the oscillations corresponding to the α orbit, and the strange behavior in the oscillations corresponding to the β orbit are related. The absence of nodes in α-oscillations was also observed in the sister compound $κ$-(BETS)$_2$FeCl$_4$ [23]. It is further to investigate why the nodes we expect from theory and the nodes we measure differ for the α-frequency.

Figure 5.14: Left: SdH oscillations of the α frequency, results of the inverse FFT for the α frequency, arranged in the same way as for β. Right enlarged window starting from $θ = 15.5°$ showing the only visible beats.
5.3 The normal metallic state

Figure 5.15: The enlarged window starting from $\theta = 15^\circ$. The crosses and filled squares mark the positions where we would expect nodes from theory.
6 Summary

In this thesis we measured the low-temperature magnetoresistance in κ-(BETS)$_2$FeBr$_4$ down to temperatures of 0.4 K and magnetic fields up to 16 T. We analyzed Shubnikov-de Haas (SdH) oscillations in the paramagnetic as well as in the antiferromagnetic (AFM) state.

In the low-temperature AFM state we have confirmed the $\delta$ frequency $F_\delta = 62$ T reported by Konoike in [10]. Moreover, we found another frequency $F_\eta = 178$ T in the AFM state. This frequency supports a theory by Mori et al. [16] predicting that the AFM ordering imposes a superstructure in the Fermi surface. The new frequency is to be further investigated to certify the area in the AFM Fermi surface which is responsible for it.

A theory [7, 8] predicted the absence of Zeeman splitting effect on the SdH oscillations. This is reflected in the absence of "spin-zeros" in the angular dependence of the oscillations amplitude. We have shown that there are, indeed, no spin zeros up to high tilt angles. Hence, we can provide experimental evidence for this theory.

In the normal metallic paramagnetic state we observed $F_\alpha = 800$ T and fast $\beta$ oscillations with $F_\beta = 4300$ T in agreement with earlier measurements [10, 19]. Both frequencies show a field-dependent spin splitting effect due to an internal magnetic field that allows us to evaluate the internal field $B_{ext}$ and the spin splitting factor $g$. Varying the angle between the magnetic field and the normal to the conducting layers, we found below 20°, $B_{ext}$ to vary from 12.3 T to 13 T and the $g$ factor to vary from 1.8 to 2.25, for the $\beta$ oscillations; for the $\alpha$ oscillations we found no beats. Above 20° $B_{ext}$ was approximately constant, $\approx 13$ T and $g \approx 2.05$ for the $\beta$ oscillations. We also saw nodes in the $\alpha$ oscillations, but were not able to fit for more than three angles. For the $\beta$ oscillations below 20° and for the $\alpha$ oscillations in general further studies are required to understand their behavior.
Bibliography


Bibliography


Acknowledgments

At the end of this thesis I want to thank all the people who helped me accomplish this master thesis. I especially want to express my gratitude to:

- Prof. Dr. Rudolf Gross for giving me the opportunity of doing this thesis
- Dr. Mark Kartsovnik, for introducing me to the subject of organic superconductors, supervising this thesis, always giving advice and sharing his knowledge.
- Dr. Werner Biberacher, who helped me throughout this thesis with many aspects and whose door was always open for asking advice.
- Michael Kunz, who introduced me to the experimental part of this thesis, for countless advice, for sharing his knowledge, for his help with everyday problems, and especially for contacting the small samples.
- H. Fujiwara for providing the samples
- the master student of this group, Sergej Fust, and all the other students and members of the WMI for the nice working atmosphere.