Effective cyclotron mass and electronic properties of \(\kappa\)-phase organic superconductors in the vicinity of the Mott-insulator transition

Master Thesis

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Garching, October 30, 2017
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1. Introduction

Superconductivity has been a highly discussed topic in the field of solid state physics, since its first observation by Heike Kamerlingh Onnes in 1911 [1]. Yet it took more than 50 years for a valid theoretical description presented by Bardeen, Cooper and Schrieffer to explain the microscopic mechanisms causing this phenomenon [2, 3]. Although their theory works well for describing superconductivity in usual metals, the idea of pairing electrons to so-called Cooper-pairs by electron-phonon-interactions does not seem to be applicable to several groups of later found "unconventional" superconductors. Some of these are heavy fermion superconductors [4, 5] (1979), high-$T_c$ cuprates [6, 7] (1986), iron pnictides [8, 9] (2006) or organic superconductors (1980) [10, 11]. Especially the latter have drawn a lot of attention, when they have been nominated as possible candidates for room temperature superconductivity by W.A. Little in 1964 [12]. Although we have not yet discovered superconductivity at temperatures above 300K, the idea sparked a hunt for new superconducting (SC) materials, which have shown to exhibit many interesting physical phenomena. The first synthesized organic metal that exhibited superconductivity was the Bechgaard salt (TMTSF)$_2$PF$_6$ [10], which shows a quasi-one-dimensional character of the charge transport. However, superconductivity in this material is only observed for pressures above 12kbar and temperatures below 0.9K.

Up to now the highest known critical temperatures amongst organic superconductors have been observed in the quasi-two-dimensional (2D) family of charge transfer salts based on the molecule BEDT-TTF [13]. Although the record for the critical temperature is with $T_c \approx 14$K [14] still well bellow room temperature, these materials have proved to be an interesting field of study. One reason for this is that their reduced dimensionality makes them relatively simple model systems to study many physical phenomena they share with other compounds of interest. An example for that is the occurrence of insulating instabilities close to the SC phase, which can be observed not only in high-$T_c$-cuprates [7], but are also known, for example, in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl [13], which will be investigated in this thesis. It has been shown that the mechanism causing the insulating phases are not of simple single particle nature, but are a result of strong interactions between the electrons, making it a many-particle problem [15]. One of the first theoretical description of such systems has been given by J. Hubbard in the so-called Hubbard model [16]. Although the Hubbard model is a good starting point to describe the general nature of Mott-insulators, it is not able to describe many observed phenomena. One theory that gained a lot of attention in recent years is the dynamic mean field theory (DMFT) [17], which offers
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A more complete picture of many Mott-insulating systems. The good description of many observed phenomena within DMFT, inspired several following experiments on Mott organics over the last years [18].

The group of organic metals is especially interesting in this respect for many reasons. The most important ones are the exceptionally good achievable crystal qualities and the high compressibility enabling one to vary the interaction strength of the electrons by moderate changes of pressure.

An especially interesting property in the vicinity of the Mott metal-insulator transition (MIT) is the charge carriers effective mass, as it is a direct measure of the interaction strength between the electrons. Nevertheless, despite big experimental and theoretical efforts, there is not yet a clear picture of how the effective mass changes, as the MIT is approached. Hence, an experimental study of this will be an important part of this thesis.

One way to study the effective mass of metallic charge carriers is by magnetic quantum oscillations (MQOs), such as the de Haas-van Alphen or the Shubnikov-de Haas effect. The latter will be the main means of investigation in this thesis. Furthermore, MQOs give us the opportunity to study the Fermi surface and learn about the scattering rate of charge carriers, which is especially interesting on the verge from delocalized to localized electrons.

The Mott-insulating systems we choose to investigate in this work are the two compounds $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)]$_2$Cl and $\kappa$-(BEDT-TSF)$_2$Mn[N(CN)$_2$]$_3$. Both materials exhibit a MIT at moderate pressures blow 1 kbar and can be grown with very good quality. Especially having very clean crystals is a very important aspect of MQO experiments, as the approaching insulating instabilities heavily reduce the observable effects of MQOs. Hence, these experiments also require special conditions, such as millikelvin temperatures and high magnetic fields.

The structure of this thesis is the following: In chapter 2 I will give more details on the organic metals investigated. I will put a special emphasize on the crystal structure and the resulting Fermi surface, as well as the differences in their phase diagrams. In the third chapter I will explain the concept of MQOs and address the main factors which dominate their appearance. Furthermore, I will introduce the reader to the Hubbard model for Mott insulators and give an insight into recent works within DMFT. This will be followed by a short part in chapter 4 in which the experimental setups will be presented to provide and measure the required pressures, low temperatures and high magnetic fields. Chapter 5 will present the experimental results, their analysis and discussion, followed by a short summary.
2. κ-Phase Charge Transfer Salts

The compounds used in this thesis are so-called charge transfer salts based on organic donor molecules. In the following sections I will give an introduction to the chemical composition and the resulting crystal structure as well as their physical and electronic properties. Further on, I will point out the differences of the used materials, especially with regard to their respective phase diagrams. As a final point I will try to convince the reader of why the family of organic superconductors are an excellent model system to study Mott physics in strongly correlated electron systems.

2.1. Crystal Structure

To understand the unique features of organic charge transfer salts, it is important to first take a look at their crystal structure. The main component of all these salts are relatively flat organic molecules e.g. bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) or bis(ethylenedithio)tetraselenafulvalene (BEDT-TSF or BETS), which are depicted in Fig. 2.1. These molecules are arranged in sheets with the longest side almost perpendicular to the resulting layer. The way the molecules are aligned to each other is responsible for different physical properties and is therefore classified into different phases\cite{13,19}. The most prominent ones are shown in Fig. 2.2, in particular the so-called κ-phase, which is present in the investigated salts. As there is a big overlap of the molecular orbitals of different ET molecules, electrons can move easily within the layers making them highly conducting. The reason why in particular the κ-phase is of so high interest, has its roots in the formation of dimers out of two donor molecules. The dimer donates one electron to the monovalent anion leaving the conducting system with exactly one electron per lattice site i.e. a half filled band. This is a key requirement for the existence of the Mott insulating state \cite{19}. The used anions heavily affect
2. κ-Phase Charge Transfer Salts

**Fig. 2.2:** Schematic drawing of the packing of ET molecules in the α-, β-, λ-, θ- and κ-phases. The red shaded areas represent the unit cell and the blue ellipses represent the dimerization of ET molecules in κ-phase salts (according to [19]).

The physical properties of the resulting salt as will be shown in Sec. 2.4. Some popular examples are Cu(NCS)$_2^-$, Cu(CN)$_3^-$ and Cu[N(CN)$_2$]X$^-$, where X can be Br, I or Cl. The materials used in this thesis are κ-(ET)$_2$Cu[N(CN)$_2$]Cl, κ-(ET)$_2$Cu(NCS)$_2$ and κ-(BETS)$_2$Mn[N(CN)$_2$]$_3$, which will further on be abbreviated as κ-Cl, κ-NCS and κ-BETS-Mn respectively.

The anions are also arranged in layers which are separating the ET sheets from each other as shown in Fig. 2.3. This leads to a small overlap of the electron orbitals in the direction perpendicular to the layers, which is called the $b$-direction, resulting in a weak interlayer conductivity. One consequence of this is a high anisotropy of electric conductivity of $\sigma_a/\sigma_b = 10^3 - 10^4$ [13], making them quasi-2D conductors.

**Fig. 2.3:** a) Crystal structure of κ-Cl (according to the crystallographic data in Ref. [20]) with the unit cell indicated as dashed line. b) Sketch of the general layered structure of κ-phase salts. The ET layers, which are parallel to the ac-plane, are highly conductive, whereas the anion layers in between are insulating.
Another important quantity in organic metals are the hopping integrals between neighboring dimers. The common notation for it is shown in Fig. 2.4. The ratio of $t/t'$ is the dominant factor determining the presence of magnetic ordering in the Mott-insulating state of these materials. The closer it is to 1, the more strongly frustrated the material is, with the extremal case for $t/t'=1$ for the regular triangular lattice \[21\]. It is usually derived from the crystal structure using theoretical models, such as first principles band calculations \[22\] \[23\] or the extended Hückel method \[24\]. Figure 2.5 depicts the results for $\kappa$-Cl, $\kappa$-NCS and $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$. As can be seen, $\kappa$-Cl is the least frustrated of the three salts, hence we expect it to exhibit more pronounced features of magnetic interactions, than $\kappa$-NCS. Further, we see $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$ to exhibit $t/t' \approx 1$, which makes it an ideal material to study the Mott-physics with minimal magnetic interaction.

![Fig. 2.4: The tight-binding hopping integrals $t$ and $t'$ of the single-band dimer model \[21\]. The circles represent the dimers.](image1)

![Fig. 2.5: The values of $t$ and $t'$ in the dimer model evaluated by different methods for $\kappa$-Cl (blue), $\kappa$-NCS (red) and $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$ (green) \[21\]. (original data from \[22\] \[24\]).](image2)
2. \(\kappa\)-Phase Charge Transfer Salts

2.2. Synthesis

As for most single crystals, the synthesis of charge transfer salts starts by purifying the base materials. This is often done by gradient sublimation on Teflon for both the donor and acceptor molecules \[25\]. In this process the material is placed in an evacuated tube and heated by a resistive heater. Due to a strong temperature gradient, the single components sublime on the Teflon along the tube with high purity.

To grow single crystals out of these components, one uses electrocrystallization, like the galvanostatic method, which is depicted in Fig. 2.6 \[13\] and will be briefly explained in the following. For this procedure we have a small H-like evacuated glass container, with the two compartments connected by a fine-porosity glass-frit. Before the crystals can be grown, the reactants have to be dissolved. Therefore one puts two magnetic stirring bars into both parts of the container and adds the crystals of neutral molecules together with some electrolytes. This mixture has to be stirred in an inert environment like \(N_2\) or \(Ar\) and at room temperature for several hours. After the stirring is switch off and the undissolved parts are subside, one exchanges the stirring bars for platinum electrodes and a constant current is applied between anode and cathode. This electrolyzation starts the Redox reaction and thereby the process of the single crystal growth. As the electrolytes are often light sensitive, this is usually done in darkness. This way of growing crystals is very demanding, as slight variations e.g. more electrolyte or varying currents, can strongly influence the resulting salt. However, it also

Fig. 2.6: a) Picture of organic metal single crystals growing in a electrocrystallization process. b) Sketch of the same setup for better illustration of the single components \[13\].
2.3. Bandstructure and Fermi Surface

The strong anisotropy of conductivity is reflected in the Fermi surface (FS) of these compounds, which is shown for the case of κ-NCS in Fig. 2.7. As one can see, the FS in the $k_x k_y$-plane consists of two open sheets (red) and a closed pocket (blue). This shape does not change strongly when moving in $k_z$-direction, as in the third dimension there is only a slight warping to be seen, which is exaggerated in this picture for better visibility [26]. This picture of the FS has been theoretically derived for κ-NCS in tight-binding bandstructure calculations [26] and also been confirmed for κ-Cl and κ-BETS-Mn by quantum oscillation experiments [27–29]. Furthermore, this quasi two dimensionality is not only a very simple case compared to often complex three dimensional (3D) FSs but also exhibits strongly enhanced quantum oscillations (see Sec. 3.1.1). This enables us to investigate electronic properties such as the FS and the effective cyclotron mass with moderate continuous fields achievable by superconducting magnets and are not dependent on higher pulsed magnetic fields necessary for most 3D systems.

Fig. 2.7: 2D (a) and 3D (b) Fermi surface of κ-NCS. The warping in $k_z$-direction is exaggerated for better visibility. Therefore the FS can be considered to be quasi-two-dimensional, consisting of a closed pocket (blue) and two open sheets (red) [26].
2. κ-Phase Charge Transfer Salts

2.4. Phase Diagram

Probably the most interesting feature about organic charge transfer salts is their rich phase diagrams, as these materials exhibit many different ground states including superconducting (SC), metallic, antiferromagnetic insulating or quantum spin-liquid [30]. Figure 2.8 illustrates a generic phase diagram of the most popular κ-ET2X salts with their ambient pressure positions marked above. As one can see, among these materials only κ-Cl shows an insulating behavior at ambient pressure and can be driven to a SC state by applying moderate pressures of about 300 bar. κ-NCS on the other hand is already SC at ambient pressure and higher pressure can drive the system only in a normal metallic state.

Another way to tune the positioning in the phase diagram is by applying chemical pressure i.e. chemical substitution. In this case, substituting Cl by Br in κ-ET2Br2Cl1−x has the same effect as applying pressure and induces a MIT for x ≈ 0.7 [31]. However, this method induces disorder into the crystal and therefore decreases the amplitude of the quantum oscillations due to increased scattering and forces one to use a different sample for each 'pressure' i.e. x.

Fig. 2.8: Generic phase diagram of ET2X-salts as a function of hydrostatic pressure, with increasing pressure from right to left. The dashed lines indicate the ambient-pressure positions for different anions X [21].
Another candidate that exhibits a pressure-induced MIT is the relatively new and lesser studied \( \kappa \)-BETS-Mn. It has a similar phase diagram to \( \kappa \)-Cl and will therefore be used to check our results for universality. It undergoes a MIT at \( p \approx 500 \) bar, which is also believed to be of Mott origin. Furthermore \( \kappa \)-BETS-Mn exhibits a SC phase on the metallic side close to the MIT. However, its critical temperature of superconductivity has a very weak pressure dependence with a maximum \( T_c \) of \( \approx 5.7 \) K \([32]\). In contrast \( \kappa \)-Cl has a maximum \( T_c \) right before the MIT of 13 K, which is among the highest for all organic charge transfer salts \([13]\). \( T_c \) decreases for higher and lower pressures, resulting in a so-called SC dome. One more feature both materials exhibit is an extended area around the MIT, at which both the SC and insulating phase coexist \([32, 33]\), which is caused by the first order character of the MIT. Despite the similarities at low temperatures, the phase diagrams show some distinct differences along the temperature axis. For pressures around \( p_c \) \( \kappa \)-Cl shows a first order transition from metal to insulator ending in a second order critical endpoint at 38 K \([34]\). For higher temperatures there is an ongoing crossover region, where the phase changes continuously, which could be ascribed to the existence of a quantum critical point around \( (p = p_c, T = 0) \) \([35]\). However, this behavior has not been observed in BETS-Mn, where the phase transition moves to lower pressures with increasing temperature and shows no endpoint for \( p > 0 \). One difference that might explain the different shapes of the phase diagrams is the existence of paramagnetic localized spins of the Mn\(^{2+}\)-ions in the insulating layers, which shows only a weak interaction with the conducting layers.

The phenomenon of adjacent insulating and SC phases is not only found in organic charge transfer salts, but also known for Fe-pnictides \([9]\) and high \( T_c \)-cuprates \([7]\), as can be seen in the \( T-x \) phase diagram of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) and \( \text{R}_{2-x}\text{Ce}_x\text{CuO}_4 \) (Fig. 2.10) where...
2. \( \kappa \)-Phase Charge Transfer Salts

\( x \) is the doping concentration. As the pairing mechanisms for these unconventional SC are still unknown it is highly desirable to understand the mechanism driving the MIT. That’s one reason why we use organic superconductors as model compounds to study the influence of the strong electron correlations on the SC state in unconventional superconductors.

\[ \text{Fig. 2.10: Temperature-doping phase diagram of the high-} T_c \text{ superconductors } \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \text{ and } \text{R}_{2-x}\text{Ce}_x\text{CuO}_4 [7].} \]
3. Theoretical Background

3.1. Magnetic Quantum Oscillations

In this section I will explain the origin of magnetic quantum oscillations (MQOs) and put special emphasis on Shubnikov-de Haas oscillations. The latter have been used in this thesis to investigate the Fermi surface and the effective cyclotron mass. We will discuss the magnetic breakdown effect, which leads to additional oscillation frequencies and also address the influence of the flux flow regime on the oscillation amplitude.

3.1.1. Landau Quantization

The origin of MQOs lies in the quantization of electron orbits under the influence of magnetic fields. For a gas of free electrons in a magnetic field the stationary Schrödinger equation is given by [36, 37]:

\[
\frac{1}{2m_0} \left( \frac{\hbar}{i} \nabla - eA \right)^2 \Psi = E\Psi. \tag{3.1}
\]

In this case \(m_0\) represents the free electron mass, \(\frac{\hbar}{i} \nabla\) is the canonical momentum operator, which becomes the kinematic momentum operator \(\frac{\hbar}{i} \nabla - eA\) under consideration of the magnetic field \(B\) with the vector potential \(A\). For a magnetic field parallel to the \(z\)-direction, we can choose the gauge:

\[A = (0, Bx, 0), \tag{3.2}\]

which turns Eq. (3.1) into:

\[
\frac{\partial^2 \Psi}{\partial x^2} + \left( \frac{\partial}{\partial y} - \frac{ieB}{\hbar} x \right)^2 \Psi + \frac{\partial^2 \Psi}{\partial z^2} + \frac{2m_0E}{\hbar} \Psi = 0. \tag{3.3}
\]

This can be solved using the ansatz \(\Psi(x, y, z) = u(x)e^{i(k_y y + k_z z)}\), where \(u(x)\) has to fulfill

\[
\frac{\partial^2 u}{\partial x^2} + \left[ \frac{2m_0\tilde{E}}{\hbar^2} - \left( k_y - \frac{eB}{\hbar} x \right)^2 \right] u = 0, \tag{3.4}
\]

and \(\tilde{E} = E - \frac{k^2}{2m_0} k_x^2\). Here we see that the electron orbit is only affected by \(B\) for the motion within the plane perpendicular to the magnetic field, whereas the motion in
3. Theoretical Background

the $z$-direction is equivalent to that of free electrons. To solve Eq. (3.1.1) in the $xy$-plane we substitute the cyclotron frequency

$$\omega_c = \frac{eB}{m_0}$$

and $\tilde{x} = x - \left( \frac{\hbar k_y}{eB} \right)$ to end up with the equation for a harmonic oscillator

$$-\frac{\hbar}{2m} \frac{\partial^2 u}{\partial x^2} + \frac{1}{2} m_0 \omega_c^2 \tilde{x}^2 u(x) = \tilde{E} u(x).$$

In this case the possible energies are given by $\tilde{E} = \left( n + \frac{1}{2} \right) \hbar \omega_c$, resulting in

$$E = \left( n + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2}{2m_0} k_z^2.$$  

This shows how the electron energy is split from a single band for $B = 0$ into several subbands, so called Landau subbands for finite magnetic fields. As a result, the electronic states in the $k_xk_y$-plane are shifted onto concentric circles (see Fig. 3.1). In the three dimensional (3D) case these circles are extended into the $z$-direction and become coaxial cylinders with steps in energy of $\delta E = \hbar \omega$ called Landau tubes.

**Fig. 3.1:** Quantization of electronic states in the $k_xk_y$-plane for free electrons a) with and b) without magnetic field applied perpendicular to the plane.

The quantization of states can also be understood in a more illustrative fashion. Thereby we imagine the electrons to move on circular orbits due to the Lorenz force, which acts only perpendicular to the electrons motion. The wave function along an
3.1. Magnetic Quantum Oscillations

A magnetic quantum oscillation orbit has to fulfill Sommerfeld quantization, i.e. it is only non-destructively interfering for orbits with

$$\oint k \, dx = 2n\pi,$$

(3.8)

where \(k\) is the particle’s wave vector and \(n \in \mathbb{N}\).

So far we only considered the case of free electrons with a quadratic dispersion relation and a spherical FS. If we expand this picture to the problem in real crystals, we have to account for a non-quadratic dispersion relation leading to a non-circular electron motion. It can be shown that the cyclotron frequency in this case is given by [38]

$$\omega_c = \frac{2\pi eB}{\hbar^2} \left( \frac{\partial S}{\partial E} \right)^{-1}_{k_z},$$

(3.9)

with \(S\) being the area in \(k\)-space enclosed by an electron orbit with constant energy \(E\) and constant \(k_z\), which is the component of \(k\) parallel to \(B\). Comparing this to Eq. (3.5), we can introduce a cyclotron mass \(m_c\) defined by

$$m_c = \frac{\hbar^2}{2\pi} \left( \frac{\partial S}{\partial E} \right)_{k_z}.$$

(3.10)

For \(T = 0\) the Landau tubes are filled with equal amounts of electrons up to the Fermi energy \(E_F\), whereas tubes of higher energy are empty. The cross section area \(S_n\) of the \(n\)-th Landau tube can be expressed by the Onsager relation [39]

$$S_n = (n + \gamma) \frac{2\pi eB}{\hbar}. $$

(3.11)

Hereby, the \(\gamma\)-factor is \(\frac{1}{2}\) for free electrons and of the order of unity for real crystals and can therefore be neglected, as the order of the tubes is usually \(n \gg 1\). It also implies that the Landau tubes increase in size by increasing the magnetic field. If \(B\) passes a value for which the size of the FS is equal to the size of the highest occupied Landau tube, the tubes can exit the FS, resulting in a sudden redistribution of the electrons onto lower levels [36, 38]. This change of the density of states at the FS results in the change of several physical properties, such as magnetization, which is known as the de Haas-van Alphen effect [40], or electrical conductivity, known as the Shubnikov-de Haas (SdH) effect [41]. Both are often referred to as magnetic quantum oscillations. If we define the surface formed by the extreme cross section of the planes with the Fermi surface as \(S_{\text{extr}}\), we see that the \(n\)-th tube crosses the FS for

$$\frac{1}{B} = (n + \gamma) \frac{2\pi e}{S_{\text{extr}} \hbar}. $$

(3.12)

Thus, this happens at equal distances in \(1/B\) and therefore we define the oscillation frequency \(F\) as

$$F = \left[ \Delta \left( \frac{1}{B} \right) \right]^{-1} = \frac{S_{\text{extr}} \hbar}{2\pi e}. $$

(3.13)
3. Theoretical Background

**Fig. 3.2:** Illustration of the Landau tubes in a) a quasi-2D FS and b) a spherical FS as in a free electron gas [42]. c) and d) depict the corresponding density of states in units of \(\hbar \omega_c\) [36]. As \(\omega_c\) increases with field, the distribution is stretched in the \(E\) direction and the Landau tubes eventually cross the FS (red). The light blue shaded area represents the distribution for \(B = 0\) T.

Consequently we are able to determine the extremal parts of the Fermi surface in the \(xy\)-plane by measuring the frequency of the MQOs. Furthermore, one can reconstruct the 3D Fermi surface by studying the oscillations at different field orientations. If we compare the situation for a 3D spherical and 2D cylindrical Fermi surface as depicted in **Fig. 3.2**, we understand, why 2D systems exhibit more pronounced quantum oscillations. Both graphs illustrate the density of states \(D(E)\) for the case with magnetic field (dark blue) and without (light blue). For a spherical FS, \(D(E_F)\) increases continuously and jumps as a Landau tube surpasses the Fermi edge. If the FS is changed into a cylindrical shape, \(D(E_F)\) will be 0 as long as the energy of the highest occupied tube is smaller than \(E_F\). Once \(E = E_F\), the whole Landau tube lies on the Fermi edge, resulting in a \(\delta\)-function for \(D(E)\) at the FS, and therefore very strongly pronounced quantum oscillations.
3.1. Magnetic Quantum Oscillations

3.1.2. Shubnikov-de Haas Effect

To understand why the resistivity oscillates, it is helpful to look at the qualitative explanation given by Pippard in 1965 [43, 44]. In his idea, the scattering probability, and therefore the resistivity, are proportional to the density of states at the FS, as the electrons need free states to scatter. The amplitude $A$ of the oscillating part of the conductivity $\tilde{\sigma}$ relative to the background conductivity $\sigma_0$ for a FS with a single extremal orbit can be shown to follow [37, 38]

$$\frac{\tilde{\sigma}}{\sigma_0} = \sum_{r=1}^{\infty} \frac{1}{r^{1/2}} a_r \cos \left[ 2\pi \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right].$$

(3.14)

Here $r$ accounts for higher harmonics and the sign of the phase shift by $\pi/4$ has to be negative for $S_{\text{extr}}$ being a maximum cross section or positive in the opposite case. This behavior has first been proposed by Lifshitz and Kosevich for the density of states [45] and has later been adapted to the conductivity by Adams [46]. Further on, the damping of the oscillations is expressed by

$$a_r \propto m_c B^{1/2} (S''_{\text{extr}})^{-1/2} R_T(r) R_D(r) R_S(r)$$

(3.15)

with $(S'')_{\text{extr}}$ being the curvature of the FS in the direction of $B$ at the extremal cross section and $R_T(r)$, $R_D(r)$ and $R_S(r)$ being the temperature, scattering and spin splitting damping factors respectively.

3.1.3. Damping of Oscillations

As Eq. (3.15) indicates, there are certain factors that influence the oscillation amplitude in real crystals. The ones included in the Lifshitz-Kosevich theory will be presented in the following:

**Temperature damping factor:** Most important for this thesis is the influence of temperature on the oscillation amplitude. As $T > 0$ leads to a softened Fermi distribution of the single electron occupation probability, also the distribution of the electrons at $E_F$ is smeared out. This can be represented by the existence of many different extremal cross sections of the FS, leading to oscillations with slightly different frequencies [38, 42]. As a result, the peak in the oscillation spectrum is broadened, which is equivalent to a smaller oscillation amplitude. It has been shown by Lifshitz and Kosevich [45] that the temperature dependence of the damping is determined by the normalized effective cyclotron mass $\mu = m_c/m_0$ according to

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

(3.16)
3. Theoretical Background

where \( K = \frac{2\pi^2 k_B m_0}{\hbar e} \approx 14.69 \text{T/K} \). Equation (3.16) can therefore be used, to evaluate \( \mu \) by measuring the temperature dependence of the amplitude of the SdH oscillations.

**Dingle damping factor:** But not only the FS can be smeared, but also the Landau tubes are not infinitely sharp, due to scattering processes. This leads to a finite relaxation time \( \tau \), and therefore softens the distribution on the Landau tubes from a \( \delta \)-function to a Lorentz distribution function with the half-width \( \Gamma = \hbar/2\tau \) \cite{38}. If we define the Dingle temperature \( T_D = \frac{\hbar}{2\pi k_B \tau} \), we can write the temperature damping factor as following \cite{47}:

\[
R_D(r) = \exp \left( -\frac{\pi r}{\omega_c \tau} \right) = \exp \left( -K r \mu T_D / B \right)
\]

(3.17)

Knowing \( \mu \) from the temperature damping described above, we can use Eq. (3.17) to evaluate \( T_D \) from the field dependence of the oscillation amplitude and therefore get an idea of the scattering rate and the quality of our samples.

**Spin splitting damping factor:** The last damping factor in Eq. (3.15) accounts for the occurrence of Zeeman splitting. As the energy of an electron with its spin parallel or antiparallel to the magnetic field is shifted by \cite{48}

\[
\Delta \epsilon = \pm g \mu B
\]

(3.18)

with Landé factor \( g \) and Bohr magneton \( \mu_B \), each Landau tube splits into two subbands. In case of free electrons \( g \approx 2 \) and therefore the energy difference is \( \Delta \epsilon = \hbar e B / m_0 = \hbar \omega_c \) which is the same as the difference between two neighboring Landau levels. Consequently the contribution of the electrons with an antiparallel spin of the \( n \)-th Landau tube are in phase with that of parallel spins on the \((n+1)\)-th tube \cite{32}. As in general \( g \neq 2 \) and \( \mu \neq 1 \), there is a phase shift of the subbands in real crystals leading to a damping factor of

\[
R_S(r) = \cos \left( \frac{\pi}{2} r g \mu \right).
\]

(3.19)

3.1.4. Magnetic Breakdown

Up to now we only considered the case for electrons in a single conduction band moving on a classical orbit. This picture changes, once we introduce further conduction bands lying close to each other at \( E_F \). As with increasing field \( \hbar \omega_c \) gets in the order of \( \epsilon^2_0 / E_F \), with \( \epsilon_0 \) being the energy gap between the neighboring conduction bands, the probability to tunnel from one band to the other is strongly increased \cite{38, 42}. This scenario is called magnetic breakdown (MB). An example similar to the one we will see in our samples is depicted in Fig. 3.3. In a semiclassical description, the electrons are only allowed to stay on one band, therefore the only possible closed orbit is the so called
\(3.1. \text{Magnetic Quantum Oscillations}\)

\(\alpha\)-orbit (red). Once the electrons are able to tunnel from one band to another, a second orbit arises called the \(\beta\)-orbit (dashed line). Consequently we will see two frequencies in our SdH spectrum. As the tunneling probability \(P\) increases exponentially with the magnetic field, we can define the magnetic breakdown field \(B_{MB}\) as

\[
P = \exp\left(-\frac{B_{MB}}{B}\right).
\]

As a consequence, the contribution of the electrons traveling on the MB orbit will increase with field, whereas the number of electrons on the classical orbits will decrease. This has to be taken into account for the evaluation of \(m_c\), as the background resistance in Eq. (3.14) is dominated by the classical orbit and the open sheet for \(B \ll B_{MB}\) and by the MB orbit for the opposite case.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Example of a 2D FS formed by two conduction bands, which results in a closed pocket (red) and two open sheets (blue). The dashed line indicates the magnetic breakdown orbit.}
\end{figure}

\subsection*{3.1.5. Oscillations in the Flux Flow Regime}

Another important effect to consider is the influence of superconductivity on the oscillation amplitude. By increasing the magnetic field, a type II superconductor undergoes a transition at the lower critical field \(B_{c1}\) from the Meißner-phase, in which all magnetic flux is expelled from the SC volume, to the Shubnikov-phase, in which magnetic flux can enter the SC volume \([49, 50]\). In this regime the resistance is dominated by the flux dynamics (for more detail I refer to Ref. \([51, 52]\)). Only when \(B\) exceeds the upper critical field \(B_{c2}\) the system turns into a normal metallic state. As \(B_{c1}\) and \(B_{c2}\) increase with decreasing temperature, the system is moving closer to the SC state for low temperatures. Therefore an enhanced or decreased damping of the oscillations in the regime dominated by the flux flow would act as an additional damping factor as long as \(B < B_{c2}\). Up to now there are different theories addressing this issue, with some predicting an additional damping \([53, 54]\) and other explaining enhanced oscillations \([55]\). Further on, there have been several experiments on organic superconductors with equally contradicting results, including enhanced damping \([56, 57]\), no additional damping \([58]\) and also weaker damping \([59]\). Hence we will try to address this issue, especially in the field range relevant for the evaluation of the effective cyclotron mass.
3. Theoretical Background

3.2. Metall-Insulator Phase Transition

One of the most interesting features in organic charge transfer salts is the occurrence of a pressure driven phase transition from an insulating state at low pressures to a metallic and even superconducting state at high pressures. To differentiate these two states we define them according to Ref. [60] by their electric conductivity for $T \to 0$ and sufficiently small electric fields to obey Ohm’s law. As one would expect in the case of an insulator, the entries in the DC conductivity tensor $\sigma_{\alpha\beta}^{DC}$ have to vanish and therefore have to fulfill:

$$\sigma_{\alpha\beta}^{DC}(T = 0) \equiv \lim_{T \to 0} \lim_{\omega \to 0} \Re\{\sigma_{\alpha\beta}(\omega)\} = 0 \quad (3.21)$$

Correspondingly the conductivity for the metallic state has to stay finite according to Drude theory:

$$\sigma_{\alpha\beta}^{DC}(T = 0, \omega \to 0) = \frac{e^2 n}{m^*} \cdot \frac{\tau}{(1 + \omega^2 \tau^2)} \quad (3.22)$$

Here $e$ is the elementary charge, $n$ the charge carrier density, $m^*$ the quasiparticle effective mass and $\tau$ the typical scattering time. In order to see non-vanishing conductivity at $T = 0$, a system needs to fulfill two requirements:

1. It needs quantum-mechanical states that can be excited by the vanishingly small electric field i.e. the Fermi energy must lie inside a band.
2. These states must be delocalized over the whole crystal.

The first criterion is also called the gap criterion and might fail in case of paired electrons like in BCS-like superconductors. Typical example insulators that do not fulfill criterion 1, are band insulators (see Fig.3.4) or Peierls insulators, whereas an example of insulators which do not fulfill condition 2, are Anderson insulators.

![Fig. 3.4: Differences between metal, semiconductor and insulator in the framework of band theory. The black frames represent possible electronic states and the blue areas are the occupied states.](image-url)
3.2.1. Mott Insulators

All the above mentioned phenomena can be explained by a single electron model with a periodic lattice potential. But there are certain materials such as transition-metal oxides and organic charge transfer salts that show insulating behavior despite having a partially filled band. To understand this phenomenon, one has to take into account the electron-electron interaction as first suggested by Mott and Peierls in 1937 \[15\]. In their understanding, the repulsion between the electrons can become so strong as to hinder the electrons from moving \[61\].

One of the first theoretical works on this have been performed by Anderson \[62\], Kanamori \[63\] and Hubbard \[16\] in the now well established Hubbard model. In this theory it was assumed that electrons can only sit on and hop between pointlike lattice sites, which can be occupied by a maximum of two electrons with different spins because of Pauli’s principle. In the case of one electron per site, we would expect a half-filled band, thus a metallic behavior. But as equal charges repel each other due to the Coulomb interaction, electrons on singly occupied sites are in an energetically lower state compared to electrons on doubly occupied sites. In the band structure picture this corresponds to the separation of the half-filled band into a full lower Hubbard band and an empty upper Hubbard band as shown in Fig.3.5. The Hamiltonian for

![Fig. 3.5: Sketch of electron distribution on lattice sites and band structure in the Mott insulating and metallic state. The arrows indicate spin up and down electrons, whereas the blue circles represent unoccupied sites.](image-url)
3. Theoretical Background

this scenario is given by [16]:

$$H = U \sum_i c_i^\dagger c_i^\dagger c_i c_i - t \sum_{\langle i,j \rangle, \sigma} (c_i^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_i)$$ \hspace{1cm} (3.23)

The sums $i$ and $\langle i, j \rangle$ are performed over all lattice sites or all pairs of neighboring lattice sites respectively and $\sigma$ accounts for both spin directions. The operators $c_i^\dagger$ and $c_i$ are the creation and annihilation operators for an electron on lattice site $i$ with spin $\sigma$. The prefactors $U$ and $t$ are measures of the Coulomb repulsion and the hopping energy. By increasing the ratio of $U/t$ one can drive the system from the metallic into the insulating state and vice versa. In real crystals this can be done by changing the bandwidth, using hydrostatic pressure or chemical substitution as discussed in Sec. 2.4.

The transition explained above is only sharp at $T = 0$ and is therefore considered to be a quantum phase transition with a quantum critical point at $T = 0$ and $U = U_c$, which is the critical value of $U$. Although there is no sharp phase transition at finite temperatures, the quantum critical point can have a big influence on the physical properties in a region for $T > 0$ as shown in Fig. 3.6a). Adopting the nomenclature of Ref. [60], we call this kind of insulator a Mott-Hubbard insulator.

![Fig. 3.6: Comparison of a generic phase diagram for a) a quantum phase transition and b) a thermodynamic phase transition as a function of temperature $T$ and external parameter $\lambda$, e.g. pressure. (Drawn according to Ref. [60])](image)

A different possibility to turn a metal into an insulator is by introducing long-range order. For example in the case of half band filling and a transition from a paramagnetic metal to an antiferromagnetic insulator. Hereby the ordering leads to a doubling of the unit cell, as the translation symmetry is now only given, if it contains electrons of both spin states. Thus the Brillouin zone is folded, resulting in two electrons per site, which is equivalent to a full band [61]. As this transition occurs at a finite temperature $T = T_c(\lambda)$ it is a thermodynamic phase transition as shown in Fig. 3.6b) and the insulating state is called Mott-Heisenberg insulator. A thermodynamic phase transition
3.2. Metall-Insulator Phase Transition

is the result of the competition between internal energy and entropy resulting in a state of higher order for \( T < T_c \). In contrast to that a quantum phase transition is driven by varying the relative strength of two non-commuting operators \([60]\). This explains the differences seen in the phase diagrams shown in Fig. 3.6. In the case of a Mott-Hubbard insulator, the energy gap in the electron excitation spectrum exists at any temperature and charge carriers can only be thermally excited, whereas in the Mott-Heisenberg insulator the gap criterion is only fulfilled below \( T_c(\lambda) \) and the gap vanishes for higher temperatures. Therefore, the influence of the phase transition disappears above \( T_c \) in the Mott-Heisenberg insulator but stays finite in the Mott-Hubbard insulator, although it is strongly smeared by temperature. It is to be mentioned that for many real-world systems it is not unusual that a quantum phase transition is accompanied and also to some degree covered by a thermodynamic phase transition \([60]\).

3.2.2. Effective Mass at the Mott-MIT

One highly discussed topic within the field of Mott transitions is the behavior of electronic properties such as the Fermi surface and especially the effective electron mass \( m^* \) when coming close to the critical value of \( U/t \), as \( m^* \) is a direct measure of the strength of electron correlations in the system. In this section I will introduce one of the most prominent theoretical predictions, since the investigation of the effective cyclotron mass will be a major topic of this thesis.

One of the most popular and fundamental theories on the behavior of the effective mass near a zero temperature MIT was published by Brinkman and Rice in 1970 \([64]\). In their work they start from the Hubbard model assuming an exactly half filled band, as discussed in section 3.2.1. By neglecting effects of magnetic ordering in the insulating state, they conclude that the renormalized mass \( m^*/m \) is inversely proportional to the discontinuity \( Z \) of the single-particle distribution function at the Fermi energy. As \( Z \) decreases by increasing the electron interaction strength \( U \) and finally vanishes at \( U = U_0 \), the effective mass has to diverge when approaching the insulator from the metallic side:

\[
\frac{m^*}{m} = Z^{-1} = \frac{1}{1 - (U/U_0)^2} \tag{3.24}
\]

Despite experimental efforts on different Mott insulating organic systems, there is not yet clear evidence for this postulation. On the one hand, experiments by Merino et al.\([65]\) seem to support the theory by Brinkman and Rice. They performed optical conductivity measurements on two different organic metals, similar to the ones used in this thesis, with different electron interaction strengths and saw an increase of the effective optical mass by almost a factor of 3 (see Fig. 3.7). However, the small amount of data and big error bar only offers a qualitative description of the change of \( m^* \) but is no evidence for a diverging behavior.

On the other hand, an earlier experiment carried out by Nakazawa et al.\([66]\) offers opposite results. The authors focused on the change of the electronic heat capacity
3. Theoretical Background

Fig. 3.7: Optical conductivity measurements performed on $\kappa$-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ crystals yield an strong increase of $m^*$. The ratio of Br to Cl was used to tune the electron interaction strength, with a smaller amounts of Br making the system more insulating.

Fig. 3.8: Electronic heat capacity coefficient for differently deuterated $\kappa$-Br samples as well as for $\kappa$-Cl and $\kappa$-NCS in vicinity of the MIT. The chemical pressure increases from right to left, so the superconducting state is on the left side of the transition boundary (thick line).
Therefore we choose MQOs for the determination of $m^*$, as they are only sensitive to metallic electrons and hence are more reliable. They already proved to be a powerful tool to evaluate $m^*$ for several other systems. One example for that is the work by Shishido et al. [67], in which they used them to investigate the heavy fermion superconductor CeRhIn$_5$ that exhibits a quantum critical point at $p \approx 2.35$ GPa. As one can see in Fig. 3.9, the mass increases by up to a factor of 10, when approaching the transition. Although this is not a classical Mott MIT, but a transition from localized electrons to 4f-itinerant heavy fermion SC electrons, it proofs the general concept of a diverging effective mass at a quantum phase transition.

![Fig. 3.9: Effective cyclotron mass of different orbits of CeRhIn$_5$ around a quantum critical point at 2.35 GPa [67].](image)

Although magnetic quantum oscillation techniques have been applied to the problem of the Mott MIT, there is not yet a clear proof or disproof of the Brinkman-Rice theory with regard to Mott transitions. This is mainly due to that fact that the oscillations become harder to detect as the amplitude is drastically decreased as the MIT is approached. Therefore the experimental results so far show either big error bars or could not be performed close enough to the transition [68]. Hence the most important point to investigate in the framework of this thesis will be the behavior of $m_c(p)$ close to the MIT.

### 3.3. Mott Transition in Dynamic Mean Field Theory

Over the last years there was a lot of theoretical progress on the Mott MIT, expanding the idea by Brinkman and Rice. One of the most successful in this respect is the dynamic mean field theory (DMFT). As it is too complex to cover in all detail in this thesis, I will only give a short insight to it and present the most important results. For further information I refer the reader to ref. [17] [69] [70]. The aim of this theory is to reduce the number of degrees of freedom of a single-site effective problem by
3. Theoretical Background

reducing the latter to a problem of interactions at a given site with an external bath. For this purpose it considers an isolated lattice site with the external bath containing all other degrees of freedom on other sites \[17\]. The resulting so-called impurity model can be solved in various ways. A common approximation to this model is to assume the lattice self-energy to be a momentum-independent (local) quantity, which becomes exact in the limit of infinite lattice coordinates. The local observable is the local Green’s function, which needs to be determined under the self-consistency condition that the impurity Green’s function reproduces the lattice local Green’s function through an effective mean field. This is usually determined by an iteration process and can be used to derive dynamical response functions and transport properties of the system. One example for that is shown in Fig.3.10 which depicts the resistivity of a half-filled Hubbard model in DMFT \[71\].

![Fig. 3.10: Resistivity in the $U$-$T$ plane of a half-filled Hubbard model according to DMFT calculations. The white lines separate orders of magnitude in resistivity \[71\].](image)

DMFT has managed, to describe a lot of observed features, such as the first order character of the Mott transition with a region of coexistence of the metallic and insulating phases. This can be understood as follows: there is a mean-field solution for the insulating case \(U > U_{c1}\) and for the metallic case \(U < U_{c2}\), with different critical values of the couplings \(U_{c1}(T) < U_{c2}(T)\). Hence there is a region, where both the metallic and insulating solutions are valid (see Fig.3.11). Since a divergence of \(m^*\) according to Eq. (3.24) is believed to occur at the \(U\), at which the Fermi liquid solution breaks down, we expect a strong increase of \(m^*\) towards \(U_{c2}\). Hence, the divergence might not be visible in experiments, as the first order transition between \(U_{c1}(T)\) and \(U_{c2}(T)\) might make the region close to \(U_{c2}(T)\) inaccessible to our methods of probing, because most of the sample is in the insulating phase.

A different approach on the description of \(m^*(U)\) has been given by Dobrosavljević \[18\]. He ascribes the enhancement of \(m^*\) to approaching a state with high residual entropy. He introduces the coherence temperature

\[
T^* \propto T_F/m^*
\]

(3.25)
at which the conducting quasiparticles of the Fermi liquid are destroyed by thermal fluctuations. Basic thermodynamics tells us that the entropy $S$ can be written as \[ S(T) = \int_0^T \frac{dT'}{T'} C_p(T') \quad (3.26) \]

with the specific heat at constant pressure $C_p(T)$. By approximating $C_p(T)$ by its leading term for Fermi liquids \[ C(T) = \gamma T + ... \quad (3.27) \]

and using the fact that the Sommerfeld coefficient $\gamma$ is directly proportional to $m^*$, we can reduce Eq. (3.26) at the coherence temperature to \[ S(T^*) \approx \gamma T^* \propto O(1), \quad (3.28) \]

where the effective mass dependence of $\gamma$ and $T^*$ cancel out. Close to $U_c$, $m^*$ becomes very big and therefore according to Eq. (3.25) $T^*$ vanishes. Hence, we conclude from \[ S(T \to 0) \propto O(1) \quad (3.29) \]

that a state with strongly enhanced $m^*$ indicates the proximity of a phase with finite residual entropy. It can be shown that $m^*$ has to increase according to \[ m^*/m = (U_c - U)^{-1} \propto (p - p_c)^{-1}, \quad (3.30) \]

assuming moderate changes in pressure \[ 18 \]. In the case of the Mott-Hubbard insulator the electrons are localized at $T = 0$. However, without magnetic ordering, every electron can be in one of two possible spin states. Hence, the system can be seen as an agglomeration of free spins with the residual entropy \[ S(0+) = R \ln(2). \quad (3.31) \]
3. Theoretical Background

This illustrates how magnetic interactions strongly affect the observable mass enhancement. In this picture especially strongly frustrated materials, such as spin liquids, should exhibit a diverging effective mass, whereas materials with finite magnetic ordering show a weakened mass enhancement.

3.3.1. Resistive Maximum

Further, Dobrosavljević connects transport properties around $T^*$ with the change of $m^*$. He explains the resistivity maximum in the temperature dependence of many Mott systems by the destruction of the heavy quasiparticles, which govern the electronic transport below $T^*$. In fact the theoretical calculations based on this idea very well reproduce the experimental findings in the 2D electron gas realized in Si MOSFETs [75]. As a result, he concludes that the temperature, at which the resistivity maximum appears $T_{\text{max}}$ is directly linked to renormalization of the effective mass of the quasiparticles by

$$\frac{T_{\text{max}}}{T_F} \approx 0.7 \frac{m_B}{m^*},$$

(3.32)

with $m_B$ being the electrons’ band mass and $T_F$ the Fermi temperature $T_F = E_F/k_B$. Although this has been obtained for a different system, he suggests for Mott organics that $T_{\text{max}}$ can be identified by the coherence temperature leading to [75]:

$$\frac{T_{\text{max}}}{T_F} \approx \text{const.} \frac{m_B}{m^*}$$

(3.33)

Another interesting prediction based on the same idea is that the resistivity curves $\rho(T)$ at different constant pressure can be collapsed onto a single function $f$ like

$$\rho(T) = (\rho_{\text{max}} - \rho_0) f \left( \frac{T}{T_{\text{max}}} \right),$$

(3.34)

**Fig. 3.12:** a) Resistivity maxima in the strongly correlated metallic regime of a half-filled Hubbard model within DMFT. b) Scaling collapse of the resistivity maxima [75].
as the resistivity around $T^*$ is governed by the same physical mechanisms. Here $\rho_{\text{max}}$ is the pressure-dependent resistivity at the maximum and $\rho_0$ is the residual resistance due to impurity scattering. Furthermore, not only $T_{\text{max}}$ has been predicted to exhibit a well defined dependence on the renormalized mass, but also $\rho_{\text{max}}$ should display a power law dependence on $m^*$ with a compound-dependent exponent \[75\]. The curves calculated by the DMFT for different positions in the phase diagram are depicted in Fig. 3.12. At low temperatures the electrons are strongly correlated and the resistivity is governed by inelastic electron-electron scattering with a quadratic temperature dependence $\rho(T) \approx AT^2$, with $A \propto (m^*)^2$ \[76\]. As $T$ approaches the coherence temperature, the thermal destruction of quasi particles sets in, breaking the $T^2$ dependence and leading to the resistive maximum. First experiments on $\kappa$-Cl showed reasonable agreement with the proposed theory as can be seen in Fig. 3.13.

![Fig. 3.13: Temperature dependence of the resistivity in $\kappa$-Cl at different pressures. The data (circles) are compared to DMFT calculations (diamonds). The measured residual resistivity $\rho_0$ has been added to the theoretical curves \[77\].](image)

### 3.3.2. Influence of Magnetic Ordering in Cluster DMFT

Since we have already seen above, that magnetic ordering can heavily influence the mass enhancement, we will use this section, to discuss the influence of magnetic frustration on the Mott MIT, which is neglected in single-site DMFT. One example for a theory including affects of magnetic frustration is cluster DMFT (CDMFT) performed by Kotliar et al. \[78\]. They achieve this by going from the single isolated lattice site in DMFT to a $2 \times 2$ cluster with a square lattice, which is the least frustrated possible case. In their findings, the addition of magnetic ordering does not change the first order character of the transition, but can have a drastic influence on the shape of the coexistence region and can reduce $U_c$ of the critical endpoint. The authors also point out that their findings more closely resemble the shape of the phase diagram found in the $\kappa$-phase organics than the single-site DMFT. About the nature of the metallic phase in the coexistence region, they postulate a strongly incoherent anomalous metallic state with a scattering rate, violating the expected quadratic temperature dependence.
3. Theoretical Background

Furthermore, they predict a remaining scattering of approximately $0.2\,t$, which is of the order of 100K for the present compounds, even at temperatures as low as $0.01\,t$. This strongly incoherent metallic state is also the reason, why the authors were not able to evaluate $Z$ at low temperatures very close to $U_{c2}$, where they cannot exclude a vanishing quasiparticle renormalization. However, in the normal metallic state, $Z$ is believed to have an almost linear dependence depicted in Fig. 3.14 similar to single site DMFT. However, it is cut off by the coexistence region and the spatial coherence is lost before the quasiparticles effective mass diverges.

Despite these striking differences at low temperatures, it is worth mentioning that CDMFT and single-site DMFT give very similar results at elevated temperatures, as the entropy of the paramagnetic insulator in CDMFT becomes similar to that of the non-magnetic one in the single-site approach.

Fig. 3.14: The quasiparticle renormalization parameter $Z$ as function of $U/t$ for different orbitals in CDMFT (blue and green). In the normal metallic state, the orbitals show essentially the same behavior as single-site DMFT (dashed line). However, the diverging effective mass is cut off by the strongly incoherent metallic solution in the coexistence region. We added the coexistence region for regular DMFT using the data provided in Ref. [78] at $T/t = 0.01$ for better understanding.
4. Experimental Setup

In this chapter I will introduce the experimental methods that have been used within this work. Namely those are the techniques for measuring and generating the required pressures, low temperatures and high magnetic fields. In this respect I will shortly discuss advantages of the different setups as well as the accompanying experimental challenges and constrains. Another important aspect will be the preparation of the samples, especially making electrical contacts and the setup for the resistive measurements.

4.1. Sample Preparation and Resistive Measurements

All our resistive measurements were performed using a four-point technique. By using one pair of leads for applying the current and one for measuring the voltage, we are able to measure only the sample resistance without additional resistances caused by the wires or contacts. This is important, as the resistance of the leads can be orders of magnitudes higher than the sample resistance and would therefore dominate the measured signal if a two-probe method was used. To provide mechanically stable and well conducting contacts to the samples, we used the commercial conducting graphite paste Dotite thinned with Du Pont thinner to glue the electrical leads to the sample. The leads are annealed 20 µm thick Pt wires, which have been connected to the surface of the samples, which are parallel to the layers. The contacts were made manually and we were able to achieve contact resistances of below 20 Ω per contact, which did not change over the course of the measurements.

For all experiments the resistance was measured in an AC configuration with Lock-in amplifiers. To ensure almost constant measurement currents we connected an ohmic resistor with up to 10 MΩ in series with the samples. For the measurements on the SdH oscillations only the out-of-plane (oop) resistance was measured, as it is significantly higher than the in-plane (ip) resistance and therefore allows for a more precise measurement.

In addition, the zero field temperature dependence of the ip and oop resistivity was studied using a so-called Montgomery method [79]. To do so, we perform simultaneously two four point measurements (see Fig. 4.1). One Lock-in measures the regular oop resistance by applying the current at contacts 1 and 2 and measuring the voltage at 3 and 4. The second Lock-in however applies the current between contacts 2 and 3 and records the potential difference between 1 and 4. As the current in this
4. Experimental Setup

direction is not equally distributed over the whole sample cross section, the quotient of the potential difference and applied current cannot be identified by the ip resistance. However, we can use a theoretical model (see appendix) implemented by L.I. Buravov [80] to calculate the ip and oop resistivity from the data obtained in this configuration. In addition, one has to take care that the Lock-ins share a common ground for the current lead and need to work at non-commensurate frequencies to avoid interference effects. As the investigated samples are highly anisotropic, it is necessary to have very thin samples and place the contacts as far apart as possible in order to have feasible ip resistances. For this experiment a sample of the dimensions $400 \times 310 \times 15 \mu m^3$ was chosen.

![Measurement circuit in the Montgomery configuration for simultaneous measurement of the ip and oop resistivity. The resistences $R_1$ and $R_2$ are 100 kΩ and $f_1 = 13.4$ and $f_2 = 23.9$.](image)

**Fig. 4.1:** Measurement circuit in the Montgomery configuration for simultaneous measurement of the ip and oop resistivity. The resistences $R_1$ and $R_2$ are 100 kΩ and $f_1 = 13.4$ and $f_2 = 23.9$.

4.2. Magnetic Field Setup

To see MQOs it is crucial to have high magnetic fields, because the leading term of the field dependent amplitude is exponential [see eq. (3.14)]. As pulsed fields are not an option at these low temperatures, due to heating effects by eddy currents, we were using continuous magnetic fields. One possibility to get fields of up to 15 T is by using a SC solenoid inside a 4.2 K-cold liquid $^4$He bath. This method was used for the measurements on $\kappa$-Cl and $\kappa$-NCS. In this case, the maximum field could further be increased to 17 T by cooling the $^4$He bath below 2 K and therefore increasing the critical current of the solenoid.

For higher fields it is necessary to use a partially or fully resistive magnet such as the ones at the LNCMI in Grenoble, shown in Fig. 4.2a. As they are operated at constant currents of up to 30 kA it is important to minimize the energy dissipation by Ohmic losses and ensure mechanical stability to withstand the ponderomotive forces induced.

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[1] Laboratoire National des Champs Magnétiques Intense
4.3. Temperature Setup

by the huge currents in high magnetic fields. Therefore one uses a special copper alloy to build up the magnet core as depicted in Fig. 4.2b). As the core produces up to 24 MW of heat, it needs to be cooled by \( \approx 300 \text{l/s} \) of water to keep the temperature below 100 \(^\circ\)C. In the given setup with a 52 mm bore hole we were able to obtain fields of up to 29 T.

![Resistive magnet](image-url)

\textbf{Fig. 4.2:} a) Picture of the resistive magnet used at the LNCMI in Grenoble. The big pipes coming out of the core are for the supply and drain of cooling water\cite{source1}. b) shows the profile of the polyhelix magnet core \cite{source2}.

4.3. Temperature Setup

Depending on the desired temperature range, we are using three different techniques to stabilize the temperature of our samples.

\textbf{\(^4\)He-VTI:} For cooling to temperatures down to 1.4 K, we are using a \(^4\)He variable temperature insert (VTI) which is placed in a bath of liquid \(^4\)He at 4.2 K [Fig. 4.3a)]. As one can see, there is an impedance connecting the \(^4\)He bath and the inner space of the VTI which are otherwise decoupled by a vacuum space in between. This impedance allows small amounts of helium to enter the inner space of the VTI. By pumping the inner space and thereby decreasing the vapor pressure inside, it is possible, to stabilize the temperature between 4.2 and 1.4 K. The constant flow of He gas furthermore ensures a steady cooling power. To stabilize higher temperatures, the pumping power is kept at a minimum and heating power is introduced by a resistive heater. The best suited way of measuring the temperature in the whole temperature range from 1.4 to 300 K is a Cernox\textsuperscript{\textregistered} thermometer,
which is a resistive sensor with a high sensitivity in the whole temperature range. This setup was used for the experiment on the ip and oop conductivity in \(\kappa\)-Cl.

Fig. 4.3: Schematic drawing of a) \(^4\)He VTI (for temperatures down to 1.4 K) and b) \(^3\)He VTI (for temperatures between 0.4 and 1.4 K).

\(^3\)He-VTI: As 1.4 K is not sufficient to study magnetic quantum oscillations in our materials, we have to use one of two other methods, to reach even lower temperatures. For the measurements on \(\kappa\)-BETS-Mn we chose a \(^3\)He-insert [Fig. 4.3b], which allows to cool down to 0.4 K. This system is similar to the above mentioned VTI, but has an additional space inside the 1.4 K cold \(^4\)He pumping space. In that part of the insert \(^3\)He is condensed at the cold plates, which are the only thermal connection to the main bath, to build up a reservoir of liquid \(^3\)He. At low temperatures the vapor pressure of \(^3\)He is much higher than of \(^4\)He and hence the accessible temperatures by pumping the \(^3\)He space are considerably lower than in a \(^4\)He-VTI. The main advantages of this technique compared to the following dilution refrigerator are a high cooling power, which allows for higher measuring currents without overheating the samples, and a much faster operating procedure. Especially the latter is the main reason, why we chose this setup for the measurements during the one week of magnet time at the LNCMI. Another ad-
vantage of using a $^3\text{He}$-insert is the possibility to evaluate the temperature by the vapor pressure of the $^3\text{He}$. As it does not depend on the applied magnetic field, we can stabilize the pressure during field sweeps by keeping the pressure in the $^3\text{He}$ space stable.

Fig. 4.4: a) Schematic drawing and b) picture of the used dilution refrigerator.
4. Experimental Setup

**Dilution refrigerator:**

As the magnetic fields produced by the SC magnets are much weaker than at the LNCMI, we used even lower temperatures, to investigate the SdH oscillations in $\kappa$-Cl and $\kappa$-NCS at the WMI. Therefore we adjusted a dilution refrigerator dip-stick (Fig. 4.4), which had been built by Dr. C. Probst and that has been used for earlier works [83, 84], to fit our needs e.g. to be able to hold the pressure cell. It is a Joule-Thomson dilution refrigerator system: $^3$He is pressurized to about 600 mbar and first purified in a liquid nitrogen cold trap and further cooled in the heat exchanger by the back flow gas. When the helium enters the mixing chamber it is liquified and at temperatures below 0.86 K a phase separation arises between a pure $^3$He phase on top and a $^3$He-$^4$He-mixed phase below. As $^4$He is superfluid at these temperatures, it acts like vacuum to $^3$He. By reducing pressure in the distillation chamber (still) one removes the warmest $^3$He-atoms from the mixture, which leads to a diffusion of $^3$He into the mixed phase inside the mixing chamber. This is equivalent to an evaporation of $^3$He, which costs latent heat and leads to a cooling power of 15 $\mu$W at 100 mK for this specific setup. For optimizing the evaporation rate a heating power of 0.3 mW is applied at the still resulting in a pressure of 0.2-0.3 mbar at the pumping line. To ensure mechanical stability but yet minimize heat inputs from the outside, the mixing chamber is connected to the distillation chamber only by Degussit \(^2\) which is a poor heat conductor and the whole space is evacuated to below $10^{-4}$ mbar.

![Fig. 4.5: Temperature damping factor for different effective masses. The blue shaded area represents the region accessible by our dilution refrigerator, whereas the red area represents the one accessible by the $^3$He-VTI.](image)

Although the dilution refrigerator setup needs considerably more time to operate, its necessity for the evaluation of the effective mass becomes obvious when we have a look at Fig. 4.5, which shows the temperature damping factor for different effective masses.

\(^2\)Degussit: sintered Al\(_2\)O\(_3\) from Friatec AG, Mannheim
4.4. Pressure Setup

As we expect masses of more than six times the free electron mass (c.f. Ref. [68]), we would loose more than 70% of the maximum amplitude in the $^3$He setup. The lowest achievable temperature of this dip-stick is about 25 mK. However, during our measurements the usual operating temperature for the mass evaluation was 70-800 mK, as field sweep induced eddy currents led to heating effects which need to be compensated.

As the expected signal were of the order of only several % of the overall resistance, the following measure had to be taken to decrease the noise as much as possible. We decoupled the setup from the power line ground and properly grounded it to a separate ground. Furthermore, we were using a signal integration time of 3 s on the lock-in synchrodetectors and changed the field with a rate of 30 mT/min. As a last measure, the applied currents to the samples were adjusted to be as high as possible without exceeding a dissipated power of 10 nW which has been determined as upper limit for avoiding overheating of the samples.

In order to stabilize temperature between 70 and 800 mK in magnetic fields, we apply up to 500 µW of heating on the cell holder plate and use a so-called "Type-C" RuO$_2$-thermometer, which has a negligible magnetoresistance compared to its temperature sensitivity as shown in works by C. Marcenat et al. [85]. These findings have been reproduced and extended to $^3$He-temperatures within the present thesis.

4.4. Pressure Setup

As we are particularly interested in the pressure dependence of several physical properties, it is important to have a reliable way of measuring and applying pressures. The latter has been done in two different ways which will be explained in the following. However, in both cases we need to lead twelve wires for the samples and the pressure sensor from the pressurized volume to the outside. Therefore we are using a feedthrough made of a CuBe alloy and Stycast 2850 epoxy with catalyst 9, which has good low temperature properties such as a high degree of hardness and small thermal expansion coefficient. Such a feedthrough is then mounted into the pressure cell and is the basis for all used pressure techniques. Since the parts used in the pressure cells have to withstand big forces and will be put into strong magnetic fields, they are also made of a very hard and non-magnetic CuBe alloy.

For studying the transport properties of the organic crystals at pressures up to 2 kbar and between 10 and 200 K, we used a helium gas pressure setup, which is shown in Fig. [4.6]. As can be seen, helium is stored at room temperature in a 150 bar bottle. From there the gas is first purified in a liquid nitrogen cold trap in order to remove other gases which might otherwise freeze inside the capillary (inner diameter 0.3 mm) and block it. To increase the pressure further, there is a compressor with a maximum output pressure of 3 kbar. By opening valve 1 between the high-pressure reservoir and the capillary or valve 3 between the capillary and the Helium recovery line, one can
4. Experimental Setup

![Diagram of gas pressure setup](image_url)

**Fig. 4.6:** Schematic drawing of the gas pressure setup.

smoothly vary and sweep the pressure. The capillary is led into the cryostat and into
the pressure cell. To stabilize the temperature of the samples and prevent the Helium
from uncontrolled freezing, there are four thermometers and heaters placed towards
the end of the capillary and on the pressure cell.

However, the gas pressure setup is not compatible with the dilution refrigerator or
$^3$He insert which are needed to reach the temperatures necessary for observing SdH
oscillations. Hence, in these experiments we used the clamp cell technique depicted in
Fig. 5.3.1b). For this technique we put the feedthrough into a Teflon cup filled with
a silicone oil called GKZh as pressure medium. Subsequently it is put into the clamp
cell and a force is applied with a hydraulic press via the "mushroom" until a certain
pressure is reached. By fixing the nut around the "mushroom", the force on the piston
is supported by the nut and the "mushroom" can be removed.

As the pressure inside the cell is temperature-dependent and decreases at lowering
temperatures, it was necessary to apply roughly 3.3 kbar more at room temperature
than we wanted to have at low temperatures. A more detailed relation between the
high and low temperature pressures is depicted in Fig. 4.8 a).

To evaluate the pressure in the cell, we used heavily n-doped InSb bars with a linear
$R(p)$-dependence of about 3.6 \%kbar$^{-1}$, which allows for a relative accuracy of a few
bars and a absolute accuracy of about 20 bar. The sensors had to be cut and ground
into suitable shapes to fit inside the clamp cells and provide sufficiently high resistances.
They were calibrated in the gas pressure setup, presented above. For further details
on the preparation and calibration see Ref. [87] Chapter 4.2. The calibration curves for
several temperatures are shown in Fig. 4.8. The calibrations obtained in this work very
4.4. Pressure Setup

well fit the data from Ref. [87] and show the expected almost linear dependence for low
pressures. Furthermore, there is no change in the sensors behavior for temperatures
below 77 K.

![Fig. 4.7: a) Schematic drawing of the CuBe-clamp cell suitable for pressures up to 20 kbar [86] and b) picture of the feedthrough with the $\kappa$-Cl and $\kappa$-NCS sample, as well as the InSb sensor connected to electric leads for resistive measurements.]

![Fig. 4.8: a) Pressure at low temperature as a function of applied pressure at room temperature for the clamp pressure cell with GKZh as pressure medium. b) Calibration curves of the used InSb pressure sensors.]

![Graphs showing pressure and resistance data.](image)
5. Results and Discussion

In this chapter I will discuss the experimental results obtained in this thesis. I will first present the findings of the SdH experiment carried out with the dilution refrigerator on κ-Cl and κ-NCS. I will start with clarifying the position in the phase diagram of κ-Cl with respect to the coexistence region. This will be followed by the analysis of the MQO spectrum and its consequences for the pressure dependence of the FS. Next, I will look at the temperature dependence of oscillations, with special emphasize on $m_c$. The clamp cell experiments will be finished with an analysis of the field dependent oscillations, used to evaluate the scattering and dimensionality near the MIT.

After that I will turn to the conducting properties in κ-Cl at elevated temperatures. We compare the anisotropy found by the SdH experiment with the one from Montgomery measurements and investigate the behavior of the resistance peak in the $R(T)$ curves in κ-Cl. Furthermore we will compare it to the predictions of DMFT.

This section will be closed by comparing the results of the SdH experiment obtained for κ-Cl to another Mott-insulating compound κ-BETS-Mn.

5.1. Metal-Insulator Coexistence Region in κ-Cl

In Fig. 5.1 we see the temperature dependence of resistance of κ-Cl under different pressures in the clamp cell. The pressures have been evaluated at 15 K and hence are higher at high temperatures, but can be assumed to be stable at low temperatures. As expected, we see a SC transition at $T \leq 13$ K for all pressures apart from 0 bar, where the sample is fully insulating. While the data at high pressures shows mostly decreasing behavior down to lowest temperature, there is a drastic increase of $R(T)$ for intermediate pressures before the SC transition, caused by the arising insulating phase.

First we want to see, at which pressure $p_{c1}$ we enter the coexistence region, as it will be of major importance for the following discussion. To define the upper critical pressure, we apply two main criteria. The first one is a differing behavior of $R(T)$ from that expected for a fully metallic system. For pressures above $p_{c1}$ we expect a Fermi liquid behavior, i.e. decreasing resistance upon cooling down to lowest temperatures. This can be observed for $p \geq 460$ bar. For lower pressures the resistance at the SC onset is increased by several times to orders of magnitudes, suggesting that big amounts of the sample are in the insulating state. Hence we assume that we enter the coexistence region for $330$ bar $\leq p \leq 460$ bar. This is in reasonable agreement with the findings of
5. Results and Discussion

![Graph showing the resistance of κ-Cl as a function of temperature under different pressures in the clamp cell.](image)

**Fig. 5.1:** Resistance of κ-Cl as a function of temperature under different pressures in the clamp cell. The color code indicates the insulating (black) and metallic (blue) state, as well as the region of coexistence (red). The inset displays the two curves closest to the upper critical pressure from both sides of the transition.

Ref. [34], where the authors claim to see the upper critical pressure at around 300 bar. The second important evidence for entering the coexistence region is the occurrence of hysteretic effects as depicted in Fig. 5.2, which can be observed in the same pressure range. The $R(T)$ curve were obtained at temperatures around the critical temperature for superconductivity starting at 8 K warming above $T_c = 13$ K and going back to 8 K. As can be seen, the resistance on the part of the curve obtained under cooling is smaller than for warming, which can be explained by the first order character of the Mott MIT and the fact that the transition favors the insulating state at low temperatures. Upon warming, all curves follow the same behavior, whereas the resistance upon cooling strongly depends on the temperature the sample was warmed up to, with higher temperatures leading to lower resistances. It is interesting to see that all data collapses on a single curve in the SC transition region, whereas the SC onset seems to shift to lower temperatures for the curves, which have been warmed to higher temperatures.

Another feature is the sudden redistribution of domains manifesting in reproducible jumps in the measured curves. These effects complicated the following analysis. To minimize the influence of these phenomena on the following experiments especially on the effective mass, all sweeps used for the mass evaluation have been done consecutively and with an equal and well defined history. Furthermore the sample was never warmed above 1 K to ensure equal phase distributions for every measurement. As there have
been intense studies on the transport properties in the coexistence region, I refer the reader to Ref. [33, 88] for further details.

Further, it is surprising to see that the resistance in the coexistence region drops by several orders of magnitude at $T < T_c$ down to unmeasurable values for all pressures. As we need itinerant electrons for superconductivity only the metallic parts of the sample can contribute to this effect. Thus despite only minor parts of the sample volume being metallic, there is still a fully metallic path through the sample shunting the insulating domains.

Another interesting aspect in the $R(T)$ curves is the presence of a resistive maximum at temperatures between 50 and 150 K. This is the peak, which is ascribed to the destruction of heavy Fermi liquid quasi-particles. As can be seen, it moves from high temperatures at high pressures to lower temperatures at lower pressures, as explained by Dobrosavljević [18]. However, we have to keep in mind that these curves are obtained in clamp cell experiments and are therefore not isobaric. Hence we will take a closer look onto the conducting properties across the phase diagram in section 5.3.1.

5.2. Shubnikov-de Haas Oscillations in κ-Cl and κ-NCS

As we have seen in Sec. 3.1.1, the frequency of the oscillations is a direct measure of the size of the quasi-2D FS. Hence, by studying the pressure dependence of the frequencies we can investigate, how the FS changes upon approaching the MIT. Moreover MQOs can be used to evaluate the effective cyclotron mass of the metallic charge carriers. Lastly the pressure dependence of the frequency of the α-orbit in κ-NCS $F_{\alpha}^\text{NCS}(p)$ is a good parameter for evaluating the precision of our pressure determination, since it is very well known.

\[ R(k\Omega) \quad T(K) \quad p = 190 \text{ bar} \]

\[ 0 \quad 50 \quad 100 \quad 150 \quad 200 \quad 250 \]

\[ 8 \quad 10 \quad 12 \quad 14 \quad 16 \quad 18 \quad 20 \quad 22 \]

Fig. 5.2: Hysteretic effects in the temperature dependence of resistance in κ-Cl. The steps seen in some curves are ascribed to sudden switching of domains from metallic to insulating phase or vise versa.
5. Results and Discussion

5.2.1. Oscillation Frequencies and Fermi Surface

In order to evaluate the frequency of the SdH oscillations from the magnetoresistance curves, we were performing the following procedure illustrated in Fig. 5.3. First, we fit the $R(B)$ curves with a polynomial function, which can be understood as the background resistance $R_{\text{bg}}(B)$ [dashed line in Fig. 5.3(a)]. Next we subtract the background from the measured signal and thereby get the oscillating part of the magnetoresistance $R_{\text{osc}}(B)$, which is further normalized to the background [Fig. 5.3(b)]. Lastly we apply a fast Fourier transformation (FFT) in $1/B$ to get the SdH spectrum.

As one can see in Fig. 5.3(c), both materials $\kappa$-Cl and $\kappa$-NCS show the expected peaks for the classical $\alpha$-orbit and the magnetic breakdown $\beta$-orbit, confirming the assumed topology of the FS. However, especially the spectrum of $\kappa$-NCS exhibits many more peaks. These can be described by linear combinations of the fundamental frequencies.

**Fig. 5.3:** a) Magnetoresistance of $\kappa$-Cl (blue) and $\kappa$-NCS (red) at the lowest temperature $T = 70$ mK. The dashed lines are polynomial fits, which are used as background resistance. b) Oscillating part of the magnetoresistance normalized to the background resistance. c) SdH spectrum obtained by a fast Fourier transformation in $1/B$. The annotations at the peaks describe the corresponding orbit on the FS.
In the semiclassical picture we can understand this by assuming that the cyclotron frequency is much higher than the scattering rate and the electrons can therefore travel along several orbits before scattering. The occurrence of this phenomenon underlines the high crystal quality and the effect of two dimensionality on the SdH oscillations. However, not all frequencies can be explained within this picture, in which electrons can only travel along the orbits in one direction according to the Lorenz force. One example for this is the $(\beta - 2\alpha)$-orbit, which does not correspond to any classical orbit. These oscillations are caused by quantum interference of the electrons’ wave function along different paths (for further information see Ref. [87]).

![Fig. 5.4: Pressure dependence of the SdH oscillations in \(\kappa\)-NCS for a) the \(\alpha\)- and b) the \(\beta\)-orbit. The data shown by the open symbols has been taken from [89] (squares) and [87] (circles).](image)

Figure 5.4 depicts the pressure dependence of the fundamental SdH oscillations observed in \(\kappa\)-NCS. The FFT was applied on the field window between 12-15 T. Both frequencies were observed over the whole pressure range and exhibit a continuous increase. The frequencies at \(p = 0\) can be extrapolated to \(F_\alpha \approx 600\) T and \(F_\beta \approx 3.88\) kT which is in good agreement with former experiments [87, 89]. As our technique of evaluating pressure has never been applied at such low pressures, we want to use the pressure dependence of \(F^\text{NCS}_\alpha\) to get an idea of how precise this technique is. As can be seen in Fig. 5.4 a), we observe the known linear dependence with a slope, which is within the error bar equal to the previous experiment carried out in a gas pressure setup [89]. The offset of about \(2\) T \(\equiv 0.3\%\) can likely be ascribed to errors in the effective magnetic field caused by misalignment or off-centered positioning.
5. Results and Discussion

of the sample or different field calibrations. Nevertheless, we see that the precision of our pressure determination is very well estimated by a 20 bar uncertainty. Since there is no available experimental data on the $\beta$-frequency in the same pressure range, we will compare our data with the extrapolation of the high pressure data obtained in Ref. [87]. In Fig. 5.4 b) we can see that the size of the $\beta$-orbit changes linearly in the whole pressure range from 0.2 to 14 kbar. As the area of the $\beta$-orbit is equal to the size of the Brillouin zone, it can be used as a direct measure of the crystal’s compressibility in the ac-plane $\kappa_{ac}$, which is given by:

$$\kappa_{ac} = -\frac{1}{\Delta p} \frac{\Delta A_{uc}}{A_{uc}} = \frac{1}{F} \frac{dF}{dp}.$$

Here $A_{uc}$ is the unit cell area and we also assume the compressibility to be constant, since $F_{\beta}(p)$ is linear within the considered region of pressure. This leads to the value $\kappa_{ac} = (4.1 \pm 0.1) \times 10^{-3}$ kbar$^{-1}$.

![Fig. 5.5: Pressure dependence of the SdH oscillation frequency corresponding to the a) $\alpha$ and b) $\beta$-orbit in $\kappa$-Cl. The high pressure data (open symbols) is taken from [68] (circles) and [27] (squares). The dashed lines in a) serve as a guide to the eye.](image)

In Fig. 5.5 we see the pressure dependence of the frequencies ascribed to the $\alpha$-orbit $F^\text{Cl}_\alpha$ and $\beta$-orbit $F^\text{Cl}_\beta$ of $\kappa$-Cl. The FFT was applied between 12-15 T for $F^\text{Cl}_\alpha$ and 13-15 T for $F^\text{Cl}_\beta$. The $\beta$-oscillations could be observed in the whole pressure range, whereas the $\alpha$-oscillations are only observable for $p \geq 270$ bar. By evaluating the pressure dependence of the frequencies seen in $\kappa$-Cl, we will now see, how the FS changes when the system approaches the transition into the insulating state.
5.2. Shubnikov-de Haas Oscillations in $\kappa$-Cl and $\kappa$-NCS

First we will have a look at $F^\text{Cl}_\beta$ [Fig. 5.5b)] and compare it to the previous experiments [27, 68]. Similarly to $\kappa$-NCS, the $\beta$-frequency is linear over the whole pressure range even in the coexistence region. However, we have to note that the point at 990 bar suggests a higher pressure than evaluated. Since we will see this in all further evaluations, we conclude that it can be ascribed to an inhomogeneous pressure distribution in the frozen pressure medium. The linear $F^\text{Cl}_\beta(p)$ dependence suggests that the compressibility of $(4.0 \pm 0.1) \times 10^{-3}$ kbar$^{-1}$ is constant even in the coexistence region and equal to $\kappa$-NCS within the experimental error bar. Additionally the sizes of the Brillouin zones and therefore the lattice parameters are very similar with the extrapolated $F^\text{Cl}_\beta(p = 0) = 3840$ T only being 1.0% smaller than for $\kappa$-NCS. This illustrates that both materials have very similar electronic properties despite only one exhibiting a MIT and underlines, why these compounds are ideal for studying the influence of the MIT on the electron correlations.

We can further compare the compressibility data to the room temperature value of $5.6 \times 10^{-3}$ kbar$^{-1}$ calculated using X-ray diffraction data on $\kappa$-Cl [90]. This data also shows a linear pressure dependence of $A_{uc}$, supporting our previous assumption of a constant $\kappa$. The difference of the compressibilities at room and low temperatures is reasonable, as a reduction of $\kappa$ is expected upon cooling. The high compressibility of the present organic compounds provides a strong advantage in comparison to inorganic Mott-insulating systems like NiS$_2$, which show much lower equivalent 2D compressibilities\(^2\): $\kappa_{2D} \approx (4.7) \times 10^{-4}$ kbar$^{-1}$ [91] and thus is much less sensitive to pressure.

Next we turn to the pressure dependence of the closed $\alpha$-pocket of the FS, which is shown in Fig. 5.5a). We see a linear dependence of $F_\alpha$ for $p \gtrsim 2$ kbar and a significantly increasing slope for lower pressures. Since the $\alpha$- and $\beta$-orbit show a significantly different pressure dependence, we can conclude that the shape of the FS changes under varying pressure. The vanishing amplitude of the $\alpha$-oscillations at lowest pressures, suggest additionally a decreasing gap at the magnetic breakdown junction upon decreasing pressure.

\[ \text{Fig. 5.6: Sketch of the suggested change of the quasi-2D FS of } \kappa\text{-Cl under approaching the Mott-MIT. The shaded areas have to be of equal sizes.} \]

\[ ^1 p = 0 \text{ kbar: } a = 12.968 \text{ Å}, c = 8.475 \text{ Å}; p = 2.65 \text{ kbar: } a = 12.872 \text{ Å}, c = 8.412 \text{ Å} \]

\[ ^2 \text{This is derived from the 3D compressibility } \kappa_{3D} = \frac{\Delta V}{V \Delta p} \text{ under the assumption of isotropic compressibility to be } \kappa_{2D} = (1 + \kappa_{3D})^{2/3} - 1. \]
5. Results and Discussion

The area outside the open sheets in the first Brillouin zone has to be of the same size as the closed pockets, because of equal number of electron- and holelike charge carriers caused by the half-filled band. Knowing this, we can explain the pressure dependence of the oscillation frequencies by the changing FS depicted in Fig. 5.2.1. The rapid decrease of $F_{1}^{\alpha}$ is caused by a downsizing of the closed pocket in the $k_y$-dimension, as otherwise the gap at the magnetic breakdown junction would increase. At the same time the open sheets need to flatten, in order to keep the shaded areas of equal sizes. It should be mentioned that the decreasing $F_{1}^{\alpha}$ could also be explained, by a reduced dimension of the closed pocket in $k_x$-direction, however this would imply a cusplike shape of the open sheets, which is rather unlikely. For a more detailed analysis of the FS, it would be desirable to investigate angle-dependent magnetoresistance oscillations (AMROs) [32]. However, the high critical fields in $\kappa$-Cl would make the use of very high fields inevitable. Hence, it is not an option to do in the 17T SC magnets at the WMI.

Another interesting feature of the SdH oscillations in $\kappa$-Cl is the presence of beating in the $\beta$-frequency. Figure 5.7 shows the $\beta$-oscillations at lowest temperatures for all pressures. In order to remove the component of the $\alpha$-oscillations, a back FFT was performed for the frequency window between 2 and 6kT. The graphs are cutoff at low fields, because the vanishing resistance in the SC state leads to a diverging signal of the normalized amplitude, due to finite noise. At all pressures, $A(B)$ exhibits points at which the oscillations disappear. As we can see, there is again one measurement at 990 bar at which the node position drastically differs from the others, which supports the assumption of an inhomogeneous pressure distribution and compression of the sample at this pressure.

The beats are the result of interference of similar frequencies $F_1$ and $F_2$, with a phase shifted by $\pi$ at the points where the oscillations vanish. The beat frequency $F_{\text{beat}}$ hereby is given by:

$$F_{\text{beat}} = \frac{|F_1 - F_2|}{2} \quad (5.2)$$

In this case the most likely explanation is that the two frequencies stem from the minimal and maximal cross sections of the FS, caused by the warping of the FS in $k_z$-direction. As the nodes shift towards lower fields for lower pressures, we can conclude that $F_{\text{beat}}$ decreases and therefore the warping of the FS decreases. This is equivalent to an increase of the resistive anisotropy $\rho_{oop}/\rho_{ip}$. We will address the pressure dependence of $F_{\text{beat}}$ in more detail in Sec. 5.2.3, since we need the effective cyclotron mass for a quantitative analysis of the field dependent oscillation amplitude.
5.2. Shubnikov-de Haas Oscillations in κ-Cl and κ-NCS

![Graph](image_url)

**Fig. 5.7:** Normalized $\beta$-oscillations in κ-Cl at temperatures below 100 mK for different pressures. The data at low pressures has been magnified for better visibility and a FFT-filter has been applied for frequencies between 2-6 kT to remove the $\alpha$-component of the resistance.
5. Results and Discussion

5.2.2. Effective Cyclotron Mass

The main aim of this thesis is to investigate the change of the effective cyclotron mass as the system undergoes the Mott MIT. Therefore I will first explain the way of evaluating \( m_c \) as illustrated in Fig. 5.8 and what has to be taken care of during the measurements. The fundamental equation for evaluating \( m_c = \mu \cdot m_0 \) is Eq. (3.16), which in combination with Eq. (3.14) and Eq. (3.15) describes the change of the oscillation amplitude \( A \) as a function of the effective mass and temperature:

\[
A \propto \frac{\mu T}{B} \sinh\left(\frac{K\mu T}{B}\right).
\]  

(5.3)

Hence, we start with recording a series of field sweeps at constant temperature [inset in Fig. 5.8a)]. Here it is worth mentioning that even in the coexistence region, the resistance exhibits a metallic temperature dependence below 1 K, suggesting a stable phase distribution at these low temperatures. Next, we analyze the magnetoresistance curves as described in Sec. 5.2.1 to get the SdH spectrum [Fig. 5.8a)]. As the noise in the field sweeps induces also a background noise in the SdH spectrum, we only used a temperature and field window, in which the oscillations are at least several times bigger than the signal’s noise. That was \( T = 100 \) to 800 mK and \( B = 12 \) to 15 T for \( \kappa \)-NCS or 14 to 15 T for \( \kappa \)-Cl respectively. At the lowest pressure \( p = 190 \) bar, the oscillation amplitude in \( \kappa \)-Cl became to small, for a reliable mass evaluation.

As Eq. (5.3) assumes only a single electron orbit, it is desirable to know the fraction of the background resistance caused by the electrons on the corresponding orbit for
normalizing the oscillation amplitude. This is not possible to all detail, however, as \( \kappa \)-Cl mainly exhibits \( \beta \)-oscillations and the \( \alpha \)-oscillations are strongly suppressed by magnetic breakdown at high fields, we associate the whole background with the electrons on the \( \beta \)-orbit. As we have seen in Sec. 5.1, \( \kappa \)-Cl does have a fully metallic path through the sample even at lowest pressures and the phase distribution is stable at low temperatures as mentioned above. Hence, a change of the background due to changes of the insulating parts of the sample can also be excluded.

In the case of \( \kappa \)-NCS we see the opposite situation with the \( \alpha \)-oscillations being several times bigger than the \( \beta \)-oscillations. Therefore, we assume the magnetic breakdown \( \beta \)-orbit only to have a small effect on the average resistance and therefore subtract the oscillations only from the background without additional normalization. It should be mentioned that the temperature dependence of the background resistance of \( \kappa \)-NCS is very small and did not change significantly with pressure. Hence our approximation has only minor effects on the evaluation of \( m_c \).

The oscillation amplitudes are then plotted as a function of temperature and fitted with Eq. (5.3) and \( m_c \) as a fitting parameter. As can be seen from Fig. 5.8b, we are able to determine the effective mass to a very high precision, thanks to the high precision data obtained in our dilution refrigerator setup.

First, we consider the cyclotron mass corresponding to the \( \alpha \)-orbit shown in Fig. 5.9: a) compared to the earlier experiment at higher pressures [68] (open circles) and b) compared to the analogous mass in \( \kappa \)-NCS obtained in the same setup and from Ref. [89] (open squares).

As one can see, the evaluated masses are in reasonable agreement with the previous

\[ \sinh(x) \approx \frac{e^x - e^{-x}}{2} \approx e^x/2. \]

3As the argument in the hyperbolic sine can be much smaller than 2 for the very low temperatures, it was not possible to apply the commonly used exponential approximation \( \sinh(x) = (e^x - e^{-x})/2 \approx e^x/2 \).
5. Results and Discussion

The mass increases continuously as the MIT is approached with no signs of divergence. However, if we compare the two materials [Fig. 5.9b)], we see a significantly stronger slope in \(\kappa\)-Cl than in \(\kappa\)-NCS. This might be due to different band masses or be in fact a sign of approaching the Mott state. Additionally we see a good agreement of our data obtained for \(\kappa\)-NCS to the former experiment [89]. However, as \(m^0_c\) shows big uncertainties due to the small oscillation amplitudes and the comparable weak temperature dependence caused by the lower cyclotron mass at high pressures, we will concentrate on the mass corresponding to the \(\beta\)-orbit in the following. As we can see in Fig. 5.10a), the data obtained in this experiment very well confirms the previous experiments carried out at higher pressures [68]. For pressures higher than \(\approx 700\) bar, we observe a gradual decrease of the effective mass. This can be explained by decreasing electron-electron interaction further away from the MIT. More interesting however, is the behavior for \(p < 700\) bar. In this range we can see a strong deviation from the linear dependence seen before. Moreover, the mass seems to increase even stronger as we lower the pressure.

![Fig. 5.10: Effective cyclotron mass for the \(\beta\)-orbit in \(\kappa\)-Cl: a) compared to the former experiment at higher pressures [68] (open circles) and b) compared to the analogous mass in \(\kappa\)-NCS obtained in the same setup.](image)

To see, if the enhancement of \(m^\beta_c\) is caused by the proximity of the MIT, we will compare the data from \(\kappa\)-Cl to that from \(\kappa\)-NCS which have been obtained under the exact same conditions. As shown in Fig. 5.10b), both materials have very similar masses at pressures above 500 bar. For lower pressures the mass of \(\kappa\)-NCS continues its approximately linear dependence down to the lowest pressure where the mass of \(\kappa\)-Cl displays a strong upturn.

To compare the obtained results to the prediction of the DMFT, we plot in Fig. 5.11 the inverse effective mass as function of pressure and compare it to Fig. 3.14. However,
5.2. Shubnikov-de Haas Oscillations in $\kappa$-Cl and $\kappa$-NCS

Fig. 5.11: Pressure dependence of the inverse effective cyclotron mass of the a) $\alpha$- and b) $\beta$-orbits for $\kappa$-Cl. The x-axis is inverted to be in $U/t$ scale, similar to Fig. 3.14. The yellow shaded area represents the region of coexistence. The inset enlarges the low pressure region for better visibility.

we have to keep in mind that the inverse effective mass is not equivalent to the renormalization factor $Z$, but needs to be multiplied by the band mass $m_B$, as $Z = m_B/m^*$. As long as $m_B$ can be considered to be constant, it only acts as a rescaling of the y-axis. Since there are no band-structure calculations on the pressure dependence of $m_B$ for $\kappa$-Cl, the only indication of the change of $m_B$ is given by the change of the FS. For only small changes in the density of states, the change of the band mass can be considered to be of the order of the change of the FS. Hence, $m_B$ of the $\beta$-orbit should only exhibit changes in the order of 1%, whereas that of the $\alpha$-orbit might change stronger, considering the change of the FS at low pressures (see Sec. 5.2.1). One finding supporting a constant $m_B$ is the fact that the ratio of $m^*_\beta/m^*_\alpha$ is constant within the error bar with $2.05 \pm 0.1$ (see dashed lines in Fig. 5.11). This means that either the main factor affecting the cyclotron mass is the same renormalization factor or both band masses happen to change similarly over the whole pressure range or a combination of both. This ratio is very close to that in similar compounds such as $\kappa$-NCS ($m^*_\beta/m^*_\alpha = 2.07 \pm 0.04$) and $\kappa$-(ET)$_2$I$_3$ ($m^*_\beta/m^*_\alpha = 2.0$) for which there have been done band-structure calculations with similar results of $m^*_\beta/m^*_\alpha = 2.2$ for $\kappa$-NCS and $m^*_\beta/m^*_\alpha = 2.3$ for $\kappa$-(ET)$_2$I$_3$. Hence, the main influence on the pressure dependence of the effective cyclotron masses stems from the renormalization factor.

If we compare our results to the behavior predicted by DMFT and CDMFT calculations (see Sec. 3.3), we can clearly see that the effective mass does not diverge at the Mott-MIT in $\kappa$-Cl as predicted by the single-site DMFT or the Brinkman-Rice

\footnote{This is in good agreement with Ref. 52.}
5. Results and Discussion

However, outside the coexistence region, both inverse masses exhibit the linear pressure dependence, which is cut off by the coexistence region, what is well consistent with CDMFT calculations (see Fig. 5.11). The critical pressure for a mass divergence would therefore be around -4 kbar, which is in this case already deep inside the insulating state. The fact that the effective mass of $\kappa$-NCS behaves very similarly, can hence be explained, by the different magnetic frustration of the systems. That means that $p_{c2}$ for the single-site DMFT case of $\kappa$-NCS is also around -4 kbar. However, since magnetic ordering is less prominent in $\kappa$-NCS compared to $\kappa$-Cl (see Fig. 2.5) it is closer to single-site scenario. As a result, the real transition occurs at lower pressure $p < 0$ bar.

Nevertheless, inside the coexistence region, the behavior strongly deviates from that expected by CDMFT. Most importantly, we are able to observe coherent transport below $p_{c1}$. Additionally the measured mass renormalization of the $\beta$-orbit decreases much faster than in the fully metallic state. As this is not observed for $m_\alpha$ and as we discussed above that the $\alpha$-orbit should be stronger affected by changes of $m_B$, we can exclude it to be an affect of increased band mass. To understand better, how the mass deviates from the expected dependence, we divide the inverse effective mass of the $\beta$-orbit by values linear extrapolated from outside the coexistence region $1/m_{\text{extra}}$ (Fig. 5.12). The increase of the effective cyclotron mass seems to accelerate, as we go deeper into the coexistence region. However, it does not seem to diverge upon approaching $U_{c2}$, as the deviation is only about 11% at 210 bar and the lower critical pressure is believed to be already very close at around 160 bar [34]. The reasons for this unexpected behavior are unknown at the current state.

5.2.3. SdH Effect in the Flux Flow Regime and Dingle Temperature

For the evaluation of the effective cyclotron mass, we assume the Lifshitz-Kosevich theory to be valid and to fully determine the oscillation amplitude. In case there are other aspects affecting the MQOs, which are not included in this theory, our evaluated masses might differ from the real value. Especially the existence of a SC phase below the upper critical field is believed to affect the oscillation amplitude [53, 55]. Thanks to the low temperatures achievable by the dilution refrigerator, we were able to trace
5.2. Shubnikov-de Haas Oscillations in $\kappa$-Cl and $\kappa$-NCS

the $\alpha$-oscillations of $\kappa$-NCS down to 5 T just above the finite resistance onset in the SC mixed state. Therefore we are using the field-dependent amplitude of $A_{\alpha}^{\text{NCS}}$ to see if it differs from the Lifshitz-Kosevich behavior. In order to simplify the fitting curve, we express the field-dependent part of the oscillation amplitude $A(B)$ for the 2D limit [42] in the following way:

$$A = R_D R_T \propto \exp(-K\mu T_D/B) \cdot \frac{\text{const.}/B}{\sinh(K\mu T/B)}$$

$$AB = \text{const.} \frac{\exp(-K\mu T_D/B)}{\sinh(K\mu T/B)} \approx \text{const.} \frac{\exp(-K\mu T_D/B)}{1/2 \exp(K\mu T/B)}$$ (5.4)

$$\ln(AB) = \text{const.} + K\mu \frac{T + T_D}{B}.$$

This way we end up with a so-called Dingle plot, which is usually a linear function in $1/B$. For the amplitude, we are using the difference between the upper and lower envelopes of the normalized oscillating resistance, as shown in Fig. 5.13(a). For $A_{\alpha}^{\text{NCS}}$ the Dingle plot is shown in Fig. 5.13(b). The corresponding magnetoresistance curve is depicted in the inset of Fig. 5.13(b) and shows a flattening between 7 and 8 T. Hence, we assume the upper critical field to be in this field range and would therefore expect a change of the slope of the Dingle plot, if superconductivity affects the oscillation amplitude. However, the field-dependence is very well described by the Lifshitz-Kosevich theory and does not show any anomalies between 5.5 and 13 T. The discrepancy at

![Fig. 5.13: a) Normalized oscillation amplitude in $\kappa$-NCS with the upper and lower envelopes at $p = 460$ bar and $T = 70$ mK. b) Dingle plot for the $\alpha$-oscillation amplitude. The so called Dingle plot is performed according to Eq. (5.4). The inset shows the corresponding field sweep. The good agreement with the linear fit indicates that the SC state does not influence the SdH oscillation amplitude.](image)
5. Results and Discussion

lower fields is caused by the decreased signal to noise ratio, as the oscillations disappear, and accompanied problems with fitting the envelopes. At fields above 13 T, the approximation \( \sinh(x) \approx \exp(x)/2 \) is no longer good, which explains the differences at high field. However, the good agreement with the linear fit at fields around the SC transition, shows that the entrance in the SC mixed state does not influence significantly the SdH oscillations. Since we see only slight effects of superconductivity on \( R(B) \) in \( \kappa \)-Cl, we conclude that it does not need to be taken into account for the mass evaluation.

Next we will use the same method to evaluate the Dingle temperature and the frequency of the nodes in of the \( \beta \)-oscillations of \( \kappa \)-Cl, shown in Fig. 5.14(a). In this case, however, we have to modify Eq. (5.4), as we cannot make the exponential approximation for the hyperbolic sine at high fields and have to add an additional term accounting for the nodes. As the nodes are obviously a result of interference of oscillations with similar frequencies, we use an additional factor of 
\[
\phi = \arctan \left( \frac{\hbar e B}{2\pi m_c t_\perp} \right)
\]  
(5.5)

to substitute it by 
\[
\frac{t_\perp}{t_\parallel} = \frac{2t_\perp}{E_F} = \frac{F_{\text{beat}}}{F}
\]  
(5.6)

to substitute it by \( t_\perp = E_F F_{\text{beat}}/2F \). Here, \( t_\parallel \) is the intralayer transfer integral and \( F = (F_1 + F_2)/2 \) is the fundamental oscillation frequency and will be taken from the

![Fig. 5.14: a) Normalized oscillation amplitude in \( \kappa \)-Cl with the upper and lower envelopes. b) Field dependent amplitude of the \( \beta \)-oscillations evaluated from the differences between the envelopes and fitted with Eq. (5.8).](image-url)
FFT results (see Chapter 5.2.1). The Fermi energy \( E_F \) can be roughly estimated by assuming a quadratic dispersion and a circular shape of the \( \beta \)-orbit (\( S_{\text{extr}} = \pi k_F^2 \)) by Eq. (3.13) as

\[
E_F = \frac{\hbar^2 k_F^2}{2m^*} = \frac{\hbar eF}{m^*}.
\]  

(5.7)

The new fitting function therefore has the form:

\[
A \propto B^{-1/2} \cdot \frac{1}{\sinh(K\mu T_B)} \cdot \exp \left(-K\mu T_B^* \right) \cdot \left| \cos \left( \frac{\pi}{F} \right) - \frac{\pi}{4} + \arctan \left( \frac{1}{\pi F_{\text{beat}}} \right) \right|
\]  

(5.8)

\( T_D, F_{\text{beat}} \) and a constant scaling factor are used as fitting parameters and \( \mu \) is known from the previous section. An example of such a fit is shown in Fig. 5.14 b). The data shows remarkably good agreement with Eq. (5.8) in a wide field range around the node. The evaluated beat frequencies and Dingle temperatures obtained at different pressures are plotted in Fig. 5.15.

![Diagram showing pressure dependence of beat frequencies and Dingle temperatures in \( \kappa \)-Cl.](image)

**Fig. 5.15:** Pressure dependence of the beat frequencies and Dingle temperature in \( \kappa \)-Cl. The fit at lowest pressure did converge for two frequencies. The dashed lines are a guide to the eye.

The beat frequency is pressure independent in the purely metallic state with \( F_{\text{beat}} = 41.4 \text{T} \) and strongly decreases by more than a factor of two inside the coexistence region. This suggest a strong decrease of the warping of the FS in \( k_z \)-direction, which is equivalent to a strong increase of the anisotropy. Furthermore, we can use this data to evaluate the resistive anisotropy \( \rho_{\text{oop}}/\rho_{\text{ip}} \) according to [42]

\[
\frac{\rho_{\text{oop}}}{\rho_{\text{ip}}} = \left( \frac{t_\parallel}{t_\perp} \right)^2 \left( \frac{a}{d} \right)^2 = \left( \frac{F}{F_{\text{beat}}} \right)^2 \left( \frac{a}{d} \right)^2
\]  

(5.9)

with \( a \) being the intralayer lattice period and \( d = b/2 \) the interlayer spacing (c.f. Fig. 2.3). We evaluate the \( \rho_{\text{oop}}/\rho_{\text{ip}} \) to be about \( 2.2 \times 10^3 \) in the fully metallic state.
5. Results and Discussion

This increases to $7.4 \times 10^3$ or $3.4 \times 10^4$ at 210 bar. The two possibilities at low pressures stem from the problem that we could not clearly identify the order of the node. At 830 bar we see two nodes enabling us to determine them to be the 4th and 5th from their frequency and the distance to $1/B = 0$. For pressures down to 270 bar, the fit to Eq. (5.5) only converged for one specific order of the node, in contrast to 210 bar, where the high uncertainty of the oscillation amplitude led to a converging fit for the node being of 0th ($F_{\text{beat}} = 11 T$) or 1st order ($F_{\text{beat}} = 22.5 T$). It is worth mentioning that the behavior of $F_{\text{beat}}$ and therefore of the anisotropy shows significant similarities to the deviation of the pressure dependence of the effective mass (see Fig. 5.12).

The Dingle temperature, however, is constant within the experimental accuracy over the whole pressure range. So we clearly see that the coherent transport survives below the upper critical pressure. Furthermore, we do not observe any significant increase of the electron scattering in the coexistence region. These results contradict the predictions of CDMFT about the electron transport within $p_c^2 < p < p_c$. However, as the calculations in Ref. [78] were performed for temperatures down to $T = 0.01T \approx 5K$, it cannot be excluded that also within this theory coherent transport sets in at lower temperatures. Therefore we evaluated $T_D$ for temperatures between 100-800 mK with similar results over the whole range.

Hence, we conclude that the transport in the metallic parts of the sample are not affected by the arising insulating domains in $\kappa$-Cl, which contradicts CDMFT.

5.3. Transport Properties at Elevated Temperatures

In order to check the predictions about the scaling phenomena around the coherence temperature [18] and to verify our findings about the change in anisotropy, we now study the conducting properties at elevated temperatures. For this purpose, we performed simultaneous ip and oop resistivity measurements of thin $\kappa$-Cl samples in the Montgomery configuration with the gas pressure technique. Although we are mainly interested in the isobaric temperature dependence of the conducting properties, we performed isothermal pressure sweeps at different temperatures, as it is easier to realize in experiments. To ensure constant temperatures during each cycle, the temperature was stabilized with an external heater and the pressure was changed slowly with about 0.7 bar/s.

5.3.1. Anisotropy Measurements in $\kappa$-Cl

The isothermal $R(p)$ curves were used to construct the resistive $T$-$p$ phase diagrams shown in Fig.5.16. Both components of the resistivity share key features predicted by DMFT calculations (see Fig.3.10). One is the fanlike shape of lines of constant resistivity and the change of orders of magnitude even well above the critical end point ($p_c = 248$ bar; $T_c = 39.7 K$ [96]). The fact that we observe these features expected for
5.3. Transport Properties at Elevated Temperatures

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![Fig. 5.16: a) ip and b) oop resistivity of κ-Cl in the p-T plane obtained in the Montgomery configuration.](image)

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The transport properties at elevated temperatures are crucial for understanding the behavior of materials under high pressures and temperatures. These properties include electrical conductivity, thermal conductivity, and the response to magnetic fields.

Fig. 5.16: a) ip and b) oop resistivity of κ-Cl in the p-T plane obtained in the Montgomery configuration.

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A quantum critical point, can be explained by a weakly first order character of the transition \[18\]. In this case, which is well known for standard critical phenomena \[97\], the first-order character is only observed very close to the critical endpoint. Everywhere else the phase transition behaves like a conventional second-order phase transition. This includes the observation of critical scaling phenomena \[98\], which have been shown for different Mott-organics \[99\], but should not be confused with the scaling around the resistive maximum, investigated below.

However, comparing our data to similar experiments shows one significant difference, which is the absolute value of conductivity, which differs by about a factor of 5 for the ip component from the findings in Ref. \[77\]. This is most likely caused by two major problems of the present measurement configuration. The first one is the problem of not perfectly parallel contacts and a broad contact area due to the conducting paste, which leads to a high uncertainty in the setup geometry. Figure 5.17 shows one of the used samples, with a contact width comparable to the spacing of the contacts. The second, probably more important factor is the inhomogeneity of the sample for the Montgomery method. As defects might cause the currents to flow in paths different from the ideal case, the effective current path and the area of the current flow might differ from the assumed values. Nevertheless, since these errors mainly cause a renormalization by an almost constant factor, they will not affect the scaling relations, which only depend on the

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![Fig. 5.17: One of the κ-Cl samples used for the Montgomery method. The area enclosed by the blue line is the contact area, which is covered with the conducting paste.](image)
5. Results and Discussion

normalized conductivities.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.18}
\caption{Resistive anisotropy of $\kappa$-Cl measured in the Montgomery configuration for a) $T > T_c$ and b) $T < T_c$. The dashed line indicates the transition into the SC state and the solid line shows the MIT according to [34] and can be seen as upper critical pressure. The different absolute values of both plots is caused by the use of different measurement setups.}
\end{figure}

But before investigating the scaling relation, we will use the resistivity data, to look at the anisotropy in the $p$-$T$ phase diagram shown in Fig.\ref{fig5.18}. Figure\ref{fig5.18}a) depicts the resistive anisotropy in temperature region above the critical endpoint. The absolute values of the anisotropy are not consistent with what we expect from the SdH experiments. This can be explained by the same reasons as the different conductivities above. Additionally, the presence of impurities leads to incoherent conduction channels\cite{100}, which decreases the value expected from the FS warping. However, we see a clear increase in anisotropy as we approach the critical point. Further, the region of increased anisotropy extends into the crossover region and converges around $p_c$ as $T$ comes close to $T_c$. This supports our assumption of the strong increase of two-dimensionality being a feature of the MIT in $\kappa$-Cl.

Figure\ref{fig5.18}b) shows the anisotropy in the low temperature regime. As helium solidifies at these high pressures for lower temperatures, it was not possible to extend the data below 11 K. However, the present data clearly indicate that the region of high anisotropy follows the transition line taken from Ref.\cite{34} before it is cut off by the SC dome. Another interesting aspect is that the area seems to follow the SC transition, suggesting that not only the Mott-MIT appears first in oop direction, approaching it from the metallic side, but also supercurrents arise only at lower pressures for the oop component.
Next we turn to the scaling relations predicted by the DMFT \[18\] for the conducting properties near the coherence temperature. We look at the ip conductivity only, in order to avoid interference of oop mechanisms such as the anisotropy. First, want to check, if it is possible, to describe the $\rho_{\text{ip}}(T)$ curves, depicted in Fig. 5.19(a), by a single function according to Eq. (3.34). For this purpose, we construct the cooling curves at different pressures from the pressure sweeps and normalize their temperature and resistivity to the respective values at the resistive maximum as shown in Fig. 5.19(b). Here, $\rho_{\text{max}}$ is the maximum value of the resistivity of the corresponding $\rho_{\text{ip}}(T)$ curve and $T_{\text{max}}$ the temperature, at which the maximum appears. The resulting curves very well fit each other in a relatively big temperature range around $T_{\text{max}}$. Only the curve at lowest pressures shows some deviation, which might be caused by the strong temperature and pressure sensitivity in this regime. Furthermore, we see a slight separation of the curves at low temperatures, with the resistivity at lower pressures decreasing faster than at high pressures. One possible explanation for that is the neglection of a residual resistivity of the metallic state, as we used $\rho_0 = 0$. This approximation acts like an offset with decreasing amplitude, as $\rho_{\text{max}}$ decreases with pressure.

Figure 5.20 depicts the pressure dependence of $\rho_{\text{max}}$ and $T_{\text{max}}$. For the conductivity we see the expected increase as we approach the MIT. The position of the resistive peak on the other hand shifts to lower temperatures supporting the DMFT predictions at first sight. As can be seen by the noticeably scattering in $T_{\text{max}}(p)$, there is an uncertainty of several K especially at higher pressures, as the maximum becomes broader and eventually vanishes for pressures above 650 bar. However, there is an observable kink between...
5. Results and Discussion

350 and 375 bar, which cannot be explained solely by scattering and happens to be in the same pressure range, in which we observe the change in dimensionality. To see if the relation between $\rho_{\text{max}}$ and $T_{\text{max}}$ to $m^*$ suggested by V. Dobrosavljević holds (see Sec. 3.3.1), we first plot $\rho_{\text{max}}(\mu_\beta)$ in the double logarithmic scale, which is shown in Fig. 5.21a. We focus only on the mass corresponding to the $\beta$-orbit, as it could have been determined more precisely and at lower pressures. The data only shows slight deviations from a linear fit, proving the power law dependence $\rho_{\text{max}} \propto \mu^\gamma$, with $\gamma = 2.6 \pm 0.2$ for this compound.

Next we look at the more interesting behavior, of the temperature at which the resistive maximum appears. For this purpose, we plot in Fig. 5.21b) $T_{\text{max}}(p)$ as obtained from the gas pressure experiment and compare it to the positions based on Eq. (3.33) using $m_c$ determined in Sec. 5.2.2. As there is no data on the band mass $m_\beta$ of $\kappa$-Cl, we will set it equal to the free electron mass $m_0$ and the Fermi energy is again estimated from Eq. (5.7).

The two sets of data show surprisingly good agreement in the normal metallic state despite our rough approximations. This suggests that the constant in Eq. (3.33) is of the order of $1/m_\beta^*$, or $T_{\text{max}}$ not being dependent on the renormalization factor, but the whole effective mass.

In the coexistence region, on the other hand, we can see some difference, with the expected $T_{\text{max}}$ being higher than the experimental data. Although this result should be seen as an argument for plausibility rather than a definite proof for Dobrosavljević’s prediction, due to the little amount of data and the mentioned approximations, we want to give some possible explanations for the discrepancy at low pressures, which are rather of speculative nature.

On the one hand it is possible that the discrepancy is not a real effect, but mainly a result of our approximations. In case of a non-constant band mass, the result implies that at lower pressures the band mass decreases, to compensate for the too high cal-

Fig. 5.20: Pressure dependence of the resistive maximum in $\kappa$-Cl. The red points show the dependence of the height of the peak, whereas the blue ones depict the temperature at which it appears. The dashed line is a guide to the eye.
5.3. Transport Properties at Elevated Temperatures

Fig. 5.21: Dependence of the resistive maximum in $\kappa$-Cl on the effective mass of the $\beta$-orbit. a) Double logarithmic plot of $\rho_{\text{max}}(m^*_\beta)$ with a linear fit, to illustrate the power law dependence. b) Position of the resistive maximum as obtained in the gas pressure experiment and as suggested by Eq. (3.33).

calculated $T_{\text{max}}$. However, such a drastic decrease of $m_B$ is rather unlikely.

In a different interpretation of this plot we could say that the overall slope of the real position is stronger than that expected from the SdH experiments and the difference at low pressures is a result of high uncertainties. In this case a possible source of error is the evaluation of $T_{\text{max}}$ from the gas pressure experiment. Around the coherence temperature, the resistivity is a superposition of the peak and the increasing resistance of metallic charge carriers with increasing temperature. Since the maximum is not very pronounced, especially at high pressures, the peak in the $\rho(T)$ curves is shifted to higher temperatures compared to the real coherence temperature. In this case, the data from the gas pressure experiment would be lower than depicted in Fig. 5.21b), but by rescaling by a smaller constant, the slope would be more similar to the calculated values.

On the other hand, if the discrepancy in the coexistence region is a real effect, we could also speculate that the increased two-dimensionality has to be considered. Therefore, we might have to add to the right-hand side of Eq. (3.33) a pre-factor $c < 1$ which decreases as the systems becomes more 2D.

Concluding this section, our data provides support to the theoretical predictions [18] of the scaling behavior of the resistivity, although some deviations for the coherence temperature from the predicted behavior are observed in the coexistence pressure range.
5. Results and Discussion

5.4. Comparison to $\kappa$-BETS-Mn

To check whether the results about $m_c$ obtained on $\kappa$-Cl are universal for organic materials with a Mott-insulating ground state, we performed similar experiments on another organic conductor, which is $\kappa$-(BETS)$_2$Mn[N(CN)$_2$)$_3$ ($\kappa$-BETS-Mn).

5.4.1. Phase Diagram

![Phase Diagram](image)

Fig. 5.22: a) Out-of-plane resistance of $\kappa$-BETS-Mn as a function of temperature under pressures in the metallic state (blue), as well as the region of coexistence (red). The inset shows the small feature in coexistence region caused by arising superconductivity. b) Pressure dependence of the SC critical temperature.

![Resistivity vs Pressure](image)

Fig. 5.23: Pressure dependence of resistance of $\kappa$-BETS-Mn at 0.4K and 27T.

Figure 5.22a) shows the low temperature part of the $R(T)$ curves around the SC-transitions upon cooling. Similarly to $\kappa$-Cl, we see only small differences in the normal metallic state. Although the curves at 720 and 800 bar show a small increase in resistance before the SC transition, the resistances right before the transition is not yet increased. This suggest it not to be a sign of the coexistence region but maybe due to anomalies caused by the arising superconductivity. A possible scenario is that the formation of Cooper-pairs decreases the amount of normal metallic charge carriers, but there are not yet supercurrents in the oop direction, leading to an increasing resistivity [101, 102]. However, for $p \leq 520$ bar, we see an increase in resistance by several times upon cooling, compared to the normal metallic state. Figure 5.23 shows the
5.4. Comparison to $\kappa$-BETS-Mn

The pressure dependence of resistance at lowest temperature and under a magnetic field of 27 T to destroy all superconductivity. The data shows significant change in resistance around 500 bar, indicating the proximity to the insulating state. Therefore we conclude the upper critical pressure to be between $520 \leq p_{c1} \leq 720$ bar, which is in good agreement with Ref. [32].

There are two differences to point out, comparing the present behavior to $\kappa$-Cl. The first one is the between 10 and 100 times higher resistance in the normal metallic state, despite similar sample dimensions. A possible explanation for this is a high anisotropy, resulting in higher out-of-plane resistivity. The second difference is the high residual resistance in the SC state in the coexistence pressure range. For $p = 520$ bar, the resistance below the SC transition decreases only to about 5% of the normal state resistance at the SC onset. This becomes even more pronounced for the lower pressures, where the transition can only be detected as a small kink around $T_c$ [see inset Fig. 5.22(a)]. One possible explanation for this might be that the insulating domains have a very flat shape, which separates the metallic domains from each other. This would also imply that we can interpret the system as a serious connection of insulatorlike and metallike resistances.

In Fig. 5.22 b) we plotted the critical temperature of the SC transition as a function of pressure. The maximal temperature of the SC onset is 5.2 K in this experiment, which is in good agreement with Ref. [32]. However, in contrast to the reported almost constant $T_c$, we see a strong decrease of the critical temperatures with a maximum at around 600 bar, resulting in a domelike shape of the SC phase similar to $\kappa$-Cl.

Further, we consider the magnetic field dependence of the resistance as depicted in Fig. 5.24(a). As one can see, fields of below 3 T are sufficient to suppress supercurrents.

**Fig. 5.24:** a) Magnetoresistance curves at a constant temperature of 0.4 K for different pressures. b) Pressure dependence of magnetic field necessary to suppress supercurrents in the out-of-plane direction.
5. Results and Discussion

at any pressure. Even at the lowest pressures, there is an increase in resistance at small fields (see inset Fig. 5.24a). The minimum seen at these curves below 0.1 T is probably caused by remnant fields in the magnet. A more detailed analysis of the critical field is presented in Fig. 5.24b). The critical field decreases gradually for pressures above 520 bar but has a discontinuity for the lowest two pressures, where supercurrents are almost fully suppressed at $B = 0$. As the critical temperature shows a significantly different behavior at low pressures, we conclude that the feature we see is caused by the breaking of weak links, like Josephson junctions between SC islands, rather than the destruction of SC electrons. This is an additional argument for our model of serial connected resistances of insulator- and metallike nature.

5.4.2. Effective Cyclotron Mass

Fig. 5.25: a) Magnetoresistance of $\kappa$-BETS-Mn at a constant temperatures of 0.4 K with the corresponding SdH spectrum in the inset. b) Dingle plot of the oscillation amplitude corresponding to the $\beta$-orbit. The linear fit between 13 and 29 T indicates a very good agreement with the 2D Lifshitz-Kosevich formula. The inset shows the original oscillations normalized to the background resistance $R_{bgr}(B)$.

Next we present the magnetoresistance of $\kappa$-BETS-Mn and analyze it in the same way as in Sec. 5.2.1. Figure 5.25a) shows a general magnetoresistance curve and the corresponding FFT. The SdH spectrum of the oscillations in the inset of 5.25a), shows two fundamental frequencies for $p = 1060$ bar. The peaks appear at $(1.21 \pm 0.05)$ kT and $(4232 \pm 3)$ T correspond to the $\alpha$- and $\beta$-orbit respectively, with the higher frequency being the dominant component. This is in reasonable agreement with the very recent first observation of these oscillations [29]. Comparing this to the frequencies seen in $\kappa$-Cl, we see that the $\beta$-orbit and therefore the first Brillouin zone is about 10% bigger in $\kappa$-BETS-Mn in agreement with structural data [32]. By contrast, the $\alpha$-orbit is more than twice the size of that in $\kappa$-Cl. The relatively big $\alpha$-orbit can be explained by a
very broad and almost rectangular closed pocket of the FS predicted by band structure calculations \[32\]. The 2D FS suggested by the authors is depicted in Figure 5.26. Due to the low amplitude of the $\alpha$-oscillations, which decreases at lower pressure, we were not able to trace $F_\alpha$ closer to the MIT.

The field-dependent amplitude in Fig. 5.25b) is plotted according to Eq. (5.4). The very good agreement with the linear fit in the field range of 13-29 T supports our assumption of the high two-dimensionality and anisotropy, as there is no sign of beating.

Next we will investigate the pressure dependence of the effective cyclotron mass. Since it is determined by the temperature dependence of the oscillations normalized to the background resistivity, we first have to clarify the role of the residual resistance in the coexistence region. As already discussed, $\tilde{\sigma}/\sigma_0$ in Eq. (3.14) only considers the ratio of the oscillating part of the signal to the conductivity of the electrons responsible for the oscillations. If the sample contains fully insulating layers, which do not contribute to the SdH oscillations, but very well influence the overall conductivity of the sample, the relevant $\sigma_0$ is different from the as-measured one. As long as the sample is fully metallic, $\tilde{\sigma}$ can be normalized by the measured $\sigma_0$. In the case of interposed insulating layers, the background resistance can be dominated by the resistivity of the insulating phase, distorting the $A(T)$ fit.

To account for all possible scenarios, we will define the upper and lower possible limits for the normalization, which are illustrated in Fig. 5.27a). The lower limit is given by assuming the background conductivity to be determined by the metallic parts of the sample, fully shunting the insulating domains. In this case, we normalize the oscillation amplitude to the entire background (see Fig. 5.27 open symbols). To evaluate the temperature dependence of $\sigma_0 = 1/\rho_0$ we used the normal-state resistance measured at a magnetic field of 27 T. The other extreme would be to assume the insulating layers to be the dominant factor of the temperature dependent conductivity. In this case we evaluate the conductivity of the metallic phase between 0.4 and 0.85 K from a linear
5. Results and Discussion

explanation of the data and discussion of the results.

As there is very sparse data on the effective cyclotron mass further away from the coexistence region [29], we performed additional measurements at the WMI at 3He-temperatures. This is especially interesting with regard to the comparison of the
CDMFT predictions. For this purpose we plot the inverse effective mass of $\kappa$-BETS-Mn in Fig. 5.28 as it has been done for $\kappa$-Cl in Sec. 5.2.2. Similarly to $\kappa$-Cl the renormalization factor exhibits the expected overall linear dependence up to the coexistence region. Below the upper critical pressure, the mass seems to be renormalized more strongly than above. This is consistent with our findings in $\kappa$-Cl, however the deviation from the linear dependence for $\kappa$-BETS-Mn is considerably smaller, with at most 7% difference. Further, the extrapolated pressure, at which $Z$ vanishes is with -6.2 kbar much lower than for $\kappa$-Cl. Despite $\kappa$-BETS-Mn apparently being further away from $U_{c2}$ in the single-site DMFT than $\kappa$-Cl, its mass seems to be renormalized more strongly.

Another interesting aspect about the cyclotron mass in $\kappa$-BETS-Mn is an unusually high $m_\alpha$. At pressures of 1.4 kbar, the ratio of $m_\beta/m_\alpha$ has been found to be 1.24 [29], which is much lower than for most $\kappa$-(ET)$_2$X salts (see Sec. 5.2.2). Although calculations within the extended Hückel method yield a theoretical ratio of the band masses of 1.55 [29], which is small compared to $\kappa$-Cl or $\kappa$-NCS, the real value significantly deviates from that. This might be a hint for an unusually strong renormalized $m_\alpha$. In order to study this phenomenon further away from the Mott MIT, we studied the SdH oscillations at $p \approx 4$ kbar. As the oscillations of the $\alpha$-orbit are strongly suppressed by magnetic breakdown, it was easier to investigate them in fields between 14 and 16 T at the WMI. The temperature dependence of the oscillation amplitude yields $m_\beta^2/m_\alpha^2 = 1.46 \pm 0.1$, which is much closer to the theoretical predictions. So the reason for the relatively big $\alpha$-mass seems to not only lie within a high band mass, but also a more strongly renormalized mass on the $\alpha$-orbit. The authors of Ref. [29] explain this by the extended flat segments of the closed pocket, leading to pronounced nesting
properties and thus enhanced electron correlations at the nesting wave vector. Hence away from the MIT the unusual high renormalization is less pronounced. This might also explain, why the amplitude of the $\alpha$-oscillations is so strongly suppressed at low pressures.

5.4.3. Dingle Temperature

Next, we want to investigate the Dingle temperature in $\kappa$-BETS-Mn, as we approach the MIT. Since we do not expect the insulating phase to show a significant magnetoresistance, it can be considered constant over the whole field range and the entire change of $R(B)$ is governed by the metallic phase. If we stay in our picture of in-series connected insulating and metallic resistances, we have to subtract the residual zero-field resistance from the measured signal for the data in the coexistence region, before analyzing it with Eq. (5.4). As we only see very weak $\alpha$-oscillations, which disappear at lower pressures and since we are operating at very high fields, we can neglect the effects of magnetic breakdown on the oscillation amplitude.

![Graph showing Dingle temperature vs pressure]

**Fig. 5.29:** a) Pressure dependence of the Dingle temperature in $\kappa$-BETS-Mn for the corrected effective mass. b) Comparison of the Dingle temperatures to the upper and lower limiting case of the effective cyclotron mass.

The results for the Dingle temperature are shown in Figure 5.29a) for the data corrected as explained above and compared in Figure 5.29b) to the limiting cases explained in the section before. The data only weakly depends on the way of evaluation, thanks to the flat magnetoresistance at high fields. The Dingle temperature is constant within the uncertainty for $p \geq 720$ bar, which is consistent with our findings in $\kappa$-Cl. In the coexistence region however, the Dingle temperature increases by up to 20%. Using the
definition of the Dingle temperature, we can apply

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

(5.10)

to estimate the energy scale of the scattering to be of the order of 0.66 meV. This might be a hint for enhanced scattering below the upper critical pressure, although it is much less than predicted by CDMFT (≈10 meV). Why this behavior cannot be seen in \( \kappa \)-Cl is unclear at this point.
6. Summary, Conclusion & Outlook

In this thesis, we studied the electronic properties of the Mott organic compound \( \kappa-(BEDT-TTF)_2Cu[N(CN)_2]Cl (\kappa-\text{Cl}) \) at low temperatures and pressure below 1 kbar by Shubnikov-de Haas (SdH) oscillations, as well as the conducting properties in an extended region of the \( p-T \) phase diagram. Additionally we performed magnetic quantum oscillation experiments on its sister compound \( \kappa-(BEDT-TTF)_2Cu(NCS)_2 (\kappa-\text{NCS}) \) to see the influence of the proximity to the Mott metal-insulator transition (MIT). Further, another Mott-insulating system, namely \( \kappa-(BEDT-TSF)_2\text{Mn}[N(CN)_2]_3 (\kappa-\text{BETS-Mn}) \) was used, to check our findings in \( \kappa-\text{Cl} \) for universality. A special emphasis was put on the evaluation of the effective cyclotron mass and its comparison to recent theoretical predictions, most importantly dynamic mean field theory (DMFT) [17] and cluster DMFT (CDMFT) [18].

The temperatures between 70 and 800 mK under changing magnetic fields up to 17 T necessary for the SdH experiments on \( \kappa-\text{Cl} \) were obtained by a dilution refrigerator dip-stick. The experiments on \( \kappa-\text{BETS-Mn} \) were performed mainly at the high field laboratory in Grenoble at magnetic fields of up to 29 T. Thanks to this opportunity we were able to study the SdH oscillations at higher temperatures between 0.4 and 1.4 K realized by a \(^{3}\text{He}\)-cryostat. For both cases we used a clamp cell technique for applying hydrostatic pressures. However, for the investigation of the conducting properties at elevated temperatures, we were using a \(^{4}\text{He}\)-cryostat together with a helium gas-pressure setup to be able to precisely control pressure and continuously change the temperature between 1.4 and 300 K. Furthermore, the use of a Montgomery-like measurement geometry [19] allowed for a simultaneous evaluation of the in-plane (ip) and out-of-plain (oop) resistivity.

In the described experiments we found the following results. We identified the region of coexisting insulating and metallic phases in \( \kappa-\text{Cl} \) and \( \kappa-\text{BETS-Mn} \) close to the MIT by the increasing resistance in the cooling curves and a hysteretic temperature dependence. We found to enter the coexistence region from the metallic side for \( \kappa-\text{Cl} \) at \( \approx 350 \) bar and for \( \kappa-\text{BETS-Mn} \) at \( \approx 600 \) bar, which is in good agreement with literature. Furthermore, we found a dome-like structure of the superconducting (SC) phase in \( \kappa-\text{BETS-Mn} \) with its peak also around the upper critical pressure.

The observation of the two fundamental frequencies in the SdH spectrum allowed us to study the FS close the MIT. \( \kappa-\text{Cl} \) and \( \kappa-\text{NCS} \) exhibit very similar FSs and the same linear pressure dependence of the oscillation frequencies, whereas \( \kappa-\text{BETS-Mn} \) shows a significantly bigger \( \alpha \)-orbit. However, as we approach the MIT in \( \kappa-\text{Cl} \) we observe a significantly decreased closed pocket of the FS and the corresponding amplitude van-
ishes at the lowest applied pressures. Hence, we assume that the quasi-two-dimensional (2D) FS of κ-Cl becomes more rectangular, as the MIT is approached. Angle-dependent magnetoresistance oscillation may be a helpful tool to investigate the FS in more detail in the future. Additionally to the change of the 2D FS, we were able to observe an increase of anisotropy of the system in the same pressure range. This was done by analyzing the beating of the β-oscillation amplitude, which suggests a decrease of the warping of the FS in the direction perpendicular to the layers. Furthermore, this change in anisotropy was also confirmed by ip and oop conductivity measurements, which show a sharply change of the anisotropy at the transition for temperature below the critical endpoint and becomes broader for $T > T_c$ following the crossover region. Hence, we suggest the increasing anisotropy to be an inherent property of the Mott-MIT in κ-Cl.

We used the temperature dependence of the oscillation amplitude at different pressures, to determine the pressure dependence of the effective cyclotron mass for all three materials. Similar to the findings on the FS, κ-Cl and κ-NCS are very similar to each other for pressures above the upper critical pressure. All three organic metals show a good agreement with the $m^* \propto Z^{-1} \propto (p - p_c)^{-1}$ dependence predicted by DMFT [18], underlining the importance of electron-electron interactions in the system. However, as $m^*$ does not diverge close to the transition, we see that magnetic interaction have to be taken into account as done in CDMFT [78]. Hence, it would be interesting to study the effective cyclotron mass on strongly magnetically frustrated materials in the future, which should exhibit the predicted mass divergence. One possible candidate for such an experiment is κ-(BEDT-TTF)$_2$Cu(CN)$_3$, which is supposed to be a spin liquid at low temperatures and pressures [30] and not an antiferromagnetic insulator, like κ-Cl or κ-BETS-Mn.

The behavior inside the coexistence region differs from that in the fully metallic state. For both κ-Cl and κ-BETS-Mn an even stronger increase of $m^c_\beta$ can be observed, which cannot be explained at the current state. Furthermore, we observe a coherent transport contrary to the theoretical predictions. Additionally, the Dingle temperatures did not show any hints for increased scattering in the coexistence region of κ-Cl and only a small increase for κ-BETS-Mn, much smaller than predicted by CDMFT.

Lastly we investigated the transport properties around the resistive maxima in the cooling curves of κ-Cl. We were able to trace the maximum for pressures between 200 and 650 bar and fit the curves onto a single function $\rho/\rho_{\text{max}} = f(T/T_{\text{max}})$. This shows that the conducting properties around $T_{\text{max}}$ are governed by a single physical mechanism, which is believed to be the destruction of heavy Fermi liquid quasi particles [75]. Further evidence for this theory is the dependence of $\rho_{\text{max}}$ and $T_{\text{max}}$ on the effective mass. For $\rho_{\text{max}}(m^*)$ we found the expected power law dependence and for $T_{\text{max}}(m^*)$ we found $T_{\text{max}} \approx T_F/m^c_\beta$, which is in good agreement with the theoretical predictions.
Altogether we can conclude that modern theories like DMFT and CDMFT offer a good description of the weakly first order Mott-MIT in organic charge transfer salts for the most parts of the phase diagram. This shows that both electron-electron correlations of the Mott-Hubbard insulating scenario and effects of magnetic ordering like in the Mott-Heisenberg insulating case are important factors for the MIT in Mott organics. However, they start to become less accurate, as we enter the coexistence region. Hence, these theories need to develop further, including the coherent transport, the mass enhancement and the increased anisotropy, observed in this region.
A. Mathcad Algorithm for Montgomery Configuration

Calculation of anisotropy and resistivities of sample using
Montgomery method (modified by Buravov)
Lx-length Lz-width Ly-thickness
Nx-(number-1) of column of Ux/ix; Ny-(number-1) of column of
Uy/ly
Temp-(number-1) of column of Temp
data-file name of stuff
file-name name of export file
a1.a2.a3.a4 - distances of contacts from the corners
a1-down-left(always current contact)
a2-down-left
a3-down-right
a4-up-right

data := "H:\1.txt" file := "H:\2.txt" Temp := 0 Nx := 2 Ny := 1
Lx := 0.04 Ly := 0.0015 Lz := 0.03 a2 := 0.008 a3 := 0.008 a1 := 0.009 a4 := 0.007

a := READPRN(data)
ii := rows(a) - 1 rows(a) := 2570 cols(a) := 3
i := 0..ii

RXi := ai.Nx RYi := ai.Ny

Δ1 := a1/Lx Δ2 := a2/Lx Δ3 := a3/Lx Δ4 := a4/Lx

q(x) := e^{(-2\pi x)}

K(x) := \frac{\pi}{2} \left( 1 + 2q(x) + 2q(x)^2 + 2q(x)^3 + 2q(x)^4 \right)

ϕ := \frac{\pi}{2} - 0.1

S(ϕ) := \sin \sqrt{\int_{0}^{\phi} \frac{1}{\sqrt{1 - \sin(θ)^2}} dθ - u}, \phi
A. Mathcad Algorithm for Montgomery Configuration

\[
\begin{align*}
\zeta_1(x) &= S[K(x) \cdot (1 - 2 \Delta_1)] \\
\zeta_2(x) &= \left(1 + 2 \cdot q(x) + 2 \cdot q(x)^4 + 2 \cdot q(x)^9 + 2 \cdot q(x)^{16}\right)^2 \\
&\quad \times \frac{1}{4 \cdot \sqrt{q(x)} \left(1 + q(x)^2 + q(x)^6 + q(x)^{12} + q(x)^{20}\right)^2} S[K(x) \cdot (1 - 2 \Delta_2)] \\
\zeta_3(x) &= -\left(1 + 2 \cdot q(x) + 2 \cdot q(x)^4 + 2 \cdot q(x)^9 + 2 \cdot q(x)^{16}\right)^2 \\
&\quad \times \frac{1}{4 \cdot \sqrt{q(x)} \left(1 + q(x)^2 + q(x)^6 + q(x)^{12} + q(x)^{20}\right)^2} S[K(x) \cdot (1 - 2 \Delta_3)] \\
\zeta_4(x) &= -S[K(x) \cdot (1 - 2 \Delta_4)] \\
F(x) &:= \left[ \begin{array}{c}
\frac{\zeta_2(x) - \zeta_1(x)}{\zeta_2(x) - \zeta_4(x)} \\
\frac{\zeta_2(x) - \zeta_4(x)}{\zeta_1(x) - \zeta_3(x)} \\
\frac{\zeta_1(x) - \zeta_3(x)}{\zeta_2(x) - \zeta_4(x)} \
\end{array} \right]
\]

\[
x_0 := \text{root}(F(x), \frac{R_x}{R_y}, xx) \quad xx := \frac{L_x}{L_y}
\]

\[
anisotropy(x) := \left(\frac{1}{x} \cdot \frac{L_x}{L_y}\right)^2 \quad \text{anisotropy} = ax/ey
\]

\[
\rho_x(x, R_x) := -R_x \cdot \pi \cdot L_z \cdot x \cdot \frac{L_y}{L_x} \cdot \frac{1}{xx} \cdot \frac{1}{\left[ \begin{array}{c}
\frac{\zeta_2(x) - \zeta_1(x)}{\zeta_2(x) - \zeta_4(x)} \\
\frac{\zeta_2(x) - \zeta_4(x)}{\zeta_1(x) - \zeta_3(x)} \\
\frac{\zeta_1(x) - \zeta_3(x)}{\zeta_2(x) - \zeta_4(x)} \
\end{array} \right]}
\]

\[
\rho_y(x, R_y) := -R_y \cdot \pi \cdot L_z \cdot x \cdot \frac{L_x}{L_y} \cdot \frac{1}{xx} \cdot \frac{1}{\left[ \begin{array}{c}
\frac{\zeta_2(x) - \zeta_3(x)}{\zeta_1(x) - \zeta_4(x)} \\
\frac{\zeta_1(x) - \zeta_3(x)}{\zeta_2(x) - \zeta_4(x)} \
\end{array} \right]}
\]

\[
\text{ff}([w, w, w]) := 0
\]

\[
b := \text{matrix}(ii + 1, 6, ff)
\]

\[
b_{i, 0} := a_{i, \text{Temp}} \quad b_{i, 1} := \text{anisotropy}(x_0) \quad b_{i, 2} := \rho_x(x_0, R_x) \quad b_{i, 3} := \rho_y(x_0, R_y) \quad b_{i, 4} := a_{i, N_x} \quad b_{i, 5} := a_{i, N_y}
\]

\[
\text{WRITEPRN(file)} := b
\]
Bibliography


Bibliography


Bibliography


Bibliography


Bibliography


[100] M. V. Kartsovnik, P. D. Grigoriev, W. Biberacher & N. D. Kushch. Magnetic field induced coherence-incoherence crossover in the interlayer conductivity of a


Acknowledgments

At the end of this work I would like to thank all the people, who helped me to make this work possible. I especially want to express my gratitude to:

- Prof. Dr. Rudolf Gross, for giving me the opportunity of doing this work at the Walther-Meißner-Institut.
- Dr. Mark Kartsovnik, for his supervision, help and plenty of interesting tea times.
- Dr. Werner Biberacher for his support in the laboratories and plenty of tasty cake.
- Dr. Michael Kunz for his introductions to all tasks in the laboratory.
- Prof. Dr. Vladimir Zverev for his assistance during the measurements at the LNCMI in Grenoble.
- Ilya Sheikin for his support and hospitality at the LNCMI.
- Paul Weinbrenner for the constructive cooperation within the framework of his bachelor thesis.
- Alma Dorantes for many interesting conversations in several tea times.
- The whole technical and administrative stuff of the WMI, who were always open to requests and help.
- My fellow students, who ensured a good working atmosphere, in particular Michaela Schleuder, Christian Besson and Lukas Liensberger.
- My family and girlfriend for supporting me in the last years and giving me the time I needed, especially in the stressful writing process.