Organic superconductor as a low-temperature pressure gauge

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1 Introduction

Organic charge transfer salts exhibit rich phase diagrams and have been extensively studied over the last few decades [1][2]. The material \( \kappa-(ET)\text{Cu}[N(CN)_2]\text{Cl} \) is one example thereof, showing an exciting interplay between the Mott insulator and superconducting instabilities of the normal metallic state, see Fig. 1.1. A newer material \( \kappa-(BETS)\text{Mn}[N(CN)_2]_3 \) is currently being studied at the organic metals group at the Walther-Meißner Institute [3]. It shows similarly metal/superconductor-insulator transitions for pressures below 1 kbar = 100 MPa, see Fig. 1.2. This illustrates the importance of experiments in this pressure range.

A conventional method for measuring in this pressure range is the He gas pressure setup. However, this apparatus is not flexible enough to perform certain types of measurements. A solution is found by employing the clamp cell technique, where samples are surrounded by a pressure medium, e.g. silicon oil and hydrostatic pressure is applied at room temperature. Then the cell can be cooled down to low temperatures in a cryostat. Due to freezing of the pressure medium during cooling, the pressure in the cell changes. This change is usually measured by putting a coil of manganin (Cu 84% Ni 4% Mn 12%) into the cell, along with the organic samples. From the pressure dependent change of its resistance the low-temperature pressure can be determined to an accuracy of \( \pm 250 \) bar. This accuracy is satisfactory when measuring pressure well above 1 kbar. However it is desirable to achieve a higher accuracy for the interesting pressure range below 1 kbar. In this thesis the organic superconductor \( \kappa-(ET)\text{Cu(NCS)}_2 \), which is very sensitive to pressure [4], has been used as a pressure gauge at low temperatures. As a first step, calibration curves for different properties at pressures below 1 kbar have been obtained in a He gas pressure setup. Afterward the samples were put into the clamp cell to observe the behavior of pressure.
1 Introduction

Figure 1.1: Phase diagram of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl [7]. (100 MPa = 1 kbar)

Figure 1.2: Phase diagram of $\kappa$-(BETS)$_2$Mn[N(CN)$_2$]$_3$ [8]. (100 MPa = 1 kbar)
2 The organic superconductor 
\(\kappa-(ET)_2Cu(NCS)_2\)

\(\kappa-(ET)_2Cu(NCS)_2\) possesses a monoclinic structure, see Fig. 2.1. It is composed of insulating anion layers and conducting ET layers, where ET is an abbreviation for the complex organic molecule BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene). In the conducting plane these ET molecules pair up in dimers that are orthogonal to each other. This stacking is called the \(\kappa\) phase.

In general the conductivity in \(\kappa-(ET)_2Cu(NCS)_2\) stems from charge transfer between ET donor molecules and the acceptor complex Cu(NCS)\(_2\). Hereby two ET molecules transfer one elemental charge into the anion layer giving rise to effectively half filled two-dimensional conducting bands in the ET layers. Since there is weak interlayer interaction, the resistivity in-plane is three to five orders of magnitude lower than out-of-plane, leading to a quasi-two-dimensional character of the conduction system [3]. This low dimensionality can be seen in the Fermi surface obtained from semi-empirical band structure calculations [3]. Parallel to the conducting planes it has the shape as shown in Fig. 2.2a. In the out-of-plane direction the Fermi surface is slightly warped, see Fig. 2.2b. As will be discussed in the following, oscillations in the magnetoresistance, so-called Shubnikov-

Figure 2.1: Crystal structure of \(\kappa-(ET)_2Cu(NCS)_2\) [1]

Figure 2.2: Two-dimensional a) and three-dimensional b) view of the Fermi Surface of \(\kappa-(ET)_2Cu(NCS)_2\). The warping in the \(k_z\)-direction is exaggerated. [9]
de Haas (SdH) oscillations, were observed [10], [11]. Generally speaking, these stem from oscillations in the density of states at the Fermi level [12]. In particular, the closed hole-like $\alpha$ pockets of the Fermi surface give rise to a certain frequency $F_\alpha$ in the spectrum of the SdH oscillations. This frequency depends on the size of the Fermi surface. It is very sensitive to pressure, because this compound has a high compressibility, in view of the weak van der Waals bonds between the ET molecules. The value is $\kappa_T = (122 \text{ kbar})^{-1}$ [1], which is about 5 times larger than for ordinary metals. The resulting pressure sensitivity of the frequency has already been demonstrated in previous studies [6], where pressure up to 18 kbar has been applied, see Fig. 2.3.

There are other frequencies in the spectrum, however. They originate from the magnetic breakdown effect. Here, at fields above 10 T, electrons from the open sheets can tunnel over the small energy gap at the boundary of the Brillouin zone onto the $\alpha$ pockets. Quantum interference can then lead to a number of additional frequencies [11]. One of these has been observed and evaluated in this work. Because of its comparatively low pressure dependence, these results will not be presented here.

Another advantage of measuring SdH oscillations is their relatively large ampli-
tude in this compound. The reason for this lies in the quasi-two-dimensionality of its Fermi surface, as explained below. From temperature damping of the amplitude it is possible to obtain the so-called effective cyclotron mass $m_c$ as a function of pressure $p$. This quantity has also been shown to be pressure-dependent in previous studies, see Fig. 2.4a. The physical reason for this is very complicated and can generally be traced back to the pressure dependence of many-body interactions and the high compressibility mentioned above. One can see in Fig. 2.3 and Fig. 2.4a that both $F_\alpha$ and $m_c$ have not been studied in detail below 1 kbar. This was one of the tasks performed in this work.

Other than a superconducting (SC) transition $\kappa$-(ET)$_2$Cu(NCS)$_2$ exhibits no other phase transitions. In addition, the resistive SC transition is also influenced by pressure. As is shown in Fig. 2.4b $T_c$ decreases linearly with pressure by about 3 K/kbar [1]. Again, this large pressure dependence stems in general from many-body interactions and a high $\kappa T$. Since the exact mechanism of superconductivity in this compound is not yet fully understood, a detailed explanation of the pressure behavior of $T_c$ is impossible. As has already been mentioned, this compound has been studied under high pressure [6], however there is no detailed data for the pressure range below 1 kbar.

Figure 2.4: Superconducting critical temperature and effective cyclotron mass as a function of pressure

(a) Effective mass $m^*$ normalized to the free electron mass $m_e$ as a function of pressure $p$

(b) $T_c$ vs $p$ for different materials [1]
3 Theoretical background

Solving the Schrödinger equation for conduction electrons in a magnetic field applied in \( z \) direction leads to the quantization of their energy spectrum. One finds for free electrons

\[
\epsilon(n, k_z) = (n + 1/2)\hbar\omega_c + \frac{(\hbar k_z)^2}{2m_e},
\]

(3.1)

where \( n = 0, 1, 2, \ldots \), and \( m_e \) is the free electron mass. The quantity \( \omega_c = eB/m_e \) is the cyclotron frequency, with \( m_e \) being the effective cyclotron mass [12]. In \( k \)-space the electrons are located on so-called Landau tubes which are coaxial cylinders, with a cross sectional area perpendicular to the magnetic field of

\[
S_n = (n + \gamma)2\pi eB/\hbar.
\]

(3.2)

This is the famous Onsager relation [13]. Here \( \gamma = 1/2 \) for free electrons. Since any deviations from this value are small in most cases, they will be neglected in the following [11]. As can be seen from Eq.3.2 the Landau tubes expand continually with increasing field, crossing the extreme Fermi surface cross section \( S_{\text{extr}} \) with a period of:

\[
1/(\Delta B) = \frac{2\pi e}{\hbar S_{\text{extr}}}.
\]

(3.3)

At \( T = 0 \) the electrons obey the Fermi-Dirac statistic. Therefore all Landau tubes with cross sections smaller than \( S_{\text{extr}} \) are occupied. The density of states on a Landau cylinder, that leaves the Fermi surface decreases infinitely rapidly, since electrons cannot have energies above the Fermi energy \( \epsilon_F \). This leads to oscillations of physical quantities, like for instance the free energy of the system. The frequency is simply

\[
F = 1/(1/(\Delta B)) = \frac{S_{\text{extr}}\hbar}{2\pi e}.
\]

(3.4)

As shown in Fig.3.1 in the 3 dimensional case many tubes cross the Fermi surface, whereas only a few Landau tubes touch the Fermi surface in the quasi-two-dimensional (q2D) case. Moreover, in q2D organic metals already at fields of 10 T the distance between two Landau tubes may become bigger than the warping of the Fermi cylinder. Electrons, on a Landau cylinder leaving the Fermi surface, jump to a lower level, causing oscillations in the density of states at the Fermi level. Since in the q2D case only few Landau tubes cross the Fermi surface at one time, the amplitude of these oscillations is larger in comparison to the 3-dimensional case.
3 Theoretical background

Using Pippard’s idea that the scattering probability is directly proportional to the density of states at the Fermi level, it can be shown \[14\] that the density of states oscillations can be expressed as a field derivation of the magnetization \[15, 16\],

\[
D(\epsilon_F) \propto (m_c B)^2 \frac{\partial \tilde{M}}{\partial B},
\]

Based on the Lifshitz-Kosevich theory \[12\], the oscillatory part of the conductivity can be expressed as:

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

where \(\sigma\) is the background conductivity. Neglecting higher harmonics, the amplitude of the oscillations is

\[
a_1 \propto m_c \sqrt{BR_T R_D R_S}.
\]

Here \(R_D\) is the Dingle factor, which accounts for damping of the oscillations, due to a finite lifetime of conduction electrons. \(R_S\), the so-called spin splitting factor, takes into account the Zeeman effect, which also leads to damping. Of particular interest for this thesis is \(R_T\) the temperature damping factor that accounts for the damping of the amplitude at finite temperature due to smearing of the Fermi surface. The exact expression is:

\[
R_T = \frac{K \mu T / B}{\sinh(K \mu T / B)}.
\]
Here $K=14.69$ T/K and $\mu = m_c/m_e$ is the cyclotron mass in units of free electron masses. By fitting $R_T$ to experimental data $m_c$ is determined.

Since the effective cyclotron mass as well as the frequency are sensitive to pressure, measuring the Shubnikov-de Haas effect was a major objective of this thesis. It should be noted that observing the SdH effect requires rather large fields of more than 10 T. Since many experiments with organics require such high fields, this does not create an additional problem.
4 Experimental Setup

In this section some general information on the experimental techniques and devices will be given. Then the He gas pressure setup and consecutively the clamp cell technique will be described.

4.1 General overview of the experiment

To record SdH oscillations one needs to obtain the resistance in the sample in dependence of the magnetic field. In order to accurately determine the out-of-plane resistance, which is significantly bigger than the in-plane resistance, see chapter 2, the four point measurement technique was employed, see Fig. 4.1. For this platinum wires of 20 µm diameter were glued onto the samples with a conducting graphite paste. One pair served to apply an alternating current \( f = 13 - 17 \text{Hz} \) of typically 10 µA for temperature sweeps and 100 µA for magnetic field sweeps, the other pair to measure the voltage giving the resistance via Ohm’s law. This voltage was read out via lock-in amplifiers.

In order to ensure reproducibility of the obtained results, two samples were measured simultaneously throughout the experiment. Additionally, a few runs at identical conditions were performed for the same purpose.

In order to avoid angular dependent effects \[11\] the samples were always oriented with the conducting layers perpendicular to the magnetic field. To create a homogeneous steady magnetic field up to 15 T a superconducting magnet from Cryogenics, consisting of two concentric coils made...
4 Experimental Setup

from Nb₃Sn and NbTi, was used. These coils, coupled in series, were submerged in a ⁴He bath, thus cooling them well below their critical temperature.

In order to evaluate the temperature damping of the SdH oscillations and thus obtain \( m_c \), one needs to control the temperature in the sample space. This is achieved by putting a variable temperature insert (VTI) into the cryostat. The VTI is composed of two concentric cylinders, see Fig. 4.2. The space between those is evacuated to ensure thermal decoupling from the environment. The inner cylinder is connected by a capillary with high flow impedance to the ⁴He bath. Constant pumping of this inner cylinder creates a constant flow of ⁴He through the impedance. After some time, liquid helium accumulates in the sample space. Now the temperature can be set by regulating the ⁴He vapor pressure in the inner cylinder. In this way temperatures between 1.4 and 4.2 K could be stabilized to within a few mK. Temperatures between 2 K and 20 K could be achieved by heating. To perform temperature sweeps and thus measure the SC resistive transition a heater controlled by a LakeShore 340 temperature controller was used.

4.2 He gas pressure setup

The first step of the experiment was to obtain calibration curves of the superconducting transition and SdH oscillations at a certain pressure at low temperatures. For this a He gas pressure setup was used, see Fig. 4.3. ⁴He under pressure of up to 180 bar flows through a nitrogen trap, where impurities are filtered out. This is important, since the Cu-Be capillary that transfers pressure into the cooled cell has a small diameter of 0.3 mm. Therefore any impurities could lead to a blockage. A compressor applies pressures up to 3 kbar. By using an amplifier, it is possible to reach pressures up to 10 kbar with this setup.

The pressure is measured by a membrane sensor at room temperature, before the capillary enters the cryostat. Since helium becomes solid above pressures of 25 bar at low temperatures, the pressure in the cell decreases during subsequent cooling below its freezing point. However, the drop in pressure amounts to 80 bar at about 1 kbar so it is very small. Additionally there exist calibration curves for this difference in pressure. Because of this the pressure can be determined to an accuracy of a couple of bars.

As has already been mentioned helium in the sample space becomes solid for most measurements. Still the pressure is assumed to be homogenous and hydrostatic in the sample space [18, 19], since solid helium is the softest solid known. Also it has a cubic structure and there is only a small volume effect at the phase transition.

The advantages of this setup are, that the low-temperature pressure can be read out while the measurement is running and can be adjusted accurately to within a couple of bars. In the Introduction it was mentioned that this setup has several disadvantages. For example it cannot be used in conjunction with a dilution fridge, the samples cannot be rotated in a magnetic field and it is not portable.

Better suited for the above mentioned applications is the clamp cell which will be described in the following.
4.2 He gas pressure setup

Figure 4.3: Sketch of the He gas pressure setup. [17]
4 Experimental Setup

4.3 Clamp Cell

Using the various calibration curves obtained from the gas pressure measurements, the samples were put into a clamp cell to observe the behavior pressure. Since many measurements are performed in strong magnetic fields, this cell is made from a non-magnetic Cu-Be alloy. As can be seen in Fig. 4.4, the samples are located inside a Teflon cup and surrounded by silicon oil GKZh. Pressure is applied at room temperature by pressing down a piston from above and locking it with a nut at the top. When cooling down the GKZh freezes between 180 and 220 K and becomes an amorphous solid, creating quasi-hydrostatic pressure in the sample space. Studies have shown, that depending on the pressure medium used, the pressure may not be homogeneously distributed throughout the cell after freezing [20]. As will be discussed later no significant pressure inhomogeneities have been observed in our experiments.

In general, the pressure changes considerably during the cooling process in comparison to the He gas pressure setup. As has been mentioned in the Introduction, one method to gauge this drop in pressure is to evaluate the difference in resistance of manganin, which changes by ±0.25 %/kbar. Taking into account the accuracy and reproducibility upon multiple thermal cycles, this sensitivity results in an error bar of typically ±250 bar, which is too large in the pressure range below 1 kbar. In addition, the difference in thermal expansion coefficients leads to different pressures on the manganin coil and the organic samples. Again this effect is especially important at low pressures of a few hundred bar. To avoid this, κ-(ET)$_2$Cu(NCS)$_2$ is an excellent candidate, since it obviously shows similar thermal contraction as other organics [1]. In the next chapter the results of our measurements will be shown, in order to demonstrate the accuracy, when gauging pressure with κ-(ET)$_2$Cu(NCS)$_2$. 

![Figure 4.4: Sketch of a clamp cell.](image)
5 Experimental Results and Discussion

First the calibration curves from the He gas pressure setup are shown and compared with respect to sensitivity and accuracy. Then the results will be used to observe pressure behavior in the clamp cell and check for consistency of the different calibration curves.

5.1 He gas pressure measurement

5.1.1 SdH oscillations

The magnetoresistance of $\kappa-(ET)_2\text{Cu(NCS)}_2$ is shown for different pressures in Fig. 5.1 at $T = 1.4$ K, that is well below its SC critical temperature. At zero field the superconducting state is observed, breaking at a critical field which is pressure dependent. The peak in the magnetoresistance immediately following the SC transition, is due to fluctuation effects in a q2D superconductor [21, 22]. From about 8 T onwards the SdH oscillations become visible. For every pressure the SdH oscillations were recorded in a temperature range from 1.4 K to 3 K.

Fig. 5.2 shows a selection of high field magnetoresistance curves, recorded at 400 bar. By normalizing the resistance to its non-oscillating component (resistance fitted
5 Experimental Results and Discussion

Figure 5.2: Magnetoresistance at $p = 400$ bar and at high fields for different temperatures between 1.4 and 3.0 K.

Figure 5.3: ShH oscillations, obtained by normalizing the magnetoresistance to the background, for different temperatures between 1.4 K and 3.0 K.
by a low order polynomial, one obtains SdH oscillations shown in Fig. 5.3. Here it is clearly visible, that at a constant pressure the amplitude decays with increasing temperature. Also, an additional SdH frequency, caused by magnetic breakdown and quantum interference becomes distinctly visible for temperatures starting from 2 K. It dominates the oscillations above 2.5 K.

To obtain $m_e$ from the experimental data, a fast Fourier transformation (FFT) was performed on the SdH oscillations between 12 and 15 T for all temperatures. Fig. 5.4 shows an example of the FFT spectrum at 400 bar and 1.4 K. One can see the large peak at a frequency of about 600 T. The above mentioned additional frequency, due to magnetic breakdown and quantum interference is visible at around 2600 T [11].

For the evaluation presented here, only the peak at 600 T will be relevant. In Fig. 5.5, one can see the FFT amplitude of the SdH oscillations divided by the temperature $T$ plotted against $T$. Then the fit $\text{Amplitude}/T \propto R_T/T = (K\mu/B)/[\sinh (K\mu T/B)]$ is used to give $\mu = m_e/m_e = 2.85(\pm 0.1)$. The frequency was read out directly from the FFT data.

The resulting pressure dependence of the frequency and the effective cyclotron mass obtained on two samples measured simultaneously is presented in Fig. 5.7 and Fig. 5.6 respectively. The frequency increases almost linearly with increasing pressure at a rate of about 0.03 kbar$^{-1}$. This is in agreement with results obtained from measurements in this compound at higher pressures where $F$ increased linearly up to about 5 kbar and showed saturation towards higher pressure, see also Fig. 2.3.

In contrast, $m_e$ decreases with pressure. Also the sensitivity is about 0.3 kbar$^{-1}$ exceeding that of the frequency by one order of magnitude. However the respective error bars are approximately $\pm 0.5$ T for $F$ and $\pm 0.1 m_e$ for $m_e$. From those error
5 Experimental Results and Discussion

Figure 5.5: Lifshitz-Kosevich fit (red curve) of the temperature-dependent amplitude (black squares) of the SdH oscillations.

Figure 5.6: Effective cyclotron mass vs pressure. The x-axis is extended below zero bar for better visibility.

bars and the respective sensitivities, errors for pressure determination of ±30 bar for the frequency and of ±130 bar for the effective mass measurements, were obtained. The error for the frequency is estimated from the accuracy of reading it out from the FFTs, since it reproduced for both samples in the second measurement at the same
pressure to within 0.5 T. The error bar for the mass was determined by repeating the measurements at ambient pressure, see Fig. 5.6. Since the mass is determined by fitting \(R_T/T\) to experimental data, numerous error sources contribute to this scattering. In particular, measurements at higher temperatures above 2.6 K sometimes did not fit perfectly and the effective mass could change by as much as 0.4 \(m_e\) in extreme cases depending on the temperature range.

5.1.2 \(T_c\) measurements

As mentioned in chapter 2, the SC critical temperature has been shown to decrease approximately linearly, at a rate of 3 K/kbar. In Fig. 5.8 the resistive SC transition is presented for various pressures between 0 and 1.2 kbar, clearly showing the decrease of \(T_c\) with pressure. Also heating and cooling curves are virtually the same, except for the 400 bar curve, where it seems that the heating rate was too fast in the temperature range above 10 K, causing kinks in the up sweep. The characteristic feature in the green curve at 8 K, the red curve between 12 and 13 K and partly the blue curve above 15 K originates from the phase transition of helium into the solid state. Unfortunately, for the 400 bar curve this melting point falls onto the SC transition, making its evaluation more difficult.

In general, all transitions were evaluated by taking the upper crossing, the midpoint and the extrapolation to zero, see inset Fig. 5.8. Plotting all three in one diagram against pressure, shows that their behavior is the same, see Fig. 5.9. They all decrease linearly with pressure. Therefore it is sufficient to take only one of those definitions for a calibration curve.
5 Experimental Results and Discussion

Figure 5.8: SC transition in the temperature-dependent interlayer resistance for various pressures; inset shows different ways to determine critical temperature.

Fig. 5.10 depicts the pressure dependence of $T_c$ determined from the upper crossing for the two different samples. At ambient pressure both $T_c$s are close to 10.4 K, the literature value [3]. For pressures above 100 bar, $T_c$ decreases fairly linearly with sample 1 having a slightly higher transition temperature. At 1.2 kbar the transition temperatures almost coincide. The data at 0 bar seem to show inverse behavior with sample 2 having the higher critical temperature. The point for sample 1 however fits nicely with all points above 200 bar.

The relative sensitivity $\frac{1}{T_c} \frac{dT_c}{dp} = 0.41$ kbar$^{-1}$ is the highest of all three quantities observed. Together with an estimated error bar of $\pm 0.2$ K, this gives an uncertainty for pressure determination of $\pm 60$ bar, which is more accurate than for $m_c$. Unfortunately $T_c$ depends on hardly controllable issues like sample quality and size, as well as the way the samples are contacted. Because of this $T_c$ was normalized to $T_c(0)$ the SC transition temperature at ambient pressure, see Fig. 5.11. In this way it becomes possible to compare $T_c$ of different samples, even after recontacting.

Equipped with these three calibration curves, we transferred the same two samples to the clamp cell for test measurements.
5.1 He gas pressure measurement

Figure 5.9: SC critical temperature at the upper crossing (black), midpoint (red) and extrapolation to zero (green) vs pressure.

Figure 5.10: SC critical temperature determined from upper crossing vs pressure for two different samples.
5 Experimental Results and Discussion

Figure 5.11: Upper crossing of $T_c$ normalized to the ambient pressure value as a function of pressure; two samples measured simultaneously.

Figure 5.12: Superconducting transition at 800 bar in the He gas pressure setup (red curve) and at similar pressure in the clamp cell (black).
Since helium is believed to give quasi-hydrostatic pressure in its solid state, the pressure during the calibration should be homogeneous in the sample space. Therefore, any broadening of the superconducting transition in the clamp cell would indicate pressure inhomogeneity. However, the transitions differ by less than 0.1 K in broadness between the He gas and the clamp cell pressure setup. In Fig. [5.12] one can see the transition at 800 bar in the He gas pressure setup and the transition at similar pressure in the clamp cell.

The results of the experiments are summarized in Table [5.1].

<table>
<thead>
<tr>
<th>$F$ [kN]</th>
<th>$p(300\text{K})$ [kbar]</th>
<th>$p(T_c/T_c(0\text{bar}))$ [bar]</th>
<th>$p(F)$ [bar]</th>
<th>$p(m_c)$ [bar]</th>
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<td>4.08</td>
<td>1500</td>
<td>1560</td>
<td>916</td>
</tr>
</tbody>
</table>

Table 5.1: Pressure in the clamp cell at room and at low temperatures (see text).

In the first column the applied force at room temperature is shown. The second column contains the resulting pressure, determined by measuring the resistance of a manganin coil. The further columns show the resulting pressure at low temperatures obtained from measuring $T_c$, $F$ and $m_c$, respectively. For all low temperature pressures below 1 kbar, the SdH frequency and effective cyclotron mass show pressure within a 100-140 bar from one another. Considering the above estimated error bar of ±130 bar from the effective mass measurement, the present data are in reasonable agreement with each other. The critical temperature shows pressures very similar to the SdH frequency.

To apply zero bar room temperature pressure, the samples were put into the clamp cell surrounded by GKZh as usual. The nut was then very softly fixed by hand. However when cooling down, all quantities show some small pressure, as can be seen in the first row of Table [5.1]. This is due to different thermal expansion coefficients of the samples and the GKZh. Within the error bars, the pressure at low-temperature does not change when applying a pressure at room temperature of about 1.6 kbar. This can be attributed to different roles of compressibilities and thermal expansion coefficients of both the samples and GKZh. A possible effect could for instance be that the samples contract stronger than GKZh, to the point of breaking. Indeed this happened to one of the samples when making the final measurement for $p(300\text{K}) = 1.57$ kbar.

One can see in Table [5.1] a large discrepancy between the pressure values estimated from the frequency and effective mass measurements for the highest pressure applied. However, it should be noted that 1500 bar is well out of the range studied in the He-gas pressure setup. Therefore, this pressure was estimated by linear extrapolation of the calibration curve, thereby enhancing the error bar. Also $m_c$ hardly changes
between 1 kbar and 1.2 kbar and the behavior at 1.5 kbar is unknown. Thus, the values themselves might not be correct. Since the main pressure range of interest lies well below 1 kbar this is not a problem for the present study.

Most importantly, the pressure drop at cooling may reach as much as 3 kbar. In Fig. 5.13 one can see the decrease in pressure determined from $F, T_c$ and $m_c$ plotted against pressure at room temperature. All quantities show the same decrease in pressure within error bars with the exception of the point at 4 kbar as discussed above.

In conclusion, measuring the SdH oscillations can be used to gauge the pressure with an accuracy of $\pm 30$ bar when evaluating the frequency. As a backup $T_c$ and $m_c$ provide an accuracy of $\pm 60$ bar and $\pm 130$ bar, respectively. This considerably exceeds the accuracy of $\pm 250$ bar when using a manganin coil. A possibility to apply this method, would be to put a sample of $\kappa-(ET)_2\text{Cu(NCS)}_2$ along with the main sample into the clamp cell. Upon cooling, one can then gauge the pressure by performing a field sweep between 12 and 15 T and evaluating $F$. By performing temperature sweeps and further field sweeps at different temperatures, $T_c$ and $m_c$ can be extracted, in order to check the obtained pressure values for consistency.
The goal of this thesis was to test the organic superconductor $\kappa$-(ET)$_2$Cu(NCS)$_2$ as a low-temperature pressure gauge in order to accurately determine pressures below 1 kbar in a clamp cell. The motivation for this is, that conventional methods have an accuracy of ±250 bar, which is too low in the pressure range of interest. By measuring pressure dependence of the resistive SC critical temperature, the SdH frequency and effective cyclotron mass of two samples of $\kappa$-(ET)$_2$Cu(NCS)$_2$ in a He gas pressure setup, calibration curves for the low temperature pressure were obtained. As a result, an accuracy between ±30 bar and ±130 bar was achieved. This is at least a factor of two better than usually possible.

As the second step, the samples were transferred to a clamp cell to observe the pressure behavior. In Fig. 5.13 the drop in pressure from room to low temperatures is presented. With the exception of one point at the highest pressure, all quantities measured show consistent results. In future this method can be used for studying interesting phase transitions in low-dimensional organic conductors at low pressures and low temperatures.
Bibliography


