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Magnetotransport in Quasi-Two-Dimensional Organic Conductors Based on BEDT-TTF and its Derivatives

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Abstract. — In this short review we discuss the magnetotransport properties of the most popular series of quasi-two-dimensional organic metals and superconductors, namely β-, κ- and α-salts of BEDT-TTF (shortly, ET) and some compounds based on the ET derivatives, BEDT-TTF and BEDT-TSeF. We concentrate on the results of the Fermi surface studies obtained by means of Shubnikov-de Haas as well as a new very informative angle-dependent semi-classical magnetoresistance oscillations (AMRO) experiments. The results reported here were obtained mainly due to close collaboration of different physical and chemical groups in Chernogolovka (Russia), which have been organized and led by Prof. I.F. Schegolev.

1. Introduction

The organic conductors based on the bis(ethylenedithio)tetrathiafulvalene molecule (BEDTTTF, or, shorter, ET) have initially attracted attention due to the discovery of the ambient pressure superconductivity in a layered cation radical salt β-(ET)2I3 in 1984 [1]. Further extensive efforts on the synthesis and studies of new salts of ET and its derivatives gave rise to a new generation of quasi-two-dimensional compounds [2] with properties ranging from magnetic dielectric to superconducting, depending on the chemical composition and external conditions such as temperature, pressure and magnetic field.

It is essential to know the electronic band structure of these materials in order to understand the nature and specific properties of their normal and superconducting states. A direct information on the Fermi surface (FS), one of the most important characteristics of the electronic system, can be obtained from the magnetic field studies. This, however, requires the fields strong enough to provide the Larmor radius, \( r_L \sim c p_F/eB \) (where \( B \) is the magnetic field induction, \( p_F \) is the characteristic Fermi momentum in the plane perpendicular to the field direction, \( c \) is the light velocity and \( e \) is the electron charge) sufficiently smaller than the electron mean free path \( l \), \( \gamma = r_L/l \ll 1 \). The ratio \( r_L/l \) can be estimated from the resistivity \( \rho \)

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and carrier concentration \( n \), using the standard kinetic model, \( \gamma \sim \rho \text{necc}/B \). Taking the lowest resistivity value known among the ET-based metals, \( \rho \geq 10^{-5} \, \Omega \, \text{cm} \), that is characteristic of high-quality single crystals of \( \beta_{\text{H}}-(\text{ET})_2\text{I}_3 \) and \( \beta-(\text{ET})_2\text{IBr}_2 \) at low temperatures [3], and a typical concentration \( n \simeq 10^{24} \, \text{cm}^{-3} \), one has \( \gamma \sim 20/B \), where \( B \) is measured in teslas. For many other ET salts, such as superconductors \( \kappa-(\text{ET})_2\text{X} \), this ratio is expected to be even an order of magnitude large because of their higher resistivity. Therefore, according to these estimations, the strong-field limit, \( \gamma < 1 \) can be hardly achieved in the available steady fields, \( \leq 20 - 30 \, \text{T} \).

Notwithstanding the initial expectations had been rather pessimistic, prominent Shubnikov-de Haas (SdH) oscillations were discovered in 1988 in the magnetoresistance of \( \beta-(\text{ET})_2\text{IBr}_2 \) [4] and \( \kappa-(\text{ET})_2\text{Cu(NCS)}_2 \) [5] in moderate fields of \( \sim 10 - 15 \, \text{T} \). These observations gave the first direct evidence for the existence of a well-defined FS, provided quantitative information on the FS parameters and, hence, stimulated a tremendous surge of interest to the magnetic field studies of the organic metals based on the ET molecule and its derivatives.

A great deal of the experimental data obtained to date (see, e.g. [6]) have considerably contributed to understanding the electronic properties of these materials and, in particular, proved that the rather simple extended Hückel model calculations in many cases give a surprisingly good description of the electronic band structures. In spite of their complicated chemical compositions, their FS can be basically represented by one or several slightly warped cylinders with the axes perpendicular to the crystal highly conducting plane. Sometimes the cylinders cross the first Brillouin zone boundary, giving rise to a multiply connected FS consisting of both cylindrical and open parts. Due to the extremely high anisotropy (the ratio between the in-plane and inter-plane resistivities is typically \( \sim 10^{-5} - 10^{-3} \)), these compounds may be regarded as quasi-two-dimensional (Q2D) metals, thus representing an intermediate class between the conventional three-dimensional metals and artificial two-dimensional structures. This, of course, directly influences all the magnetotransport properties, often leading to a non-conventional behaviour of both the semiclassical magnetoresistance (MR) and SdH oscillations and causing a number of novel phenomena, for example, semiclassical angle-dependent MR oscillations (AMRO) which have proven themselves to be a powerful tool for the FS investigation of these compounds.

This paper presents a brief review of the magnetotransport studies of Q2D organic metals based on the ET molecule and its derivatives, which were carried out by the Chernogolovka group (ISSP and ICP) led by I.F. Schegolev for many years. Some of recent results were obtained during a close collaboration of the Chernogolovka group and the groups from the Kyoto University (Kyoto), Walther-Meissner-Institut (Garching), Laboratoire de Physique des Solides et SNCMP (Toulouse), Laboratoire de Physique des Solides (Orsay) and State University of New York (Buffalo).

In Section 2 we will present SdH oscillations and semiclassical MR studies in apparently the simplest Q2D metals, \( \beta-(\text{ET})_2\text{X} \) with \( \text{X} = \text{IBr}_2 \) and \( \text{I}_3 \), with the FS mainly characterized by a single cylinder. We will also briefly review our understanding of the AMRO originating from the specifics of the electron motion on the slightly warped cylindrical FS which were found for the first time in \( \beta-(\text{ET})_2\text{IBr}_2 \). In Section 3 the compounds of the \( \kappa-(\text{ET})_2\text{X} \) family will be discussed. As shown by numerous experiments, the FS of the salt with \( \text{X} = \text{Cu(NCS)}_2 \) consists of both a cylinder and open sheets separated from each other by a small energy gap, being especially suitable for studying magnetic breakdown (MB) phenomena, in particular, the quantum interference effect in the coherent MB regime. The semiclassical AMRO demonstrate a rather complicated behaviour reflecting most likely the electron orbits on the closed cylindrical (2D AMRO) and open (1D AMRO) parts of the FS. Very recent results on the FS studies of the highest-\( T_c \) organic superconductors, \( \kappa-(\text{ET})_2\text{Cu[N(CN)}_2\text{]}\text{X} \) with \( \text{X} = \text{Cl} \) and \( \text{Br} \) will be
Fig. 1. — The magnetic field dependence of the resistance measured along the a-axis of $\beta$-(ET)$_2$IBr$_2$ in magnetic field tilted, in the plane perpendicular to the a-axis, by 11° from the normal to the ab-plane; $T = 1.45$ K.

also presented in Section 3. Section 4 is devoted to the $\alpha$-(ET)$_2$MHg(XCN)$_4$ compounds. Their behaviour in magnetic fields is currently of special interest due to a number of puzzling anomalies originated most likely from a unique co-existence of Q2D and quasi-one-dimensional (Q1D) FS parts. Section 5 will describe the MR properties of some new compounds, based on the ET derivatives: (BEDO-TTF)$_2$ReO$_4 \cdot 2$H$_2$O, $\lambda$-(BETS)$_2$FeCl$_4$.

2. $\beta$-(ET)$_2$X Salts with $X = \text{IBr}_2$ and I$_3$

2.1. SdH Oscillations in $\beta$-(ET)$_2$IBr$_2$. — Since the discovery of the superconductivity in the salts $\beta$-(ET)$_2$X with $X = \text{I}_3$ [1] and IBr$_2$ [7], the progress in the sample preparation technique led to the synthesis of high quality crystals of these compounds [8] and enabled the observation of the SdH oscillations of two different series and other galvanomagnetic effects reflecting the Q2D nature of their electronic systems.

A general view of the fast SdH oscillations in the in-plane, i.e. parallel to the highly conducting ab-plane, is displayed in Figure 1. The oscillation frequency, $F = F_0 / \cos \theta$, where $F_0 = 3900$ T and $\theta$ is the angle between the field direction and the normal to the ab-plane, corresponds to the FS cylinder occupying $\approx 55\%$ of the Brillouin zone (BZ) [9]. A rather heavy cyclotron mass, $m_c \approx 4.5 m_0$ ($m_0$ is the free electron mass), and Dingle temperature, $T_D \approx 0.4$ K, have been estimated from the temperature and field dependencies of the SdH amplitude according to the well-known formula (see e.g. [10]),

$$A_p \propto \frac{T \exp(-2\pi^2 p k_B T_D / \hbar \omega_c)}{\sqrt{B} \sinh(2\pi^2 p k_B T / \hbar \omega_c)},$$

(1)

where $\omega_c = eB / m_c c$, the cyclotron frequency and $p$ is the harmonic index (in the present case $p = 1$).

The warping of the FS cylinder is very small and has no considerable effect on the angular dependence of the oscillation frequency [9, 11]. However, as seen in Figure 1, it causes a prominent beating with the frequency $F_{\text{beat}}(\theta = 0^\circ) \approx 30$ T. This means that in fact two
Fig. 2. — The superposition of the fast and slow SdH oscillations in $\beta$-(ET)$_2$IBr$_2$ in the field tilted by $\theta = 17^\circ$ from the normal to the ab-plane towards the a-axis; $T = 1.45$ K.

extremal areas, $\frac{2\pi\psi}{c}\left(F_0 - F_\text{beat}\right)$ and $\frac{2\pi\psi}{c}\left(F_0 + F_\text{beat}\right)$, contribute to the SdH effect. Assuming the electron dispersion law in the form,

$$\varepsilon(k) = \varepsilon(k_x, k_y) - 2t_z \cos(k_z d),$$

where the $x$ and $y$ axes are directed in the crystal ab-plane. $z \perp x, y$ and $d$ is the interlayer spacing, the ratio between the transverse overlap integral $t_z$ and the Fermi energy $\varepsilon_F$ is estimated as $t_z/\varepsilon_F = F_\text{beat}/2F_0 \approx 4 \times 10^{-3}$. The absolute values of $\varepsilon_F$ and the bandwidth in the z-direction, $4t_z$, can be roughly evaluated under the assumption of the quadratic isotropic in-plane dispersion, $\varepsilon_F \approx \hbar F_0/m_e c \approx 10^3$ K; $4t_z \approx 15$ K, in fair agreement with other estimations.

In contrast to the frequency of the oscillations, their amplitude exhibits strongly non-monotonous dependence on the tilting angle $\theta$. In particular, a strong enhancement of the amplitude was found at the angles $\theta \approx -27^\circ$ and $+30^\circ$ when the field was rotated in the plane perpendicular to the a-axis [9,11]. This behaviour, as was first noted by Yamaji [12], is closely related to the Q2D nature of the FS and will be discussed later.

In addition to the fast SdH oscillations with the frequency $F_0$, much slower oscillations were found under the field applied at small $\theta$ [4,9]. A typical example of the superposition of the two series is shown in Figure 2. The periodicity in scale $1/B$, independence of the phase on temperature and gradual increase of the amplitude at cooling the sample allow us to attribute the slow oscillations to the SdH effect. The frequency, $F_{\text{slow}} \approx 50$ T corresponds to the k-space area of $4.8 \times 10^{13}$ cm$^{-2}$ or $\approx 0.6\%$ of the BZ cross-section. The existence of such a small FS cross-section is not predicted by the band structure calculations [13]. The Shoenberg effect (magnetic interaction) [10] can be ruled out as a possible explanation due to the following reason: the influence of the magnetic interaction should increase with lowering the temperature; in the contrary, the amplitude of the slow oscillations changes with temperature much slower than that of the fast ones, yielding the cyclotron mass of only $\approx 0.5m_c$ [4,9]. Above 3 K only the slow oscillations have been detected so far. Another possibility to explain
the slow oscillations could be an interference of different cyclotron orbits (this effect will be considered in Sect. 3). This would imply a more complicated multiply connected FS that, again, disagrees with the theoretical prediction [13].

Therefore, although the existence of a slightly warped cylinder as a main motif of the FS is proved by the SdH experiments, some details are not clear yet and need further investigation.

2.2. SEMI-CLASSICAL MR ANISOTROPY AND AMRO IN β-(ET)2IBr2. — The most remarkable feature found in the semi-classical MR was strong AMRO periodic in scale of $\tan \theta$ [9,11]. These oscillations are shown in Figure 3 for the magnetic field rotating in the $bc$-plane. The position of the oscillations does not depend on the field or temperature. Increasing the temperature from 1.5 to 4.2 K reduces their amplitude by a factor of $\sim 1.5$ [11].

Yamaji [12] was the first who suggested that the strong periodic increase in MR of a Q2D metal at rotating the magnetic field may be caused by a simple geometrical reason. He noted that at certain angles satisfying the condition,

$$dk_F \tan \theta_n = \pi(n - 1/4), \quad n = 1, 2, \ldots, \quad \tan \theta > 1,$$

(3)

the areas of the cyclotron orbits on the FS determined by the dispersion law (2) with $\epsilon(k_x, k_y) = \hbar^2 k_y^2 / 2m$ do not depend on the transverse wave vector $k_x$, to the accuracy of the ratio $\eta = t_x / \varepsilon_F \ll 1$. Of course this should lead to a considerable enhancement of the SdH amplitude and disappearance of the beat-like behaviour, in agreement with the experimental result mentioned above. As for the semi-classical MR, the numerical calculations by Yagi et al. [14] indeed showed a strong increase of the interlayer MR at the angles (3). Further, a detailed analytical

Fig. 3. — Angular dependence of the interlayer MR of β-(ET)2IBr2 in the field $B = 14$ T rotating in the plane nearly perpendicular to the $a$-axis ($\varphi = 95^\circ$); $T = 1.4$ K.
consideration of a Q2D metal with a general form in-plane dispersion made by Peschansky et al. [15] in the semi-classical approximation confirmed this result. A more transparent interpretation was done by Yakovenko et al. in [16] in the following way. Under the conditions $\eta, \gamma \ll 1$, the transverse resistivity may be written as

$$\rho_{zz} = \frac{1}{\sigma_{zz}^{(0)} + O(\eta^2\gamma^2)}, \quad (4)$$

where $\sigma_{zz}^{(0)} \propto \langle \hat{p}_z^2 \rangle$ (angle brackets mean the average over $k_z$). At a common field direction, $\rho_{zz}$, is determined only by a finite transverse velocity, $\langle \hat{p}_z^2 \rangle$, and saturates in strong field. However, at the special field directions at which the cyclotron orbit area does not depend on the position of the orbit plane $K_z$ the time averaged transverse velocity for any of the orbits vanishes:

$$\bar{v}_z(K_z) = \frac{1}{\hbar} \cdot \frac{\partial \varepsilon}{\partial k_z} = \frac{1}{\hbar} \cdot \frac{\partial S(K_z)}{\partial k_z} = \frac{1}{\hbar} \cdot \frac{\partial S(K_z)}{\partial \varepsilon} - \frac{1}{2\pi m_\varepsilon} \frac{\partial S(K_z)}{\partial k_z} = 0, \quad (5)$$

and so does $\sigma_{zz}^{(0)}$. In that case, the resistivity, $\rho_{zz}$, is determined by the small second term in the denominator of (4) and grows up as $\gamma^2 \propto H^2$. Indeed, the sharp change to a non-saturating field dependence was found in the transverse resistance of $\beta$-(ET)$_2$IBr$_2$ at turning the field to the angles corresponding to the AMRO peaks [11].

The condition (3) for the critical angles $\theta_n$ was generalized in [16] for the dispersion law written in the form,

$$\varepsilon = \varepsilon(k_z, k_y) = 2t_z \cos(k_z d + k_x u_x + k_y u_y), \quad (6)$$

characteristic of a low-symmetric system in which electrons hop between the 2D layers along the vector $\mathbf{h} = (u_x, u_y, d)$:

$$|\tan \theta_n| = \frac{\pi(n - 1/4) \pm (k_{\parallel}^{(\text{max})}, \mathbf{u})}{k_{\parallel}^{(\text{max})} d}, \quad (7)$$

where $\mathbf{u} = (u_x, u_y)$, $k_{\parallel}^{(\text{max})}$ is the Fermi wave vector component in the 2D plane whose projection on the field rotation plane, $k_{\parallel}^{(\text{max})}$, is maximal, and the signs $\pm$ correspond to the positive and negative $\theta$, respectively. Using the relation (7), it is possible to determine the FS cross-section and the direction of the electron hopping vector from the AMRO positions found in the experiment [16]. Figure 4 shows the result for $\beta$-(ET)$_2$IBr$_2$ [16] which is in good agreement with the SdH data and the band structure calculations. Later detailed studies of the angular dependence of the dHvA effect [17] have also confirmed the predicted behaviour of the quantum oscillations at the critical angles (7).

Worth of noting, the periodicity of AMRO in $\tan \theta$ is found experimentally to hold even better than predicted by theory. The conditions (3) and (7) are obtained assuming $\tan \theta > 1$. However, the AMRO observed in $\beta$-(ET)$_2$IBr$_2$ keep the periodicity down to the lowest critical angles for which $\tan \theta < 1$ [16].

Turning now to the dependence of the transverse MR on the field direction in the highly conducting $ab$-plane, a surprisingly strong anisotropy has been found for $\beta$-(ET)$_2$IBr$_2$ [11]. As is seen in Figure 5, the maximum to minimum MR ratio is $\sim 10$. This result was reproduced on several samples and can be hardly explained within the isotropic relaxation time approximation for a simple cylindrical FS presented in Figure 4. A possible reason for this anisotropy may be a highly anisotropic in the $ab$-plane relaxation time. On the other hand, a qualitatively different character of the field dependencies of the MR [11], may reflect changes in the electron orbit topology, depending on the field orientation in the $ab$-plane. Another argument in favor of a topological reason of the anisotropy may be a sudden vanishing, at some field orientations,
Fig. 4. — The transverse cross-section of the FS cylinder in $\beta$-(ET)$_2$IBr$_2$ (thick line) deduced from the AMRO parameters using the equation (7). The thin line interpolates the experimental points $\vec{k}_B^{(\text{max})}(\theta)$ (see text).

of the sharp peak in the $R(\theta)$ curves which is normally observed at $\theta \to 90^\circ$ and corresponds to switching from closed to open orbits [16].

Thus, like in the SdH studies, the results on the semi-classical MR, establishing the weakly corrugated FS cylinder as a main motif of the FS, suggest the existence of fine details which are not yet resolved.

2.3. THE $\beta$-(ET)$_2$I$_3$ SALT. — It is well known that this compound can exist at low temperatures in either of two states, $\beta_L$- and $\beta_H$-states, which are characterized by very different superconducting transition temperatures, $T_c \approx 1.4$ and 8 K, respectively [18,19]. The difference in $T_c$ is caused by a small difference in the crystal structures; whereas the positions of the terminal ethylene groups of the ET molecules are completely ordered in the $\beta_H$-state [20], there is an incommensurate superstructure [21] leading to a weak disorder of these positions and, hence, to a weak random potential in the $\beta_L$-state.

The existence of the cylindrical FS in the $\beta_H$-(ET)$_2$I$_3$ was established by Kang et al. [22] by means of the SdH experiment. The frequency of the fundamental harmonic, $F = 3700$ T, beat-like behaviour, cyclotron mass, $m_c \approx 4 - 4.5m_0$ and even the Dingle temperature, $T'_D \approx 0.5$ K are very similar to those obtained for the $\beta$-IBr$_2$ salt, revealing the similarity of their FS.
Fig. 5. — The interlayer MR of $\beta$-(ET)$_2$IBr$_2$ as a function of the orientation of the field rotating in the 2D $ab$-plane. The inset shows the same dependence in the polar co-ordinates.

Fig. 6. — The oscillatory part of the MR in $\beta_L$-(ET)$_2$I$_3$ vs. the inverse field.

The AMRO have not been observed directly in the $\beta_H$-(ET)$_2$I$_3$ but the angular behaviour of the dHvA oscillations [6] suggests the likely existence of the critical angles (7). The giant amplitude of the SdH oscillations and their U-shape form [22] at $\approx 0.4$ K reflect most likely a high two-dimensionality of the FS, however no quantitative explanation have been proposed as yet.

The relatively strong scattering on the random potential resulting in the increase of the resistivity in the $\beta_L$-phase, is most likely responsible for the lack of the fast SdH oscillations. On the other hand, prominent slow oscillations with the frequency $F_{\text{slow}} \approx 110$ T [23] have been observed (see Fig. 6). Like in the case of $\beta$-(ET)$_2$IBr$_2$, the small FS parts which could give rise to these oscillations are not predicted by the extended Hückel model calculations (see e.g. [24]) and their origin is not clear. One could suppose them to come from a minor amon
Fig. 7. — Polar co-ordinate plots of the angular dependence of the slow SdH oscillation frequencies in β-(ET)$_2$IBr$_2$ (a) and β$_1$-(ET)$_2$I$_3$ (b) for the field rotating in the ac*-plane, where c* is the normal to the ab-plane.

contribution to the conducting system. (The contribution of the I$_3^-$ anion to the DOS at $\varepsilon_F$ was suggested by first-principle band structure calculations [25], however the main structure of the FS predicted by these calculations is unlikely realistic.) In that case, the choice of anion should considerably affect the parameters of the slow oscillations. The considerable difference in the absolute values of the frequencies and their angular dependencies shown in Figure 7 might support this supposition.
We should note that although the results of the SdH studies of the $\beta_L$- and $\beta_H$-states are very different, this does not necessarily mean the considerable difference of their FS. As mentioned above, the absence of the fast oscillations in the $\beta_L$-state is most likely caused by the higher scattering. On the other hand, the slow oscillations, having lower cyclotron mass, may easily be hidden behind the extraordinary strong fast oscillations in the low-temperature measurements of the $\beta_H$-phase [22].

3. $\kappa$-(ET)$_2$X Salts

3.1. Quantum Interference in $\kappa$-(ET)$_2$Cu(NCS)$_2$. — The $\kappa$-(ET)$_2$Cu(NCS)$_2$ salt has been subjected extensive magnetic-field studies revealing various kinds of magnetic oscillations. This includes the conventional SdH [5] and dHvA [17,26] effects and magnetic-breakdown (MB) oscillations [27,28] revealing the FS consisting of a cylinder occupying $\approx 16\%$ of the BZ area and a pair of corrugated open sheets extended parallel to the $k_x k_z$-plane and separated from the cylinder by a small gap of $\approx 5-6$ meV [29]. Here we will concentrate on a specific phenomenon, namely quantum interference (QI) of electrons traversing different paths in magnetic field.

A particular case of QI between the electrons passing through open orbits connecting two MB junctions was investigated in detail by Stark and co-workers [30]. A generalized theory of QI oscillations of kinetic coefficients in a common case of a coherent MB network was developed by Kaganov and Slutskin [31]. Recently Kishigi et al. [32], basing on a numerical analysis of linear chain MB networks, proposed the QI oscillations to exist also in thermodynamic properties. From the experimental point of view, QI remains an exotic phenomenon. Among the conventional metals, only pure Mg and some of its diluted alloys have shown a simplest case of QI, so-called Stark interferometer [30]. The main reason for the lack of the experimental observations is that the MB networks normally include orbits too large to achieve the electron phase coherence on a sufficient part of the FS including several MB junctions. Besides, the strong 3D dispersion leads to an exceptionally high sensitivity of the effect to the field orientation: a small tilting of the field from a symmetry direction breaks the total orbit periodicity, smears the phase and hence results in a rapid damping of the oscillations [30].

The FS of $\kappa$-(ET)$_2$Cu(NCS)$_2$ depicted schematically in Figure 8 is particularly suited for the observation of the QI effect, representing a linear chain MB network coherent within at least one whole unit cell of the reciprocal space and almost independent of $k_z$. Indeed, besides two fundamental frequencies, $F_\alpha \approx 600$ T and $F_\beta \approx 3850$ T, corresponding to the
classical (α) and MB (β) orbits, respectively, and their higher harmonics, small signs of the difference frequency harmonics, $F_β - nF_α$, with $n = 1, 2$ have been detected in low-temperature experiments [27, 28, 33]. However their origin was unclear because their very low amplitudes, which were superimposed by much stronger fundamental harmonics, did not allow to get a reliable quantitative information on them. Very recently, the oscillations with the frequency $F_β - 2F_α$ were directly observed in MR studies at temperatures above 2 K [34]. Figure 9 shows the oscillatory MR in the field normal to the highly conducting bc-plane, at different temperatures. The slow SdH oscillations, $F_α = 605$ T, which dominate below 2 K, fade away as the temperature increases and new rapid with the frequency of $F_β - 2F_α = 2630$ T become clearly visible. The amplitude of the rapid oscillations is very low, $\sim 10^{-4}$ of the background resistance, nevertheless they have been reproduced on all the studied samples both in the inter- and in-plane resistance. As discussed in detail in [34], the difference frequency harmonic $F_β - 2F_α$ can be realized in the MB network shown in Figure 8 if the electrons keep the phase coherence within at least one unit cell of the k-space. The oscillatory amplitude estimated according the theoretical models [30, 31] is in good agreement with that found in the experiment [34].

A remarkable feature of the $(β - 2α)$-oscillations is that they are characterized by an extremely small effective mass. Indeed, as noted in [31], the temperature dependence of the QI oscillation amplitude is determined, like in the standard Lifshitz-Kosevich (LK) theory, by the energy dependence of the oscillation phase. In the QI case that is the energy dependence of the difference between the phase changes on the interfering trajectories $\lambda$ and $\lambda'$,

$$\left[ \frac{\partial (\phi_λ - \phi_λ')}{\partial \varepsilon} \right]_{k_D} = \left( \frac{\partial \phi_λ}{\partial \varepsilon} \right)_{k_B} - \left( \frac{\partial \phi_λ'}{\partial \varepsilon} \right)_{k_B} = \frac{2\pi c}{\hbar B}(m_λ - m_λ'),$$

where $\phi_λ$ and $\phi_λ'$ are the changes of the quasi-classical phase of the electron wave packet at
its evolution along the paths \( \lambda \) and \( \lambda' \).

\[
\phi_\lambda = \int_\lambda k_x dk_y
\]

Therefore the corresponding thermal factor contains the effective mass equal to the difference between the cyclotron masses on the paths \( \lambda \) and \( \lambda' \). For the \((\beta - 2\alpha)\)-oscillations, the effective mass
\[
m_{\beta - 2\alpha}^* = m_\beta - m_\alpha,
\]
in agreement with the experiment [34], in which the oscillation effective mass was obtained to be \(0.9m_0\), a factor of 4 smaller than the cyclotron mass of the classical \(\alpha\)-orbit, \(m_\alpha \approx 3.5m_0\).

It is interesting to note that \(m_{\beta - 2\alpha}^*\) can be further reduced and likely even tuned to zero by applying a moderate quasi-hydrostatic pressure. As found by Caulfield et al. [35], the areas of the \(\alpha\)- and \(\beta\)-orbits have considerably different dependencies on pressure. Therefore, one can expect the relation between the masses to change with pressure. Indeed, \(m_{\beta - 2\alpha}^*\) was found to decrease under pressure and constitute \(\leq 0.3m_0\) at \(P = 3\) kbar [34] that is at least an order of magnitude lower than \(m_0\). This extremely low effective mass allows one to directly observe the \((\beta - 2\alpha)\)-oscillations up to temperatures as high as 9 K whereas all the thermodynamic quantum oscillations are essentially damped above 2-3 K due to the temperature smearing of the Fermi level.

3.2. AMRO in \(\kappa-(\text{ET})_2\text{Cu(NCS)}_2\). — At ambient pressure, the AMRO are not very pronounced in this compound at fields below 15 T, partly due to the masking effect of the superconducting transition which causes rapid vanishing of the resistance at the angles \(\theta\) above \(\approx 60^\circ\) at 1.5 K and \(\approx 70^\circ\) at 4.2 K [36]. A moderate pressure effectively suppresses the superconductivity and enables one to observe relatively complicated AMRO [36]. An example of these angular oscillations is shown in Figure 10. The positions of most of the MR dips are found to satisfy a simple relation.

\[
\tan \theta_n \cos \varphi = \cot \beta + n \frac{K_\alpha}{K_c \sin \beta}, \quad n = 0, \pm 1, \pm 2. \tag{9}
\]

Fig. 10. — The angular dependence of the interplane MR of \(\kappa-(\text{ET})_2\text{Cu(NCS)}_2\) at \(P = 1.2\) kbar. Inset: fragments of AMRO for two field rotation planes forming the angles \(\varphi = 30^\circ\) and \(36^\circ\) with the \(ac\)-plane, respectively.
where $\theta_n$ is the polar angle between the field direction and the normal to the conducting $bc$-plane giving the $n$-th MR dip, $\varphi$ is the azimuthal angle between the field rotation axis and the crystal $b$-axis, $K_a$ and $K_c$ are the reciprocal lattice periods and $\beta$ is the angles between them. These dips can be fairly explained by a semi-classical 1D AMRO model proposed by Maki [37] and, independently, by Osada et al. [38], predicting that MR of a 1D metal measured perpendicular to the 1D axis should exhibit sharp minima at rotating the magnetic field in the plane parallel to the FS plane, i.e. perpendicular to the 1D axis. A qualitative interpretation of this result was first given in [39,40] and then reproduced in several works (see e.g. [6]). The critical angles were predicted to be determined by the reciprocal lattice periods in the FS plane.

$$\tan \theta = \frac{p}{q} \frac{K_z}{K_y}, \quad p, q = 0, 1, 2, \ldots$$

where $y$- and $z$-axes are normal to the 1D axis. In a more general case, when the field rotation axis forms an angle $\varphi$ with the 1D axis and the elementary translation vectors, $K_1$ and $K_2$, lying in the FS plane do not coincide with the orthogonal $y$- and $z$-axes, the condition (10) is obviously modified to the form [40]:

$$\tan \theta \cos \varphi = \frac{pK_{1z} + qK_{2z}}{pK_{1y} + qK_{2y}}$$

or, if $K_{1y} = 0$,

$$\tan \theta \cos \varphi = \cot \beta + \frac{p}{q} \frac{K_1}{K_2 \sin \beta},$$

where $\beta$ is the angle between $K_1$ and $K_2$. Taking into account that, if the FS corrugation in the $z$-direction is much smaller than in the $y$-direction, only the integer index AMRO, $q = 1$, are expected [37], we come to the experimentally observed relation (9). Thus, the AMRO dips observed in the $R(\theta)$ dependence of $\kappa$-(ET)$_2$Cu(NCS)$_2$ directly indicate the existence of the open FS sheets parallel to the $k_yk_z$-plane.

We note that, besides the 1D AMRO, additional features associated most likely with the Q2D FS cylinder, have been found in [36]. These features are, however, superimposed by the considerably stronger 1D AMRO that makes their accurate analysis problematic.

The further increase of pressure leads to the enhancement of AMRO [41]. An example of the angle-dependent MR at $P = 8.5$ kbar is illustrated in Figure 11. The behaviour of these oscillations is even more complicated than at lower pressure most likely due to the reducing of the MB gap under pressure and consequent arising of cyclotron orbits with different topologies.

3.3. FS Studies of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]X with X = Cl and Br. — The crystal structures of the highest-$T_c$ organic superconductors $\kappa$-(ET)$_2$Cu[N(CN)$_2$]X with X = Cl and Br (hereafter referred to as the Cl and Br salts, respectively) are very similar to that of the $\kappa$-(ET)$_2$Cu(NCS)$_2$. Therefore, their FS are expected to be similar as well [2]. However, in contrast to the latter compound, neither quantum nor classical MR oscillations have been found in these two salts at ambient pressure up to the fields $\sim 40$ T. It is not surprising for the Cl salt which is known to be a magnetically ordered dielectric at ambient pressure [42]. Recent measurements under pressure above 2 kbar have revealed clear SdH oscillations in the metallic state of this salt [43]. The oscillatory part of MR shown for several pressures in Figure 12 clearly exhibits two different frequencies, in accordance with the band structure calculations [44]. The lower frequency extrapolated to $P = 0$ kbar equals to 540 T corresponding to the classical orbit $\alpha$ on the FS cylinder occupying 14.4% of the BZ, and the higher frequency, $F(P \rightarrow 0) = 3750$ T, comes from the MB $\beta$-orbit like that shown in Figure 8 and
envelopes 100% of the BZ cross-section area. Both SdH frequencies and the cyclotron masses as well as their pressure dependencies [43] resemble those found earlier on $\kappa$-(ET)$_2$Cu(NCS)$_2$, in agreement with the theoretical predictions. The only considerable difference between the calculations [44] and experiment [43] consists in the existence of a finite MB gap between the open and cylindrical FS that is reflected in the prominent $\alpha$-oscillations seen in Figure 12. This discrepancy might be explained by the spin-orbit interaction which was not taken into account.
in the calculation [44]. On the other hand, one could propose that pressure lowers the crystal symmetry, thus removing the band degeneracy at the BZ boundary. The latter supposition is corroborated by a very recent observation of the 2D AMRO associated with the MB $\beta$-orbit in the Cl salt under pressure [45]. Their analysis reveals the direction of the interlayer hopping vector $\mathbf{h} = (u_x, u_y, d)$ (see (7)) to be tilted from the normal to the 2D $ac$-plane. This means that the orthorhombic symmetry characteristic of the room-temperature crystal structure is most likely broken at low temperatures (and under pressure) that gives rise to a finite gap between the FS cylinder and open sheets [45].

Unlike the Cl salt, its Br-containing analog is metallic already at ambient pressure. Nevertheless, only under high pressure, above $\sim 8$ kbar, weak oscillations attributed to the SdH effect have been found in the latter compound [46]. A typical example of these oscillations at three different temperatures is shown in Figure 13. Surprisingly the oscillation behaviour is quite different from that observed in the isostructural Cl salt or similar $\kappa$-(ET)$_2$Cu(NCS)$_2$. The oscillation frequency at 9 kbar is only $\approx 160$ T (in the field normal to the $ac$-plane), corresponding to FS cylinder with the cross-section $\approx 4.4\%$ of the BZ area, a factor of 4 smaller than expected from the calculations [47]. The cyclotron mass, $m_\circ \approx 0.95m_0$, is also considerably lower than in the case of the other $\kappa$-phase salts. Again, despite the predicted degeneracy of the conducting bands at the BZ boundary, the high-frequency oscillations corresponding to the $\beta$-orbit become visible only at very high fields, above 23 T [48]. One can propose that these discrepancies are associated with the high pressure used in the experiment [46]. Indeed, the pressure of $\sim 9$ kbar may be enough to induce the lattice deformation leading to a considerable gap at the BZ boundary, thus depressing the $\beta$-oscillations. However, the large difference between the predicted and observed sizes of the $\alpha$-orbits can be hardly explained by a smooth variation of the crystal lattice parameters under pressure. The calculated [44] for the isostructural Cl salt and experimentally obtained for both the Cl salt [43] and $\kappa$-(ET)$_2$Cu(NCS)$_2$ [35] pressure dependencies of the band structure yield only at most 30$\%$ variation of the FS size at

$$\frac{1}{B}, \text{T}^{-1}$$

$R_{ac}$, mO

1.45K

1.7K

2.3K

$\frac{1}{B}, \text{T}^{-1}$

$R_{ac}$, mO

Fig. 13. — The SdH oscillations in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br at $P = 9$ kbar, $B \perp ac$. 

...
Fig. 14. — The 2D plane cross-section of the FS in \( \alpha-(ET)_2\text{MHg(XCN)}_4 \) according to the band structure calculations [50].

\( P \approx 10 \text{ kbar} \). Therefore, assuming that the ambient pressure band structure of the Br salt is similar to those of the other two compounds, the present result suggests either an unusually high sensitivity of the electronic system to the pressure or a pressure-induced phase transition.

Turning to the very low amplitude of the oscillations which constitutes only \( \sim 10^{-4} \) of the background resistance, it can be caused by magnetic correlations in the Br salt. Indeed, recent experiments [49] give evidences for a low-temperature magnetic ordering at the ambient pressure. This may lead to a highly non-homogeneous local magnetic induction in the sample, thus killing the SdH effect. One can imagine that the low amplitude of the oscillations at 9 kbar is also related to the magnetic correlations which may be not completely suppressed by this pressure.

It is interesting to note that, assuming the Br salt to be a compensated metal and have the same FS topology as the Cl and Cu(NCS)_2 salts and taking into account the very small \( \alpha \)-orbit area, we come to a FS consisting of a very narrow cylinder with cross-section elongated along \( k_c \) and only very weakly corrugated open sheets along the \( k_a k_b \)-plane. The flattened form of the FS would provide favorable nesting conditions and therefore be unstable against the charge- or spin-density-wave formation. This could cause the above mentioned magnetic ordering. To clarify the nature of the electronic state in Br salt and its difference from the Cl and Cu(NCS)_2 ones, further experiments including detailed structure analysis, magnetotransport studies and band structure calculations, all at various pressures and temperatures, are necessary.

4. Magnetotransport in the \( \alpha-(ET)_2\text{MHg(XCN)}_4 \) Family, \( M = K, \text{ Tl, Rb; } X = S, \text{ Se} \)

The family of isostructural compounds \( \alpha-(ET)_2\text{MHg(XCN)}_4 \) with \( M = K, \text{ Tl, Rb, NH}_4; X = S, \text{ Se} \) has been of special interest during the last years, challenging the capabilities of the magnetotransport and other magnetic field methods in probing the electronic system of the Q2D organic metals. According to the band structure calculations [50,51], these compounds are characterized by a FS consisting of a slightly warped cylinder and open sheets, thus representing a unique combination of Q2D and Q1D electronic systems (Fig. 14). As it stands, this family can be subdivided into two groups: (i) salts with \( M = \text{NH}_4, X = S \) [52] and \( M = \text{Tl, K,} \)
Fig. 15. — Angular dependence of MR of $\alpha$-(ET)$_2$TlHg(SeCN)$_4$. Both SdH oscillations and 2D AMRO are seen. Inset shows the cross-section of the slightly warped FS cylinder, calculated from the AMRO experiment.

$X = \text{Se} \,[53,54]$ (hereafter referred to as the NH$_4$, Tl-Se and K-Se salts, respectively) which exhibit a "normal metallic" behaviour, the former compound becoming a superconductor below $\sim 2 \, \text{K} \,[55,56]$; (ii) salts with $M = \text{K}, \text{Tl}, \text{Rb}, \text{X} = \text{S} \,[50,52,57]$ which undergo a low-temperature phase transition entailing a variety of puzzling anomalies in magnetic field.

In order to understand which anomalies of the latter group really originate from the specific low-temperature (LT) electronic state, it is natural to discuss first the properties of the "normal metallic" compounds.

4.1. SALTS WITHOUT THE LT PHASE TRANSITION. — Here we will concentrate on the Tl-Se salt as a typical representative of the group (i). The resistance of this salt exhibits a smooth behaviour [53] characteristic of many other stable ET based metals. The only specific feature of the $R(T)$ dependence consists in a small upturn below 2-3 K observed in some samples and attributed to a partial charge localization in the radical cation layer. Both SdH and semiclassical AMRO can be readily seen in the low-temperature angular sweep of the interlayer MR shown in Figure 15. The semi-classical MR [58] is fairly explained by the 2D AMRO model (see Sect. 2.2) and yields a slightly warped FS cylinder with the cross-section shown in the inset in Figure 15, in good agreement with the band structure calculations.

The SdH oscillations are found to be very strong, amounting to more than 20% of the background resistance already at 1.3 K, 14 T [58]. Their frequency, $(650 \pm 10)[T]/\cos \theta$, is consistent with the AMRO data. Temperature and field dependencies of their amplitude measured in the range $T = 1.3 - 4.2 \, \text{K}$, $H = 3 - 14 \, \text{T}$ yield the values $m_c = (2.05 \pm 0.05)m_0$, and $T_D = 0.6 \, \text{K}$. As noted in [58], the very strong oscillation amplitude implies an extremely weak warping of the FS cylinder, namely smaller than the Landau level separation already at fields 10-14 T; the transverse overlap integral, $t_b \leq \hbar \omega_c/4 \approx 1.5 \, \text{K}$. In this case, not only the
extremal cross-sections but the whole FS cylinder contributes to the SdH oscillations. This is likely the reason why the SdH oscillation amplitude is not enhanced at the 2D AMRO peaks as expected from the consideration in Section 2.2. A similar MR behaviour is observed also in the NH$_4$ [59] and K-Se [54] salts.

We note that although the SdH oscillation amplitude is not essentially affected by the semi-classical AMRO, it still has a non-monotonic angular dependence [58], exhibiting sharp dips at certain angles $\theta$ between the field direction and the normal to the highly conducting $ac$-plane. These dips, being associated with the spin-splitting effect, enable us to determine the $g$-factor, $g = 1.7 \pm 0.1$. It is considerably smaller than the free electron $g$-factor, indicating an essential role of many-body interactions. If one neglects the electron correlations, the electron-phonon coupling constant $\lambda$ can be roughly estimated from the ratio $m_e/m_b = 1 + \lambda$, where $m_b$ is a bare mass defined using an approximate relationship [10] $gm_e \approx g_s m_b$ (here $g_s$ is the $g$-factor obtained from ESR and expected to be very close to 2 [60]). This gives $m_b \approx 1.7m_0$ and $\lambda \approx 0.17$. This value is somewhat different from that given by Wosnita [6] and more similar to his estimation of $\lambda$ in the NH$_4$ salt. The reason for this discrepancy is not quite clear. Since the orientation of the field rotation axis was not specified in [6], the discrepancy might be attributed to anisotropic $g$-factor that is not unlikely in the present system. We remind that the estimations of $\lambda$ from the spin-splitting effect are based on neglecting of the electron-electron interaction that may be not correct for organic metals.

Recently, a series of SdH experiments using TI-Se crystals of extra-high quality has been carried out in pulsed fields up to 36 T [61] and 50 T [62]. It was shown that the sample quality significantly affects the amplitude and wave form of the oscillations. For the samples of ordinary quality, with the resistance minimum below 2-4 K and ratio $R(300 \text{ K})/R(0.5 \text{ K}) = 30 \div 50$, the ordinary symmetric SdH oscillations, although of a rather big amplitude, have been observed at least in field up to 36 T and temperatures down to 0.1 K [62]. The standard LK analysis of these oscillations yields the mass agreeing with the previous measurements [58] and independent on the field. On the other hand, the high quality samples, with the residual resistance ratio $R(300 \text{ K})/R(0.5 \text{ K}) = 165 \div 175$, show no minimum at the $R(T)$ dependencies and exhibit giant oscillations (Fig. 16) with a high harmonic content and the amplitude more 100 times higher (at $T = 1.1 \text{ K}$ and $B = 50 \text{ T}$) than the zero field resistance of the sample, while the field dependence of background MR reveals a saturation reaching $\sim 3R_0$ near 10 T [62]. This result resembles the behaviour of $\beta_{\text{H-(ET)$_2$Hg(XCN)$_4$}}$ reported by Kang $et$ $al.$ [22]. Like in [61], applying the standard LK formula (1) to extract the cyclotron mass, one gets the value increasing from $2.1m_0$ at $B = 18 - 20 \text{ T}$ to $4.2m_0$ at 43.5 T [62]. This indicates the invalidity of the standard LK formula for the high quality samples. Of course, the correct analysis should be made for the conductivity rather than resistivity oscillations. This, however, requires the knowledge of the Hall conductivity which is not available, to date. Anyway, the observed features evidence that under present conditions both the transverse overlap integral $t_h$ and the Landau level broadening due to scattering become much smaller than the distance between two successive Landau levels. As shown by numerical modelling of the dHvA wave form, taking into account the existence of the Q1D FS part [63], this may lead to a specific shape and harmonic content higher than in the standard LK result. Therefore, the resistive oscillations are expected to have similar specifics although their numerical modelling is much more difficult.

Since the compounds of the $\alpha-(\text{ET})_2\text{MHg(XCN)$_4$}$ family demonstrate rather different properties (from antiferromagnetic to superconducting) despite the close similarity of their crystal structures, one can expect that even subtle changes in the lattice parameters induced, say, by pressure may modify the overlap integral strongly enough to entail considerable changes of the electronic properties. The pressure studies of the NH$_4$ salt [64] have revealed additional slow oscillations under $2 < P < 12 \text{ kbar}$ attributed to a pressure-induced nesting.
Fig. 16. — An example of the gigantic SdH oscillations when current and pulsed magnetic field are applied perpendicular to the conducting ac-plane in the super-high quality single crystal of α-(ET)$_2$TIHg(SeCN)$_4$ salt.

of the FS. Similar slow oscillations with the frequency $F \approx 47 \, \text{T}$ were found in the Tl-Se salt at ambient pressure [61,65,66]. Therefore an imperfect nesting probably takes place in this compound already at ambient pressure that can be a reason for the lack of superconductivity in contrast to the NH$_4$ salt. Under pressure, the slow oscillations were not observed in Tl-Se salt up to at least 11 kbar [65]. As for the fundamental frequency, it gradually increases with the rate, $d(\ln F)/dP \approx 0.02 \, \text{kbar}^{-1}$ [65]. The same and slightly higher, $d(\ln F)/dP \approx 0.03 \, \text{kbar}^{-1}$, pressure dependencies of that have been observed in the sulphur-analog compounds α-(ET)$_2$MHg(SCN)$_4$: with $M = K$ [67] and $M = NH_4$ [64], respectively. As shown in [65] by numerical modelling of the pressure dependence of the electronic band structure, the behaviour of the fundamental frequency under pressure can be fairly explained by the sliding motion of the molecules in the ET donor chains containing only one type of the molecules.

Only a small pressure dependence of the cyclotron mass has been detected for the NH$_4$ and Tl-Se salts [64,65], in contrast to the case of the K-S, Tl-S and Rb-S salts [68] which undergo the LT phase transition.

4.2. SALTS WITH THE LT PHASE TRANSITION. — The α-salts with $M = K$, Tl, and Rb, $X = S$, show a resistive hump at $T_p \approx 8 - 10 \, \text{K}$ [57,69,70]. The first magnetotransport studies performed on the K-S salt [67,69,71–73] revealed a number of anomalies in magnetic field below
this temperature. This includes a complicated field-dependent SdH spectrum, enormously high semi-classical MR in the field below 10-15 T perpendicular the highly conducting ac-plane, which is followed by a sharp MR drop, so-called \textit{kink}, accompanied by a considerable hysteresis and, finally, strong angle-dependent MR oscillations which were initially attributed to the 2D effect. Based on the MR behaviour, it was proposed in several works that these compounds undergo a phase transition into a specific LT state which can be suppressed by applying a sufficient pressure [56,74] or magnetic field [67,75,76]. The corresponding phase diagrams were proposed by Sasaki and Toyota [75], Brooks et al. [67] and Kouno et al. [74]. According to the anisotropic change of the magnetic susceptibility reminiscent of the spin-density-wave (SDW) formation [77], the LT state is considered to be a SDW-like antiferromagnetic.

The behaviour of the Ti-S salt in the LT state was found very similar to that of the K-S with even sharper MR features due to, most likely, better crystal quality. In particular, the resistance changes stronger with magnetic field exceeding the zero-field value by two orders of magnitude at 10 T (Fig. 17). Detailed measurements of the MR anisotropy in Ti-S have shown that the AMRO in them cannot be explained by the 2D model but reveal the existence of a specific plane in the electronic system [39,40]. Indeed, MR dips rather than peaks are characteristic points of the oscillations shown in Figure 18 and the positions of the dips can be fairly fitted by the expression (9) which describes 1D AMRO. It is important that, according to the AMRO parameters, the specific plane orientation does not coincide with any principle orientation in the reciprocal lattice corresponding to the room temperature structure and therefore cannot be directly associated with the FS shown in Figure 14. Practically the same behaviour of AMRO was detected later in the K-S and Rb-S salts [59,78–80]. To explain this result, the antiferromagnetic character of the magnetic susceptibility was taken into account and the specific plane was proposed to be formed by the magnetic ordering wave vector $Q$ and the reciprocal lattice period $K_b$ perpendicular to the 2D plane [40]. Assuming $Q$ to be commensurate to the original reciprocal lattice and using the AMRO parameters, the wave

Fig. 17. — Pulsed-field MR traces for $\alpha$-(ET)$_2$TlHg(SCN)$_4$ at temperatures 1.6 and 4.2 K, $B \perp ac$. Arrows indicate the field sweep direction. $B_a$ and $B_p$ indicate the transition region with a hysteresis.
vector was proposed to have the form,

\[ \mathbf{Q}_{\text{TL,Rb}}^{\text{Tl,Rb}} = \zeta \frac{\mathbf{K}_a}{6} + \frac{\mathbf{K}_c}{3} + \frac{(\eta - 1/2)\mathbf{K}_b}{3} \] (12)

for the Tl-S and Rb-S salts [40, 81] and

\[ \mathbf{Q}^K = \zeta \frac{\mathbf{K}_a}{8} + 3\frac{\mathbf{K}_c}{8} + \frac{3(\eta - 1/2)\mathbf{K}_b}{8} \] (13)

for the K-S salt [78]. Here \( \zeta, \eta = +1 \) or \(-1\). The latter uncertainty comes from the fact that the real triclinic structure is very close to a more symmetrical orthorhombic side-centered one and the difference could not be resolved within the experimental accuracy. The relatively complicated form (13) for \( \mathbf{Q}^K \) may be a sign that it is only an approximation for an actually incommensurate superstructure \(^{(1)}\). In particular, such incommensurability maybe a reason why the LT instability is weaker \( \text{(i.e. the transition temperature is lower)} \) in K-S than in the other two salts. Noting that the components of \( \mathbf{Q} \) along the \( k_a \)-direction are close to the distance between the predicted FS sheets, \( 2k_F \), it was suggested [40] that \( \mathbf{Q} \) is the wave vector of a charge- or spin-density wave leading to the nesting of the open FS. The periodic superstructure potential may also influence the 2D band, resulting in a new BZ in which the FS cylinders form a self-intersecting network with the distinguished direction according to the observed AMRO. In the case of the Tl-S salt, new open FS sheets are expected to arise as shown in Figure 19. This would agree with the proposition that the oscillations originate from

\(^{(1)}\) Although the principal AMRO behaviour is already well established, there is some discrepancy between the AMRO parameters reported for the K-S salt in references [59, 78, 79]. In particular, the parameters given in [79] lead to the same \( \mathbf{Q} \) as for the Tl-S and Rb-S (12). The difference is not big but likely exceeds the experimental error and has not clear explanation at the moment.
Fig. 19. — The reconstruction of the FS of $\alpha$-(ET)$_2$TlHg(SCN)$_4$ at the phase transition taking into account the electronic superstructure wave vector $Q$ derived from the 1D AMRO. a) $T > T_p$. b) $T < T_p$.

the semi-classical electron motion on the open FS, i.e. 1D AMRO [37, 38]. On the other hand, the superstructure in the K-S salt is hardly expected to produce new open FS [78] that makes questionable the applicability of the 1D AMRO model. We note, however, that, irrespectively of the detailed mechanism responsible for the LT AMRO in these compounds, the conclusion about the superstructure vector $Q$ most likely stays correct.

The suggestion that the LT AMRO are inherently attributed to the electronic state below the phase transition was directly proved by detailed comparison of the AMRO below and above critical temperature [78, 79] and pressure [82, 83]. The AMRO behaviour was also found to drastically change at increasing the magnetic field above the kink field [76, 79, 80]. However no complete set of measurements in the high-field state which could be compared with those at the high temperature ($> T_p$) is available to date.

The proposed model of the reconstructed FS [40] can, in principle, explain many of the observed MR anomalies [76, 79, 82]. However, there are still several questions which is difficult to understand at the moment. In particular, the origin of the high SdH frequency corresponding to 100% of the BZ area [84] is not clear. To explain it, Athas et al. [85] have suggested a co-existence of the LT and HT (high-temperature) phases in the sample, ascribing the rapid oscillations to the MB orbit in the non-reconstructed HT FS. We note, however, that the energy gap between the 1D and 2D bands in the calculated FS [50, 51] is too large to expect the MB effect to be seen at field $\sim 10$ T at which these oscillations were found. Furthermore, it is not clear why the rapid oscillations are hardly detected in the high fields, above the kink field, despite the expected exponential enhancement of the MB probability.

Concerning the intrinsic nature of the LT state, it was assumed to be determined by the SDW formation [77] or co-existence of SDW and CDW (charge-density wave) [79]. However, NMR [86] experiments were unable to detect any sign of magnetic ordering. Only a very small magnetic moment has been found in the K-S salt in the $\mu$SR study [87]. Furthermore, recent torque measurements [88] give evidence for an “easy-plane” magnetic ordering rather than the “easy-axis” one expected for the usual SDW state.

Another problem is to understand the effect of magnetic field on the LT state. As was proposed by the $T - B$ phase diagram [67, 74, 75], the high field suppresses the LT state leading to a re-entrant transition into the HT one. On the other hand, the SDW instability in Q1D systems is known [89] to be enhanced in magnetic field. Very recently, Sasaki et al. [90] proposed that the real phase diagram is more complicated and the SDW indeed becomes more stable with increasing field. In order to clarify the $T - B$ phase diagram, a series of resistance vs. temperature measurements was done in magnetic fields up to 28 T [91]. The field direction
corresponded to the first dip in the LT AMRO. Figure 20 represents some of the $R(T)$ curves at different fields. The curves are strongly non-monotonic, revealing that the electronic system undergoes considerable changes even at the highest field. Basing on these measurements, a refined phase diagram is proposed (Fig. 21). At least three phases are detected in the studied range of temperature and field, the high-field state being not identical to the high-temperature one [91]. This corroborates an earlier suggestion by Christ et al. [92] that the high-field state is not a normal metal.

On the other hand, the new phase diagram does not imply the narrowing of the normal HT state under magnetic field, in contradiction with the ordinary SDW model. Due to temperature resistance background, it is obviously difficult to determine the correct absolute value of the transition temperature from the resistive data. To make a more definite conclusion about the effect of magnetic field on $T_p$, the torque was measured as a function of temperature under the same as for the resistive experiment conditions [91]. The transition temperatures determined for different fields from the torque curves and represented in Figure 21 by open circles agree, in principle, with those obtained from the resistive experiment.

Of course, it would be very desirable to expand the field range of the torque measurements. Such an experiment is in progress, however the problem consists in a very strong temperature

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Fig. 20. — Temperature sweeps of the interlayer MR of $\alpha$-(ET)$_2$KHg(SCN)$_4$ at various fields. Arrows indicate the inflection points of the $R(T)$ curves which are assumed to correspond to the phase transitions.
dependence of the dHvA signal which becomes much stronger than the steady torque change in the fields above $\sim 20$ T.

Summarizing this Section, we conclude that, despite a large number of experimental data, the present understanding of the LT state in the $\alpha$-(ET)$_2$MHg(SCN)$_4$ family is rather controversial. It is more or less clear that the electronic band structure is considerably modified below the transition and the superstructure can be obviously determined from the LT AMRO studies. Nevertheless, the intrinsic mechanism determining the specifics of the LT state is not clear yet, neither is the effect of magnetic field on it. Further experiments, especially in the high magnetic field, are expected to clarify the mysterious nature of these compounds.

5. Compounds Based on BEDT-TTF Derivatives

5.1. (BEDO-TTF)$_2$ReO$_4$ * H$_2$O. — Bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) is an isostructural analog of BEDT-TTF which allows the synthesis of a number of conducting
MAGNETORESISTANCE IN Q2D ORGANIC CONDUCTORS

Fig. 22. — The oscillatory part of the interplane resistance of (BEDO-TTF)$_2$ReO$_4$·H$_2$O, where $c^*$ is the normal to the ab-plane. In the insets: a) Fourier analysis of SdH oscillations, b) polar co-ordinate plots of the angular dependence of the SdH oscillation frequencies coming from both electron and hole orbits (from [97])

salts as well. However, for a given anion, the BEDO-TTF salts are not isostructural to the BEDT-TTF ones and have different FS. One of them, (BEDO-TTF)$_2$ReO$_4$·H$_2$O is a Q2D organic metal down to $\sim$ 35 K, which undergoes several phase transitions as the temperature decreases [93–95]. Below 35 K, as was assumed in [94], a SDW condensation takes place. However, this SDW state is not very stable since it is suppressed by a rather low (1 kbar) hydrostatic pressure [96] and it competes or co-exists with a superconducting state the onset temperature of which is 2.4 K [93, 94].

According to calculations, the room temperature FS consists of one hole and two electron tubes, their cross-section area amounting to 3.4% and 1.7% of the BZ cross-section area, respectively [95]. Two SdH oscillations series have been observed at ambient pressure with frequency of $F_h = (76 \pm 2)$ T [95] (or 81 T [97]) and $F_e = (37 \pm 3)$ T [95, 97], respectively (Fig. 22). These frequencies correspond to cylindrical tubes, with their axes perpendicular to the conducting planes and with extremal cross section areas equal to 1.5 (1.6) % and 0.73% of the BZ, respectively. The discrepancy by a factor of more than two between these values and the calculated ones can be ascribed to the phase transitions which, as mentioned above, occur on cooling.

The FS nesting at the SDW condensation in (BEDO-TTF)$_2$ReO$_4$·H$_2$O has been interpreted [95] on the basis of the hidden nesting concept [98] in which the 2D FS is regarded as composed
Fig. 23. — The low-temperature dependence of the resistance of \((\text{BEDO-TTF})_2\text{ReO}_4 \cdot \text{H}_2\text{O}\), normalized at 30 K, in different magnetic fields under pressure of 11 kbar.

of several sheets crossing each others, the 1D character of them being hidden by degeneracy removals. However, it seems more likely that a given pair of hidden 1D sheets can involve only one type of carriers (electrons or holes). Moreover, the anisotropy of the semiclassical MR at ambient pressure [97] is typical to be originated from 1D sheets, so that the nesting may be not hidden. Whatever the nesting process, it certainly leads to a rather imperfect nesting, which accounts for the lack of stability of the SDW state. It is thus likely that the SDW condensation, which is suppressed by a very moderate hydrostatic pressure of 1 kbar only [96], may be recovered under magnetic field.

Indeed, as was shown in [99], when hydrostatic pressure is applied, the temperature dependence of the resistance in magnetic field reveals a large non-monotonous MR with a steep rise below 4 K (Fig. 23). This is reminiscent of the field-induced SDW effect observed in conducting compounds of the \((\text{TMTSF})_2X\) series when the magnetic field is parallel to the lowest conductivity direction [100]. Hence, the data obtained in [99] suggest the stabilization of a field-induced SDW state in \((\text{BEDO-TTF})_2\text{ReO}_4 \cdot \text{H}_2\text{O}\) under pressure at low temperature. It is known [101] that SDW state in Q1D compounds is sensitive to both hydrostatic pressure and magnetic field which respectively deteriorates and improves the nesting of the Q1D sheets.

We now turn to the MR as a function of magnetic field. The field dependence of the normalized resistance is displayed in Figure 24, where \(R\) and \(R_N\) stand for the field-dependent resistance and the extrapolated value of the zero-field resistance in the normal-state, respectively, at the considered temperature and pressure values. It can be seen that the almost linear semiclassical part of the MR \(((R_{SC} - R(B = 0))/R_N)\) increases with increasing pressure and decreasing temperature, while the SdH oscillation amplitude decreases with increasing pressure or temperature.

The Fourier analysis of the data reveals two series of SdH oscillations (Fig. 25) like in the ambient pressure experiment. As the pressure increases, the oscillation frequencies of both series increase linearly, \(F_h\) remaining higher than \(F_o\) by a factor of about 2, from ambient pressure up to 11 kbar [99]. It can be noticed that the sensitivity of the oscillation frequency
Fig. 24. — The field dependence of MR of (BEDO-TTF)$_2$ReO$_4 \cdot$ H$_2$O at different temperatures and pressures. $R$ is the field-dependent resistance and $R_N$ is the extrapolated value of the zero-field resistance in the normal state under the given pressure.

to the pressure (dln $F$/d$P$ = 0.07 kbar$^{-1}$) is very high when compared with $\kappa$- or $\alpha$-salts [35,64,65,67]. This can be understood taking into account that in the present compound the orbits involved in the SdH oscillations result from the imperfect nesting of the Q2D tubes, which make them certainly very sensitive to the details of the FS. The SdH oscillation amplitude ratio, $A_h/A_e$, strongly decreases as the pressure increases (see inset in Fig. 25), that may reflect a different pressure induced warping of the hole and electron tubes. The Dingle temperatures are (1.6 ± 0.2) K and (0.9 ± 0.2) K for the e- and h-orbits, respectively, in the pressure range covered by the experiments. In this pressure range the cyclotron masses related to both orbits slightly decrease, $m_{ee}$ remaining higher than $m_{ch}$ roughly by a factor of two ($m_{ee} = 1.5m_0$ and $m_{ch} = 0.8m_0$ at 3.5 kbar) [99].

It can also be remarked that the competition between SDW state and superconductivity in this compound is strongly influenced by pressure, leading to a low pressure dependence of the superconducting transition temperature ($T_c$). Indeed, d$T_c$/d$P$ = 0.2 K/kbar is one order of magnitude lower than for $\kappa$-(ET)$_2$Cu(SCN)$_2$ [35].

5.2. $\lambda$-(BEDT-TSeF)$_2$FeCl$_4$. — $\lambda$-(BEDT-TSeF)$_2$FeCl$_4$, or, shorter, $\lambda$-(BETS)$_2$FeCl$_4$ salt, where BEDT-TSeF or BETS stands for bis(ethylenedithio)tetrathiafulvalene, belongs to a new class of fascinating compounds (BETS)$_2$MCl$_4$, where M = Ga, Fe [102]. In contrast to the diamagnetic Ga$^{3+}$ ions, the Fe$^{3+}$ ones are magnetic and, whereas a superconducting ground state appears for M = Ga [103], an insulating ground state takes place for M = Fe [102] below the same temperature (8 K at ambient pressure). The fact of such remarkably different instabilities in these isostructural salts offers an unique opportunity to study the interplay between magnetism and superconductivity. Here we will consider some magnetotransport properties of the first organic conductor containing magnetic Fe$^{3+}$ ions.
The insulating ground state of the $\lambda$-(BETS)$_2$FeCl$_4$ salt was suggested to have a non-magnetic spin-Peierls-like origin [104] or be induced by an antiferromagnetic (AF) ordering of the localized magnetic moments of the Fe$^{3+}$ ions [105]. Like in the case of (BEDO-TTF)$_2$ReO$_4$*H$_2$O (Sect. 5.1) and other salts with SDW-like ground state [89], the very sharp metal-insulator (M-I) phase transition occurring at 8 K at ambient pressure in $\lambda$-(BETS)$_2$FeCl$_4$ is easily suppressed by applying pressure $> 3.5$ kbar [104]. As was mentioned above, applying pressure should increase the dimensionality of the electron system that in most cases results in a suppression of the SDW-like state, while applying a magnetic field under some conditions can stabilize or even induce this kind of isolating ground state (see e.g. [89]). Therefore, the most striking result obtained for the first time in [105] is the magnetic-field-induced suppression of the M-I phase transition in $\lambda$-(BETS)$_2$FeCl$_4$ whatever the direction of the field is. Figure 26 shows a low temperature behaviour of the normalized resistance in different magnetic fields [106]. The M-I phase transition is shifted to lower temperature as the field increases and, according to the resistive measurements, is accompanied by a hysteresis which increases with increasing field. We note that magnetization measurements using a very sensitive cantilever [106] have shown the results which agree with the resistive ones. But it was not found any sign for a ferromagnetic ordering of the Fe$^{3+}$ ions moments along the field direction, which was suggested in [105] and could induce a field-restored highly conducting state (FRHCS) in the field $> 12$ T.

The extended Hückel tight-binding band calculations on the basis of both the 298 and 10 K structures yield a Q2D closed FS with 23% of the BZ and a corrugated extended FS [104].

![Figure 25](image_url)

**Fig. 25.** The Fourier transformation of SdH data for (BEDO-TTF)$_2$ReO$_4$*H$_2$O under different pressures at a fixed temperature. Inset: the pressure dependence of the oscillation amplitude ratio for the hole and electron orbits. The ambient pressure value was deduced from data of reference [95].
The low-temperature dependence of the normalized resistance of $\lambda$-(BETS)$_2$FeCl$_4$ in different magnetic fields.

gap between the two parts of the FS becomes very small at 10 K, that suggests the system to become more 2D at cooling [104]. On the other hand, the oscillations of MR, which have been observed for one direction of the field only (up to 36 T) [107], suggest a small 2D closed FS with the area of about 2% of the BZ (Fig. 27). Such a small 2D FS does not agree with the FS derived from the 10 K structure [104]. This discrepancy probably result from the difference between zero-field-high-temperature metallic states and the FRHCS (and consequently, different FS). Very strong angular variations of the MR with additional local maximum which appears in magnetic field $> 15$ T [107] seems to support this suggestion.

So far the nature of both insulating ground state and FRHCS of $\lambda$-(BETS)$_2$FeCl$_4$ salt remains unclear. Additional SQUID, ESR, AFR, etc. studies performed very recently are presented and discussed in [106].

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Fig. 27. — The magnetic field dependence of the interplane resistance of \((\text{BETS})_2\text{FeCl}_4\) at \(T = 2\) K. Note that curve 1 was obtained just after the first cooling of the sample, while the curve 2 was recorded after heating the same sample up to 77 K and keeping it during one week at this temperature. Insert shows a periodicity of both maxima (\(\bigcirc\)) and minima (\(\times\)) of the oscillations vs. the inverse field.

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