GALVANOMAGNETIC PROPERTIES OF THE NEW ORGANIC METAL
ET$_2$TlHg(S$_{0.45}$Se$_{0.55}$CN)$_4$

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Magnetoresistance and magnetic torque have been studied in the single crystals of the mixed complex (ET)$_2$TlHg(S$_{0.45}$Se$_{0.55}$CN)$_4$. The quantum oscillations (Shubnikov–de Haas and de Haas–van Alphen) have been observed and investigated in details in this compound. The behaviour of these oscillations is close to that in the complex (ET)$_2$TlHg(SeCN)$_4$ but is characterized by a stronger carrier scattering induced by the disordered positions of the S and Se atoms in the anion.

1. INTRODUCTION

In recent years the isostructural organic metals of the α-ET$_2$XHg(YCN)$_4$ series, where ET stands for bis(ethylenedithio)tetrathiafulvalene (C$_{10}$H$_8$S$_8$), X = K, Tl, Rb, NH$_4$, and Y = S, Se, have been a subject of intensive studies [1]. These compounds have revealed a variety of surprising properties in high magnetic fields, arising from the specifics of their electronic band structure. The Fermi surface (FS) [2], essentially the same in all these metals, uniquely combines features characteristic of quasi-one- (Q1D) and quasi-two-dimensional (Q2D) systems being represented by the coexistence of a slightly warped cylinder and a pair of open sheets. The series can be subdivided into two groups: One of them includes the salts with X = K, Tl, Rb and Y = S which undergo a phase transition into an antiferromagnetic groundstate which is believed to be driven by a Peierls-like instability of the Q1D FS part. However, unlike in most other Q1D metals, the transition does not lead to an insulating state [3–5] although it brings about an essential rearrangement of the FS [6]. In contrast, no transition is observed in the salts of the other group with X = NH$_4$, Y = S and X = Tl, K, Y = Se and the FS retains its initial shape at low temperatures [7–9]. As a result, the metals of the two groups exhibit very different properties in magnetic fields.

In particular, the salt ET$_2$TlHg(SCN)$_4$ belonging to the first group exhibits the following

properties. (1) The phase transition into an antiferromagnetic groundstate at $T_p \approx 10$ K [5]; (2) Strong angle-dependent magnetoresistance oscillations (AMRO) which are presumed to originate from the electron motion along new open sheets of the reconstructed FS [6]; (3) Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) oscillations with fundamental frequency $F_0 = 670$ T at $\mathbf{H} \parallel \mathbf{b}^*$ (where $\mathbf{b}^*$ is the normal to the crystal highly-conducting ac-plane) demonstrating enormously high second harmonic contribution at low temperature, in fields above 10 T [10]. On the other hand, the selenium-containing complex, $ET_2TlHg(SeCN)_4$, is characterized by (1) the absence of the phase transition; (2) AMRO associated with the electron orbits on the cylindrical FS; and (3) strong SdH and dHvA oscillations ($F_0 = 650$ T) with a normal harmonic content described by the standard Lifshitz–Kosevich formula in the field up to 15 T [8].

In order to obtain more information on the effect of subtle structural changes in the elctronic band structure and the groundstate properties induced by the substitution of the S atoms by the Se ones in the anion, we have carried out magnetic-field studies of a new organic conductor of the mixed composition, $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$ [11].

2. EXPERIMENT AND SAMPLES

In the experiment, single crystals of the mixed salt $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$ having a typical size of $\approx 1 \times 1 \times 0.2$ mm^3 were used. The samples were prepared by the electrocrystallization in benzonitrile as decribed in [11] or in trichlorethane with the addition of ethanol abs (10 vol.%) at 20° under constant current, $I = 0.5\mu A$. In the latter case the electrolyte was the mixture of cyclic 18-crown-6 ether and TlSCN and Hg(SeCN)$_2$ salts in the ratio of 1:3:1. The samples obtained from different batches had different qualitiy. Nevertheless, the microprobe analysis has shown the same chemical composition for all of them, giving a stable S:Se ratio of 8:1, in agreement with the chemical formula of the complex. A X-ray photomethod test has confirmed that these samples are single crystals isostructural to the other metals of the α-phase series.

The magnetoresistance and torque measurements were carried out as functions of the direction and strength of the magnetic field and the temperature. The magnetoresistance was measured by the standard a.c. technique at 330 Hz with the current, $I = 100\mu A$, directed perpendicular to the highly-conducting layers. Such geometry provides the best conditions for observation of AMRO [6, 12]. The magnetic field up to 15 T was generated by a superconducting solenoid. The measurements of magnetoresistance were performed at temperatures down 1.5 K. The dHvA effect was studied by a cantilever torquemeter as described in [13]. These measurements were carried out in magnetic fields up to 14 T and temperatures down to 0.5 K.

3. RESULTS AND DISCUSSION

As in the case of the selenium salt [8], the samples of the mixed complex do not show any sign of the phase transition characteristic of its sulfur analog [5].

The SdH and dHvA oscillations in the samples of the mixed salt are clearly exhibited in the field dependence of the resistance and magnetic torque in fields ≥ 10 T (see Figs. 1 and 2). FFT analysis yields the oscillation fundamental frequency of 650 ± 10 T for $\mathbf{H} \parallel \mathbf{b}^*$. This value is close to those obtained for both the pure sulfur and selenium salts [8, 10]. Neither SdH nor dHvA
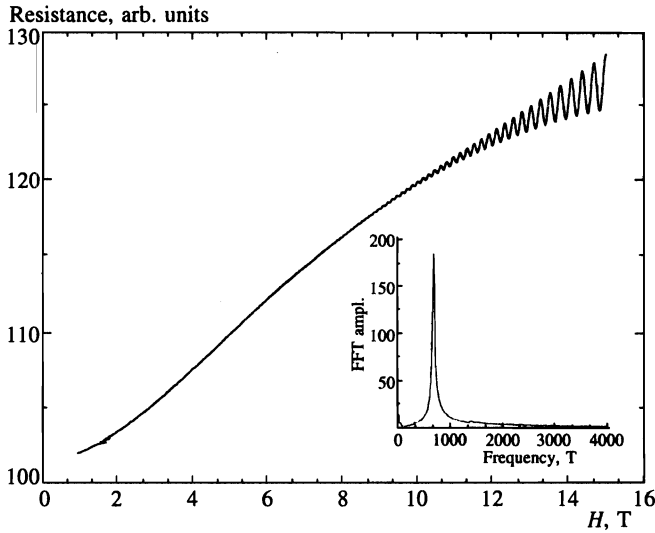
Fig. 1. Shubnikov–de Haas oscillations in $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$; $\mathbf{H} \parallel \mathbf{b}^*$, $T = 1.5$ K, $\mathbf{I} \parallel \mathbf{b}^*$. Inset: FFT of the oscillations
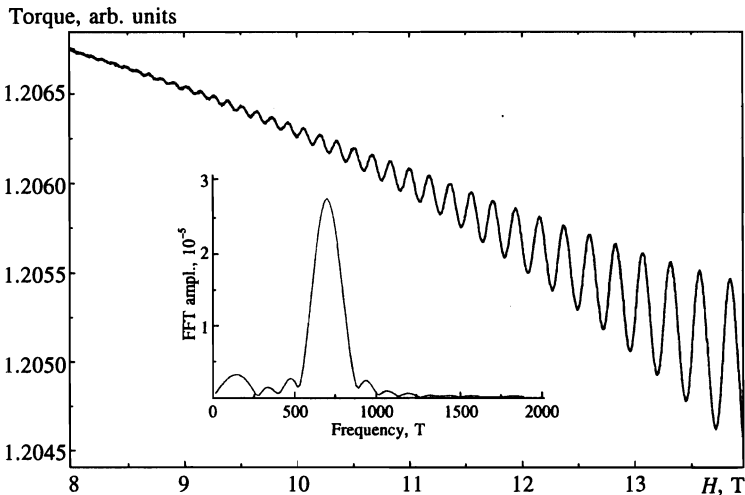

Fig. 2. De Haas–van Alphen oscillations in $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$. The magnetic field is tilted by the angle $-21.6°$ with respect to the $\mathbf{b}^*$ direction; $T = 0.5$ K. Inset: FFT of the oscillations

oscillations show any significant contribution of frequencies other than the fundamental within the field and temperature range studied. The angle dependence of the oscillation frequency is well described by the expression $F(\theta) = F_0/\cos\theta$, where θ is the angle between the field and $\mathbf{b}^*$ directions (Fig. 3), in accordance with the cylindrical shape of the corresponding FS part. Basically, the described behaviour is very similar to that found for the selenium salt. We only note that the value of the background magnetoresistance and the SdH amplitude in the
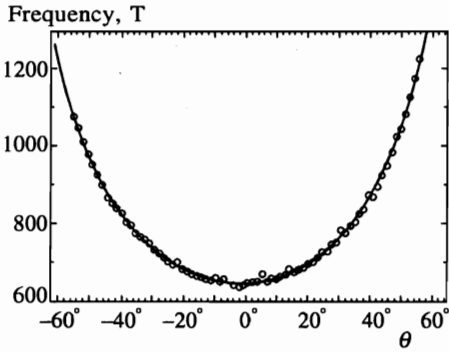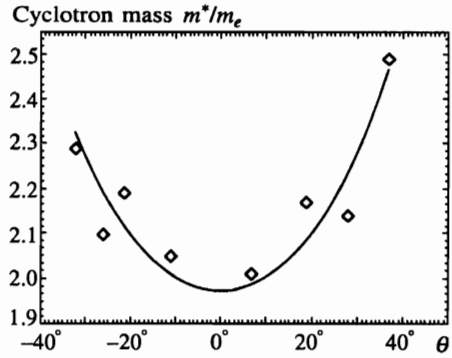
Frequency, T

Cyclotron mass m^*/m_e

Рис. 3

Рис. 4

Fig. 3.   Angular dependence of dHvA frequency.   The solid line corresponds to the relation
$$F(\theta) = 650T/\cos\theta$$

Fig. 4.   Angular dependence of the cyclotron mass.   The solid line corresponds to the relation
$$m^*(\theta) = 2.0m_e/\cos\theta$$

mixed complex are, respectively, a factor of three and a factor of six lower than in the selenium analog [8].

From the temperature dependence of the SdH and dHvA amplitudes we estimate the cyclotron mass of the carriers (m^*) on the cylindrical part of the FS. In the conducting plane it satisfies $m_0^* = (2.0 \pm 0.1)m_e$, where m_e is the free electron mass. The mass of the carriers in the selenium salt has of the same value [8]. The dependence of the cyclotron mass on the field direction for the dHvA oscillations (Fig. 4) obeys the relation $m^*(\theta) = m_0^*/\cos\theta$, within the experimental error, in agreement with the cylindrical shape of the FS.

The angle dependence of the dHvA amplitude in the mixed complex is shown in Fig. 5. There are two pairs of angles, $\theta \approx \pm42°$ and $\theta \approx \pm58°$, at which the amplitude vanishes due to the spin-splitting effect [14]. Using the experimentally obtained cyclotron mass, we evaluate the g-factor from the condition for the spin-splitting zeros [14], taking into account the cylindrical shape of the FS,

$$\cos\left(\frac{\pi}{2}\, pg\frac{m_0^*}{m_e\cos\theta}\right) = 0,$$

where $p = 1$ for the fundamental harmonic, $g \approx 1.7$. This value is very close to that found for the selenium analog [8]. As in the latter case, we attribute the deviation from the free electron g-factor to the substantiel effect of the electron–phonon interaction.

The Dingle temperature obtained from the field dependence of the oscillation amplitude in various samples of the mixed complex varies from 1.4 to 2.2 K, which is much higher than the value $T_D \approx 0.6$ K reported for the selenium salt [9]. The high Dingle temperature explains the relatively low magnetoresistance and the SdH amplitude in the mixed complex as compared to the selenium salt.

These results suggest that the mixed complex, $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$, is a «dirty version»
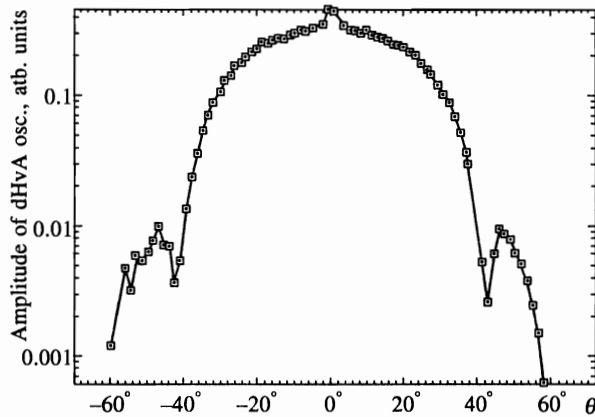
Fig. 5. Angular dependence of dHvA amplitude. $T = 0.5$ K
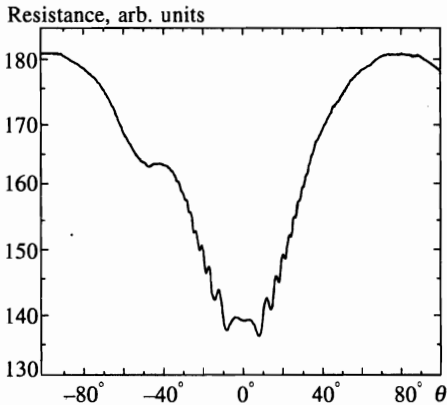

Fig. 6. Angular dependence of the magnetoresistance. $H = 15$ T, $T = 1.5$ K, $I \parallel b^*$

of the pure selenium salt $ET_2TlHg(SeCN)_4$. This conclusion, in principle, is consistent with the absence of the AMRO like those found in the pure selenium salt [8]. Indeed, the amplitude of the AMRO is expected to depend on magnetic field and the sample quality as $\sim (\omega\tau)^2$ where ω is the cyclotron frequency, $\omega = eH/m^*c$, and τ is the relaxation time. Using the Dingle temperature to estimate the relaxation time, one obtains an $\omega\tau$ value in the mixed salt an order of magnitude lower than that obtained for the pure selenium analog at the same magnetic field. Therefore, the AMRO amplitude is expected to be an order of magnitude lower in the compound studied. Figure 6, which illustrates the angular dependence of the magnetoresistance at an arbitrary azimuthal angle in ac-plane shows only one shallow maximum at around $-40°$ which could be attributed to the AMRO effect, in agreement with the above consideration. (A picture like Fig. 6 was observed at the different azimuthal angles.) Note, however, that a different (in comparison with the selenium salt) shape or degree of duistortion of the FS cannot be completely ruled out as possible reasons for the weakness of AMRO in the present case. Thus, the reason for the absence of AMRO in the mixed complex is still obscure and a more detailed study is needed for its clarification.

Summarizing, we have studied the magnetoresistance and magnetic torque of the mixed complex $ET_2TlHg(S_{0.45}Se_{0.55}CN)_4$. The complex is found to closely resemble its pure selenium analog, $ET_2TlHg(SeCN)_4$ but is likely characterized by a stronger carrier scattering induced by the disordered positions of the S and Se atoms in the anion. The disorder may be a reason for the suppression of the density-wave instability at low temperatures. On the other hand, unrelated to the disorder, the low-temperature properties are determined by the details of the inherent electronic band structure of the material. The latters could be essentially different from those of $ET_2TlHg(SCN)_4$ due to the presence of the Se atoms. Further studies are necessary to understand the crucial factors responsible for the low-temperature ground state in the system.

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