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Shubnikov-de Haas Oscillations in New Organic Conductors 
$(ET)_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ and $(ET)_8[Hg_4Cl_{12}(C_6H_5Br)_2]$

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Abstract. — The results of the investigations of Shubnikov-de Haas oscillations in the quasi-two-dimensional organic complexes $(ET)_8[Hg_4Cl_{12}(C_6H_5X)_2]$, where $X = Cl, Br$ in the magnetic fields up to 40 T were reported. These results allow one to obtain some information about Fermi surface in the mentioned complexes. Shubnikov-de Haas oscillations in the compound with $X = Cl$ correspond at least to two different cylindrical sheets of Fermi surface with the cross-section in $(bc)$-plane of 13% and 20% Brillouin zone cross-section. Shubnikov-de Haas oscillations in the complex with $X = Br$ correspond to one cylindrical sheet with the cross-section in $(bc)$-plane of 13% of Brillouin zone cross-section. The experimental results for the complex with $X = Br$ more agree with the theoretical calculations of Fermi surface than for the complex with $X = Cl$

Introduction

In the late 80ies the family of quasi-two-dimensional organic superconductors based on bis-(ethylenedithio)tetrathiafulvalene) $(ET)$ was filled up by two new superconductors with polymerized halomercurate anions, namely $(ET)_4Hg_{2.78}Cl_8$ and $(ET)_4Hg_{2.88}Br_8$ with $T_c = 1.8 K$ and 4.3 K, respectively [1,2]. The work with the anions of this type seemed to be promising due to the unusual properties of the superconductors. In particular, a record value of the derivative of the upper critical field $dH_{c2}/dT \sim 10$ T/K along the conducting sheets registered in $(ET)_4Hg_{2.88}Br_8$ at a relatively low critical temperature, leads to a record excess of a paramagnetic limit in organic superconductors [3]. Besides, an unusual growth of critical temperature with an external pressure noncharacteristic of normal superconductors was observed in this compound at a pressure up to 3-5 kbar [4]. The electron structure of these compounds was of importance, however its detailed investigation with using a magnetic field was restricted by an internal random potential inherent in these compounds, which results in the value $\omega \tau \ll 1$ in the total range of really existing fields. Such a potential is a result of that

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Hg atoms form their own sublattice in (ET)$_4$Hg$_{2.75}$Cl$_8$ and (ET)$_4$Hg$_{2.89}$Br$_8$ single crystals which is incommensurate with the lattice of the basic matrix [5]. Therefore it is quite reasonable to synthesize the conductors with halomercurate anions without a random potential. This opportunity was realized in the synthesis of a family of isostructural organic conductors (ET)$_8$[Hg$_4$Cl$_{12}$ (C$_6$H$_5$Cl)$_2$] (I), (ET)$_8$[Hg$_4$Cl$_{12}$ (C$_6$H$_5$Br)$_2$] (II), (ET)$_8$[Hg$_4$Br$_{12}$ (C$_6$H$_5$Cl)$_2$] (III) and (ET)$_8$[Hg$_4$Br$_{12}$ (C$_6$H$_5$Br)$_2$] (IV) [6]. The crystal lattices are regular in these salts which are metals at room temperatures [7]. However III and IV become dielectrics below 90 K and 160 K, respectively. II is characterized by a weak growth of the resistance below 10 K and only I keeps a metallic behaviour down to 1.4 K [8].

The magnetoresistance of the salt I denoted below as (Cl, Cl) and that of the salt II, denoted below as (Cl, Br) was studied in this work. We reported earlier about the observation of Shubnikov-de Haas (SdH) oscillations in these complexes [9,10]. The present work exhibits more detailed investigations of SdH oscillations and first of all the detailed comparative analysis of SdH oscillations in the compounds (Cl, Cl) and (Cl, Br) and their Fermi surfaces (FS).

Experimental

The objects under study were the samples of (ET)$_8$[Hg$_4$Cl$_{12}$ (C$_6$H$_5$Cl)$_2$] single crystals which appear as irregular parallelepipeds with 1.0 x 1.0 x 0.1 mm$^3$ characteristic sizes. The total X-ray analysis of this compound made at room temperature is described in [7]. (Cl, Cl) single crystals have a layered structure analogous with that of the other ET-based conductors. ET layers are located in (bc) plane. All ET molecules are parallel to each other in the layer that is characteristic of β-type packing. ET layers alternate along a$^*$ direction and are separated by polymerized [Hg$_4$Cl$_{12}$ (C$_6$H$_5$Cl)$_4$] anions. The unit cell is triclinic with Z = 1 and contains 8 ET molecules per cell. (Cl, Br) complex is isostructural to (Cl, Cl) one. The conductivity of both salts in (bc) plane, i.e. in the plane of ET layers constitutes $s = 10$ S/cm and that between the layers, i.e. along a$^*$ direction, is 3-4 orders lower. The temperature dependence of the resistance for (Cl, Cl) complex is metal-like without any peculiarities within 1.4-300 K at the measuring current I || (bc). At the same direction of the current a weak growth of the resistance was observed below 10 K in (Cl, Br) complex [8].

Magnetoresistance measurements were carried out by using a standard four-probe technique at an alternating current of 330 Hz. Both a longitudinal resistance at I || (bc) and a transverse one at I || a$^*$ were measured. For measuring a magnetoresistance a magnetic field up to 15 T was generated by a superconducting solenoid and that up to 40 T was generated by a pulse solenoid. Only in the case of a superconducting solenoid one could rotate a sample varying its orientation in a magnetic field. SdH oscillations of the resistance found in these measurements were analyzed by using a standard method of fast Fourier transform (FFT).

Results

Figure 1 shows the field dependence of magnetoresistance for (Cl, Cl) single crystals at field direction perpendicular to (bc) plane and at current direction along this plane. SdH oscillations are observed even at 7-8 T and appear as almost an ideal sinusoid with 250 T frequency. FFT of this curve (see insert A in Fig. 1) confirms this fact demonstrating a very weak contribution of the second harmonic. However at the same field and current directions the contribution of SdH oscillations with higher frequencies grows quickly in the fields higher than 15 T (pulse fields up to 40 T) (see insert B in Fig. 1).

The presence of SdH oscillations with other frequencies can be also observed in the fields up to 15 T but in the conditions distinct from those presented in Figure 1. Figure 2 displays SdH
oscillations at current direction $I \parallel a^*$ and at $\varphi = 25^\circ$, where $\varphi$ is the angle between the field direction and the direction $a^*$ ($\varphi = 0$ at $H \parallel a^*$). FFT represented in the insert to Figure 2 indicates that the curve shown in the Figure is a superposition of SdH oscillations of at least five frequencies.

Figure 3 shows SdH oscillations in (Cl, Br) single crystal at the direction of the measuring current $I \parallel a^*$ and at $H \parallel a^*$. These oscillations together with their Fourier spectrum (see the insert to Fig. 3) are similar to those observed for (Cl, Cl) samples at the same field direction. Moreover, the frequency of SdH oscillations ($F = 235$ T) in (Cl, Br) is close to that of the oscillations found in (Cl, Cl) at $H \parallel a^*$ and $I \parallel (bc)$. However, in contrast to (Cl, Cl) FFT yields only one frequency of SdH oscillations in (Cl, Br) crystals at all orientations of a magnetic field (the contributions of the other frequencies or higher harmonics are rather small).

The angular dependence of SdH frequency was studied quite in detail in a wide range of the angles $\varphi = \pm 70^\circ$. The results of the measurements are shown in Figure 4 in polar coordinates for (Cl, Cl) samples and in Figure 3 (see insert B) for (Cl, Br) ones. The following peculiarities of these measurements should be noted: 1) SdH oscillations are characterized in (Cl, Br) by the only frequency, whose angular dependency appears as a straight line perpendicular to $a^*$; 2) in (Cl, Cl) SdH oscillations are characterized by six frequencies whose angular dependence are also more or less correctly described by straight lines perpendicular to $a^*$; 3) at $H \parallel a^*$ the values of these frequencies constitute $F_1 = 150$ T, $F_2 = 250$ T, $F_3 = 400$ T, $F_4 = 500$ T,
\[ F_5 = 650 \text{ T and } F_6 = 910 \text{ T, respectively (this is the result of the interpolation of the linear dependencies in Fig. 4 on the field direction } H \parallel a^*); 4) \text{ the contribution of oscillations of each frequency to the resulting oscillation curve essentially depends on } \varphi \text{ and current direction in (Cl, Cl).} \]

At \( I \parallel (bc) \) the oscillations with \( F_2 \) frequency dominate significantly at almost all angles \( \varphi \). The contribution of SdH oscillations with other frequencies is not large, moreover the oscillations with \( F_1 \) and \( F_6 \) frequencies were not observed at any angle \( \varphi \). At \( I \parallel a^* \) SdH oscillations with \( F_2 \) frequency dominate as well. However for most \( \varphi \) values, especially if they are not close to \( \varphi = 0^\circ \), the contribution of oscillations with other frequencies is significant and even compatible with that of the main frequency \( F_2 \) (see the insert in Fig. 2).

The fact that under certain conditions the contribution of SdH oscillations in (Cl, Cl) is made only by the main frequency \( F_2 \), enables the evaluation of cyclotron mass of the carriers associated with the oscillations of this frequency. The insert in Figure 5 shows the temperature dependence of logarithm of the reduced amplitude of SdH oscillations at \( I \parallel (bc) \) and \( \varphi = 0^\circ \). The dependence is well approximated by a straight line within the experimental error. Thus one can use a standard relationship for the evaluation of a cyclotron mass:

\[
\ln(A/T) = \text{const} - 2n^2c_kBm^*(T - T_D)/e\hbar H
\]

where \( A \) is an oscillation amplitude, \( m^* \) is a cyclotron mass, \( T_D \) is Dingle temperature. The evaluation yields \( m^* = 1.35 \, m_0 \).
Fig. 3. — Shubnikov-de Haas oscillations in the single crystal \((\text{ET})_8\text{Hg}_4\text{Cl}_{12}(\text{C}_6\text{H}_5\text{Br})_2\) with the field orientation \(H \parallel a^*\) and temperature \(T = 1.45\) K. Insert A: FFT for the oscillations displayed in the figure, insert B: angular dependence of the frequency of Shubnikov-de Haas oscillations in polar coordinates.

The insert in Figure 6 shows that the application of the relationship (1) to SdH oscillations in \((\text{Cl}, \text{Br})\) complex is quite correct. The evaluation of a cyclotron mass in this compound yields \(m^* = 1.25\ m_0\) which is close to the analogous one in \((\text{Cl}, \text{Cl})\).

Figures 5 and 6 exhibit the angular dependences of the amplitudes of SdH oscillations of the main frequency \(F_2\) in \((\text{Cl}, \text{Cl})\) at \(I \parallel (bc)\) and those of the frequency \(F\) in \((\text{Cl}, \text{Br})\) at \(I \parallel a^*\), respectively. The amplitudes of oscillations have a maximum in both compounds which does not coincide with the direction \(H \parallel a^*\). The amplitude becomes almost equal to zero in each compound at \(\varphi > \pm 60^\circ\). Besides the intermediate minima in which the amplitude is close to zero, are quite of importance. These minima appear at the angles \(\varphi = \pm 28^\circ\) for \((\text{Cl}, \text{Cl})\) and at \(\varphi = \pm 35^\circ\) for \((\text{Cl}, \text{Br})\).

Discussion

The analysis of X-ray data [7] enabled one to calculate a zone structure of \((\text{Cl}, \text{Cl})\) salt [11]. Its unit cell contains 8 donor ET molecules, therefore the interaction between 8 highest occupied molecular orbitals (HOMO) results in the formation of 8 energy zones. According to a stoichiometric formula each ET molecule has 1.5 electron in the unit cell and therefore 12 electrons are to be populated at 8 energy levels. The system under study may be either a two-dimensional semiconductor or a two-dimensional metal depending on the degree of the
overlapping or the availability of the energy gap between the 6th zone and the 7th one. The calculations [11] showed that there is a small overlapping between these zones which defines their partial occupation by electrons and consequently a metallic behaviour of conductivity of this salt down to helium temperatures. The calculated Fermi surface (FS) was found to consist of two cylinders whose axes are parallel to \( a^* \). The cross-section of these cylinders in bc plane is shown in Figure 7. The calculations yielded the rigorously equal values for the areas of the sections for these cylinders which constitute 13% of the area of a corresponding section of the first Brillouin zone. However the cylinder A is associated with electrons as carriers and the cylinder B is associated with holes. It is stated in [11] that these closed FS appeared as a result of the hybridization of two hidden one-dimensional FS. One could expect quantum oscillations only with the frequency of about 250 T at \( H \parallel a^* \) from FS of such a shape (not considering the possible contribution of the harmonics and magnetic breakdown orbits).

These calculations are qualitatively and quantitatively in agreement with the experimental data on SdH oscillations in (Cl, Br). The angular dependence of the frequency of SdH oscillations apparently enables the imagination of FS in this compound as one cylinder (or several cylinders with equal areas of cross-sections) with the axis directed along the direction \( a^* \). At \( H \parallel a^* \) the frequency of SdH oscillations is 235 T that is close to the calculated value.

A significantly more complicated case is for (Cl, Cl) compound for which the calculation of FS was made [11]. The study of SdH oscillations at various field and measuring current orientations revealed the existence of oscillations with six different frequencies. All these frequencies have the dependences on the angle corresponding to the cylindrical sheets of FS (see Fig. 4). However only a part of them corresponds to really existing closed orbits. It obviously follows from the fact that the sum of all frequencies is more than the frequency corresponding to 100% of the first Brillouin zone. One can see that all frequencies are a linear combination of two frequencies \( F_1 \) and \( F_2 \): \( F_3 = F_1 + F_2, F_4 = 2F_2, F_5 = F_1 + 2F_2 \) and \( F_6 = F_1 + 3F_2 \). Figure 4 demonstrates that the frequency \( F_1 \) is observed in a very narrow range of the angles, at the same time

Fig. 4. — Anglular dependence of the frequencies of Shubnikov-de Haas oscillations in (ET)₈ [H₆Cl₁₂(C₆H₅Cl)₂] in polar coordinates.
Fig. 5. — Angular dependence of the amplitude of Shubnikov-de Haas oscillations at the fundamental frequency $F_2$ in $(ET)_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ single crystal when current is parallel to the $bc$ plane and $T = 1.45$ K. Insert: temperature dependence of the reduced amplitude of Shubnikov-de Haas oscillations at the basic frequency $F_2$.

The following problem is not also quite clear: how many cylindric sheets of FS which possess the equal areas of cross-sections, are responsible for the oscillations with the main frequency $F_2$ in (Cl, Cl) and for the oscillations with the frequency $F$ in (Cl, Br). According to the theoretical calculations of FS for (Cl, Cl) [11] one can expect that two Fermi-cylinders with the equal areas of cross-sections in every compound contribute to the oscillations with these frequencies. In this case the relationship (1) for the temperature dependence of the amplitude of SdH oscillations is valid only providing that both in (Cl, Cl) and (Cl, Br) Fermi-cylinders with equal areas are associated with the carriers which have equal cyclotron masses. It is seen from the inserts in Figures 5 and 6 that the relationship (1) holds quite well for both complexes. Therefore the conclusion may be drawn that either the contribution to SdH oscillations with the frequency $F_3$ appears at FFT significantly more frequently. Therefore we suppose that the frequencies $F_2$ and $F_3$ correspond to the real closed orbits. The frequency $F_4$ is most probably the second harmonic of $F_2$. The other frequencies are probably so called combined frequencies: $F_1 = F_3 - F_2$, $F_5 = F_3 + F_2$, $F_6 = F_3 + 2F_2$, which can arise for example due to a magnetic interaction [12]. It also cannot be excluded that the frequency $F_5$ is associated with the magnetic breakdown orbit. Thus SdH oscillations show the existence of at least two different cylindrical FS sheets in the complex (Cl, Cl) which have the cross-section in $bc$ plane equal to 13% and 20% of the first Brillouin zone cross-section and correspond to the frequencies $F_2$ and $F_3$. However a more detailed investigation will be enough to confirm this fact.

It is seen from the inserts in Figures 5 and 6 that the relationship (1) holds quite well for both complexes. Therefore the conclusion may be drawn that either the contribution to SdH oscillations with
Fig. 6. — Angular dependence of the amplitude of Shubnikov-de Haas oscillations in (ET)$_8$ [Hg$_4$Cl$_{12}$($C_6$H$_5$Br)$_2$] at the $T = 1.45$ K. Insert: temperature dependence of the reduced amplitude of the oscillations with the field orientation $H \parallel a^*$.

Fig. 7. — The cross-section of Fermi surface in the bc plane in (ET)$_8$[Hg$_4$Cl$_{12}$($C_6$H$_5$Cl)$_2$] at room temperature [11].
the frequency \( F_2 \) in (Cl, Cl) and the frequency \( F \) in (Cl, Br) is made by only one corresponding Fermi-cylinder in each complex, or such a contribution is realized by several cylinders which are characterized by equal areas of cross-sections and equal cyclotron masses of the carriers.

This is confirmed by the angular dependences of the amplitudes of SdH oscillations with the frequency \( F_2 \) in (Cl, Cl) and the frequency \( F \) in (Cl, Br) represented in Figures 5 and 6, respectively. Both dependences are quite similar qualitatively. They both are characterized by incoincidence of the maximum of the amplitude with the direction of the field \( H \parallel a^* \). This incoincidence is associated probably with a low symmetry of crystal lattice of the samples studied. Both dependences demonstrate the intermediate minima of the amplitude which the most probably arise because of a spin splitting of Landau levels. Keeping this splitting in mind one can introduce a lowering multiplier in the expression for the amplitude of SdH oscillations [12]

\[
\cos(\pi g pm^*/2m_0)
\]

where \( p \) is harmonic’s number and \( g \) is \( g \)-factor. It is reduced to zero providing that

\[
g pm^*/m_0 = 2n + 1
\]

where \( n \) is an integer. Considering that a cyclotron mass depends on \( \varphi \) as the area enveloped by the corresponding orbit, i.e. \( m^*(\varphi) = m^* (0)/\cos \varphi \) and taking into account \( m^*(0) = 1.35m_0 \) obtained earlier for (Cl, Cl) and \( m^*(0) = 1.25m_0 \) for (Cl, Br), one obtains that at \( g = 2 \) the amplitudes of the first harmonics of SdH oscillations with \( F_2 \) and \( F \) frequencies vanish at \( n = 1 \) and \( \varphi = \pm 28^\circ \) and \( \varphi = \pm 34^\circ \) respectively, that agrees well with the experimental results obtained for both complexes (see Figs. 5 and 6). It is obvious that the superposition of SdH oscillations with equal frequencies but different cyclotron masses could hardly enable one to observe such very well resolved pictures of “spin zeros” which were found in (Cl, Cl) and (Cl, Br).

**Conclusion**

The study of the behaviour of SdH oscillations in the isostructural organic conductors ET\(_3\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Cl)\(_2\)] and ET\(_8\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Br)\(_2\)] permitted one to obtain the preliminary visualization on FS in these compounds. In ET\(_3\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Br)\(_2\)] it consists of one or several cylindrical sheets with the axes directed along \( a^* \) and the equal areas of cross-sections constituting approximately 13% of the area of the corresponding cross-section of the first Brillouin zone in (bc) plane. In ET\(_3\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Cl)\(_2\)] FS the most probably contains at least two cylindrical sheets with different areas of cross-sections constituting approximately 13% and 20% of the area of the cross-section of the first Brillouin zone in (bc) plane. For ET\(_8\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Br)\(_2\)] the data obtained are in a qualitative and quantitative agreement with the theoretical calculations of FS whereas the results obtained for ET\(_8\) [Hg\(_4\)Cl\(_{12}\)(C\(_6\)H\(_5\)Cl)\(_2\)] are only partially in agreement with these calculations.

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