# Shubnikov-de Haas oscillations in the new organic conductor$(ET)_8[Hg_4Cl_{12}(C_6H_5Br)_2]$

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The behavior of the magnetoresistance in a quasi-two-dimensional organic conductor $(ET)_8[Hg_4Cl_8(C_6H_5Br)_2]$ with different orientations of the magnetic field and at different temperatures was investigated. Shubnikov–de Haas oscillations were observed for $\mathbf{H} \parallel \mathbf{a}^* \pm 60°$. The sheet of the Fermi surface corresponding to these oscillations is a cylinder whose axis is oriented along **a*** and with the area of the section in the ( **bc**) plane is equal to approximately 13% of the corresponding section of the Brillouin zone. An estimate of the cyclotron mass of the carriers responsible for the observed oscillation gives $m^* = 1.25 m_0$. The representation obtained for the Fermi surface in the experimental material agrees with the theoretical calculations. © *1995 American Institute of Physics.*

It is well known that in crystals of organic quasi-two-dimensional conductors, which are cation-radical salts of ET (bis-(ethylenedithio)tetrathiofulvalene), even very small changes in the composition of the anion can produce very large changes in the low-temperature state, while the lattice structure remains constant (see, for example, Ref. 1). The most striking example of this are, apparently, the isostructural conductors $(ET)_2Cu[N(CN)_2]X$, where X=Cl, Br. At low temperatures and normal pressure the chloride is in a dielectric state,[2] whereas the bromide undergoes a superconducting transition at the temperature[3] $T \cong 12$ K. It is therefore very important to determine, if possible, the changes produced in the electronic structure and, specifically, the Fermi surface (FS) by a change in the anion composition. In this connection, the recently synthesized family of organic quasi-two-dimensional conductors $ET_8[Hg_4X_{12}(C_6H_5Y)_2]$, where X, Y=Cl, Br, is especially interesting.[4] All salts of this family are isostructural and they are metals at room temperature. The compound with X=Y=Cl manifests metallic temperature-dependence of the resistance in the entire experimental temperature range 1.4–300 K. However, when the chlorine atoms in the anion are systematically replaced by bromine atoms, new compounds exhibiting increasingly less pronounced metallic behavior form in the same systematic manner. For the conductor with X=Cl and Y=Br the resistance characteristically increases slightly with decreasing temperature below 10 K. In the salt with X=Br and Y=Cl dielectrization occurs even below 90 K, and in the case X=Y=Br the dielectric state occurs below[5] 160 K.

The observation of Shubnikov–de Haas (SdH) oscillations in the compound $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ [designated below as (Cl, Cl)] and a detailed study of these oscillations gave some idea of the Fermi surface in this compound.[6] In the present paper we report the first observation of SdH oscillations in the compound $ET_8[Hg_4Cl_{12}(C_6H_5Br)_2]$ [designated below as (Cl, Br)]. Investigations of such oscillations for different orientations of the magnetic field and different temperatures made it possible to perform a comparative analysis of the Fermi surface in the salts (Cl, Cl) and (Cl, Br).

Single-crystal samples of (Cl, Br) with the shape of an irregular parallelepiped with the characteristic dimensions $1.5\times 1.0\times 0.05$ mm were investigated. According to x-ray crystallographic analysis,[7] the plane of the samples coincided with the (**bc**) plane of the conducting layers. The magnetoresistance measurements were performed by the standard four-contact method on 330 Hz ac current at normal pressure. The measuring current in the series of measurements presented below flowed along the **a*** direction, perpendicular to the conducting layers. Magnetic fields of up to 15 T were produced with a superconducting solenoid. The SdH oscillations observed were analyzed by the FTT method.

Figure 1 shows the SdH oscillations observed in the (Cl, Br) single crystal with the field orientation $\mathbf{H} \parallel \mathbf{a}^*$. The fast Fourier transform of these oscillations, which is shown in the inset a in Fig. 1, shows that only one frequency is present in these oscillations: $F=235$ T. Oscillations with other frequencies, including also higher-order harmonics, make virtually no contribution. The SdH oscillations were observed for angles between **a*** and the direction of the field in the range $\varphi=\pm 60°$. For all directions of the magnetic field the FTT recorded the presence of oscillations at only one frequency. This dependence on the angle $\varphi$ is described well by the relation $F(\varphi)=F(0)/\cos\varphi$ (Fig. 1, inset b). This dependence corresponds to a single cylindrical sheet of the Fermi surface (or several sheets with the same section areas) with axis along **a***.

The results obtained, on the one hand, demonstrate that the conductor investigated is different from its isostructural analog (Cl, Cl), in which several (as a minimum two) cylindrical sheets of the Fermi surface with different section areas have been observed.[6] On the other hand, the results obtained for (Cl, Br) agree fairly well with the theoretical calculation of the Fermi surface in the compound[8] (Cl, Cl). According to this calculation, the Fermi surface consists of two cylindrical sheets—one hole sheet and one electron sheet—with the same section area which in the (**bc**) plane is equal to 13% of the corresponding section of the Brillouin zone. Such a Fermi surface corresponds to SdH oscillations with one frequency of the order of 250 T with the field oriented parallel to **a***.

It is not entirely clear how many cylinders of the Fermi surface with the same section areas contribute to the SdH oscillations observed experimentally in (Cl, Br). If several Fermi cylinders contribute and the carriers corresponding to different sheets have different cyclotron mass, then there is no hope that the standard relation for the amplitude of the SdH oscillations is satisfied:

$$\ln(A/T)=\text{const}-2\pi^2 c k_B m^*(T-T_D)/e\hbar H,$$

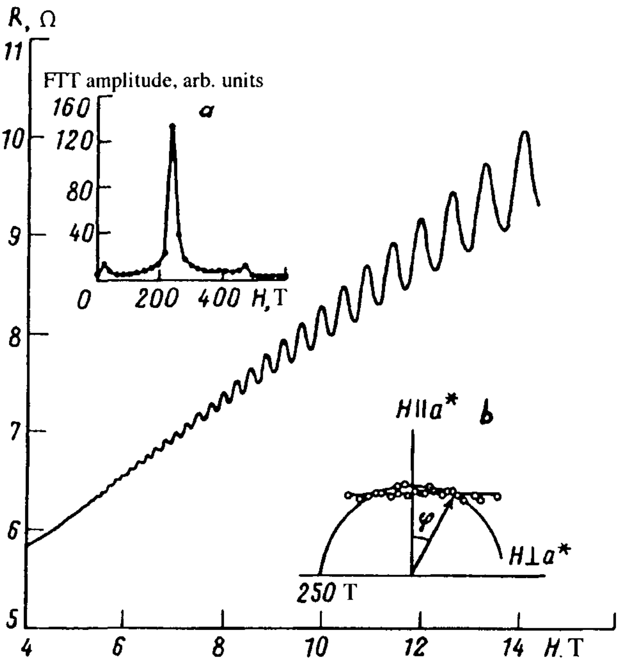

FIG. 1. Shubnikov–de Haas oscillations in the single crystal $(ET)_8[Hg_4Cl_{12}(C_6H_5Br)_2]$ with the field orientation H∥a* and temperature $T=1.45$ K. Inset a — FTT for the oscillations displayed in the figure; inset b — angular dependence of the frequency of the Shubnikov oscillations in polar coordinates.

where $A$ is the amplitude of the oscillations, $m^*$ is the cyclotron mass, and $T_D$ is the Dingle temperature. Judging from the inset in Fig. 2, however, this relation is satisfied well. This makes it possible to estimate the cyclotron mass of the carriers responsible for the observed SdH oscillations. This mass is equal to $m^*=1.25m_0$ in the (**bc**) plane and is somewhat different from the cyclotron mass of the carriers in (Cl, Cl) which are responsible for the SdH oscillations with the fundamental frequency[6] 250 T. Therefore, either several cylindrical sheets of the Fermi surface with the same section areas and the same cyclotron masses of the carriers associated with them contribute to the SdH oscillations in the conductor (Cl, Br) or only one Fermi cylinder contributes to the SdH oscillations.

Evidence for the considerations stated above is also provided by the angular dependence (shown in Fig. 2) of the amplitude of the SdH oscillations in (Cl, Br). It is characterized by the fact that the maximum of the amplitude does not occur with the field orientation **H** ∥ **a***, probably because of the low symmetry of the experimental crystal, the amplitude drops virtually to zero at angles $\varphi > \pm 60°$, and there are intermediate minima at which the amplitude is close to zero for angles $\varphi \cong \pm 35°$. These minima are probably associated with the spin splitting of the Landau levels. When this splitting is taken into account, the reducing factor $\cos(\pi gpm^*/2m_0)$, where $g$ is the $g$-factor and $p$ is the number of the harmonic, appears in the expression for the amplitude of the SdH oscillations. This factor vanishes when $gpm^*/m_0 = 2n+1$, where $n$ is an integer. Assuming that the cyclotron mass depends on the angle $\varphi$ as the area of the corresponding

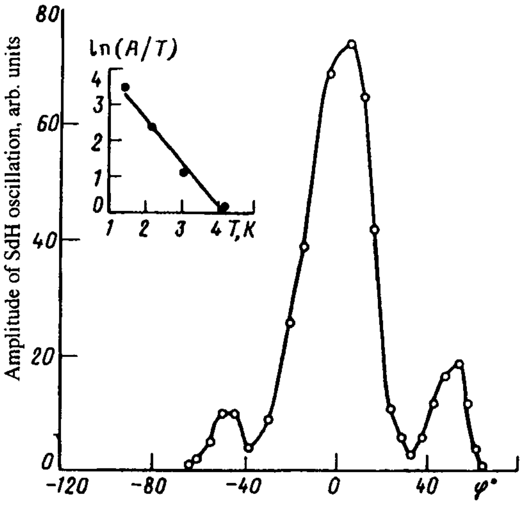

FIG. 2. Angular dependence of the amplitude of the Shubnikov–de Haas oscillations in $(ET)_8[Hg_4Cl_{12}(C_6H_5Br)_2]$ at the temperature $T=1.45$ K. Inset — Temperature dependence of the reduced amplitude of the oscillations with the field orientation **H**‖**a***.

section $m^*(\varphi)=m^*(0)/\cos\varphi$, we find that for $g=2$ the amplitude of the first harmonic of the SdH oscillations vanishes for $n=1$ at the angles $\varphi=\pm 34°$, which agrees well with the experimental results. The next pair of "spin zeros" with $n=2$ should exist at $\varphi=\pm 60°$. This pair was not recorded in the experiment, since in this range of angles the oscillations are not clearly evident. It is quite obvious that the superposition of several SdH oscillations with the same frequencies but characterized by different cyclotron masses of the carriers is unlikely to make it possible to observe a pattern of pairs of "spin zeros" as clear as the pattern shown in Fig. 2.

In summary, the Fermi surface or, at least, a portion of it in the organic quasi-two-dimensional conductor (Cl, Br) consists of one or several cylinders with the axis **a***. If there are several cylinders, then they are characterized by the same section areas and the same cyclotron masses of the carriers associated with them. This strongly distinguishes the complex (Cl, Br) from the isostructural complex (Cl, Cl), in which cylindrical sheets of the Fermi surface with different section areas have been observed. At the same time, the results obtained for (Cl, Br) agree qualitatively and quantitatively with the theoretical calculation of the Fermi surface for (Cl, Cl).

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