Galvanomagnetic properties of the new organic metal $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$: Shubnikov–de Haas oscillations and angular oscillations of the magnetoresistance

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The magnetoresistance of the new quasi-two-dimensional organic metal $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ in static magnetic fields up to 15 T and in pulsed fields up to 40 T has been investigated. Complex Shubnikov–de Haas oscillations corresponding to the superposition of oscillations with six different frequencies have been observed. The dominant contribution is made by the oscillations with the frequency F_2, which corresponds to a field of 250 T normal to the conducting layers. The Fermi surface obtained is only partially consistent with the theoretical calculations previously performed. A study of the amplitude of the Shubnikov–de Haas oscillations with fundamental frequency F_2 has made it possible to evaluate the cyclotron mass of the carriers corresponding to the respective sheet of the Fermi surface and to observe the zero-amplitude values associated with the spin splitting of the Landau levels. Angular oscillations of the classical part of the magnetoresistance, which are periodic with respect to $\tan\varphi$ (φ is the angle between the magnetic field and the **a*** axis), have been discovered, and their nature is discussed.

1. INTRODUCTION

During the latter half of the eighties, the family of quasi-two-dimensional organic superconductors synthesized on the basis of bis(ethylenedithio)tetrathiafulvalene (ET) was supplemented by two new superconductors with polymeric halomercurate anions, viz., $ET_4Hg_{2.78}Cl_8$ and $ET_4Hg_{2.89}Br_8$, which have critical temperatures equal to 1.8 K and 4.3 K, respectively.[1,2] Continuation of the work with anions of this type was prompted by the unusual properties of these superconductors. In particular, despite its comparatively low critical temperature, $ET_4Hg_{2.89}Br_8$ exhibited a record value of the derivative of the upper critical field along its conducting layers $dH_{c2}/dT \sim 10$ T/K, which, in the final analysis, is responsible for the record amount by which it exceeds the paramagnetic limit among organic superconductors.[3] In addition, an increase in the critical temperature with increasing external pressure at low pressures, which is unusual for normal superconductors, was noted for this compound.[4] The electronic structure of these compounds was of definite interest, but the detailed study employing a magnetic field was restricted to its intrinsic internal random potential, which gives $\omega\tau \ll 1$ over the entire range of actually existing fields. Such a potential appears as a consequence of the fact that the mercury atoms in single crystals of $ET_4Hg_{2.78}Cl_8$ and $ET_4Hg_{2.89}Br_8$ form their own lattice, which is not commensurate with the lattice of the main matrix.[5] The desire to create conductors with halomercurate anions without a random potential is therefore perfectly understandable. This possibility was realized as a result of the synthesis of a family of isostructural organic conductors: $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ (I), $ET_8[Hg_4Cl_{12}(C_6H_5Br)_2]$ (II), $ET_8[Hg_4Br_{12}(C_6H_5Cl)_2]$ (III), and $ET_8[Hg_4Br_{12}(C_6H_5Br)_2]$ (IV).[6] The crystal lattices of these salts are regular, and they are all metals at room temperature.[7] However, salts III and IV become insulators below 90 K and 160 K, respectively. Salt II is characterized by a slight increase in resistivity below 10 K, and only I maintains metallic resistance down to 1.4 K.[8]

The magnetoresistance of this latter metal was investigated in the present study. Shubnikov–de Haas oscillations were discovered here for the first time, and their behavior in magnetic fields with different orientations and at different temperatures was studied in detail.

2. SAMPLES AND EXPERIMENT

The objects of investigation were single-crystal samples of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$, which had the form of irregular parallelepipeds with characteristic dimensions $1.0\times1.0\times0.1$ mm^3. A complete x-ray structural investigation of this compound, which was performed at room temperature, was described in Ref. 7. According to that report, single crystals of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$, like other organic conductors based on ET, have a layered structure. The ET layers are oriented in the **bc** plane. All ET molecules in a layer are parallel to one another, as in β-type packing. The layers of ET molecules

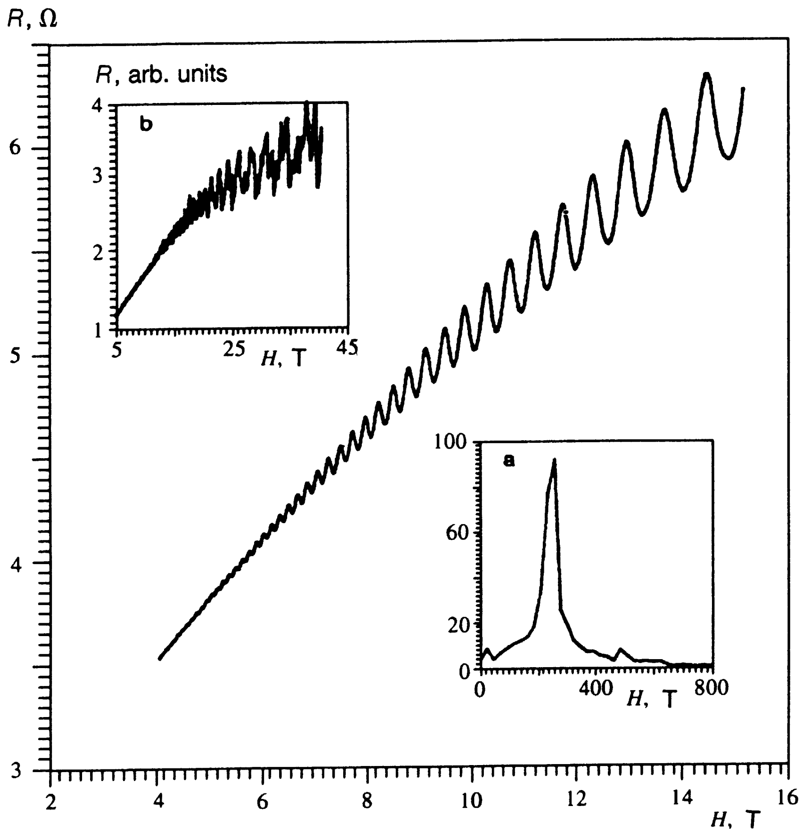

FIG. 1. Shubnikov–de Haas oscillations when **H**‖**a***, the current I is parallel to the **bc** plane, and $T=1.45$ K. Insert a—fast Fourier transform (the amplitude is in arbitrary units) for the oscillations presented in Fig. 1. Insert b—Shubnikov–de Haas oscillations in a pulsed field when **H**‖**a***, the current is parallel to the **bc** plane, and $T=1.45$ K.

alternate along the **a*** direction and are spatially separated by polymeric $[Hg_4Cl_{12}(C_6H_5Cl)_2^{4-}]$ anions. The unit cell belongs to the triclinic system with $Z=1$ and contains eight ET molecules. The conductivity σ in the **bc** plane, i.e., in the plane parallel to the ET layers, is $\sigma=10$ S/cm, and the conductivity between layers, i.e., in the **a*** direction, is three to four orders of magnitude lower. The temperature dependence of the resistivity has a metallic character without any special features in the 1.4–300 K range.[8]

The resistance measurements were performed using the standard four-contact method in an alternating current I with a frequency of 330 Hz. Both the longitudinal resistance, where the current is parallel to the **bc** plane, and the transverse resistance, where the current is parallel to the **a*** axis, were measured in various experiments. To measure the magnetoresistance, a magnetic field with a strength up to 15 T was created by a superconducting solenoid, and a field with a strength up to 40 T was created by a pulsed solenoid. Only the superconducting solenoid offered the possibility of rotating the sample to vary its orientation relative to the field. The Shubnikov resistance oscillations obtained as a result of the measurements were analyzed by a standard fast Fourier transform technique.

3. MEASUREMENT RESULTS

Figure 1 presents the field dependence of the magnetoresistance when the field is perpendicular to the **bc** plane and the measuring current is parallel to this plane. Shubnikov oscillations appear by 7–8 T, and have the form of an almost perfect sine wave with a frequency of 250 T. The fast Fourier transform of this curve (see insert a in Fig. 1) confirms this fact and reveals a very weak contribution of the second harmonic. However, if the field and the measuring current are oriented in the same direction, the contribution of Shubnikov–de Haas oscillations at higher frequencies increases rapidly in fields stronger than 15 T (in pulsed fields up to 40 T) (see insert b in Fig. 1). The presence of Shubnikov oscillations at other frequencies can also be observed in fields below 15 T, but under conditions differing from those described in Fig. 1. Figure 2 shows the Shubnikov–de Haas oscillations observed when the measuring field is parallel to **a*** and the angle φ between the field direction and **a*** equals 25° ($\varphi=0$ when **H**‖**a***). The Fourier transform shown in the insert in Fig. 2 reveals that the curve in Figure 2 is the result of the superposition of Shubnikov oscillations with at least five frequencies.

The angular dependence of the frequency of the Shubnikov–de Haas oscillations was investigated in great detail over a broad range of angles from $\varphi=-70°$ to $\varphi=+70°$. The results of the measurements are presented in polar coordinates in Fig. 3 (the results obtained when the current is parallel to the **bc** plane and parallel to **a*** have been combined. Several special features of these measurements are noteworthy.

1) The Shubnikov–de Haas oscillations in $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ correspond to the superposition of six frequencies, whose dependence on φ is described more or less accurately by a straight line in polar coordinates.

2) When **H**‖**a***, these frequencies are, respectively, $F_1=150$ T, $F_2=250$ T, $F_3=400$ T, $F_4=500$ T, $F_5=650$ T, and $F_6=910$ T.

3) The contribution of the oscillations at each frequency

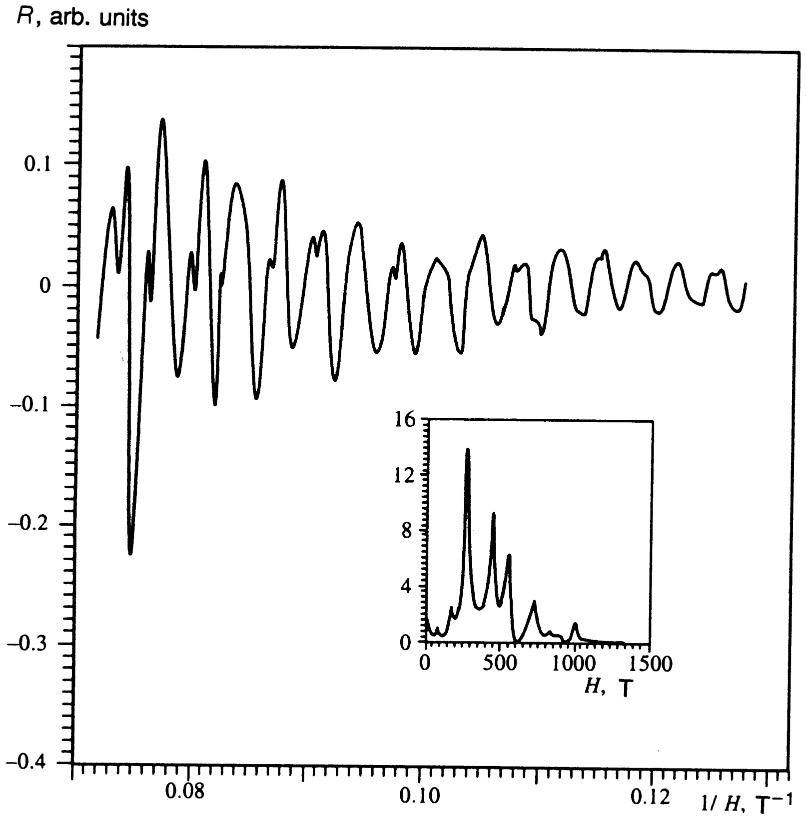

FIG. 2. Shubnikov–de Haas oscillations after subtraction of the regular part when $\varphi=25°$, the current is $\mathbf{I}\|\mathbf{a}^*$, and $T=1.45$ K. Insert—fast Fourier transform (the amplitude is in arbitrary units) for the oscillations presented in Fig. 2.

to the resultant curve depends significantly on φ and the direction of the measuring current. When the current is parallel to the **bc** plane, the F_2 oscillations clearly dominate at almost all values of φ. The contribution of the Shubnikov–de Haas oscillations at other frequencies is small, and the F_1 and F_6 oscillations are not reliably observed at any values of φ. When the current is parallel to $\mathbf{a}^*$, the F_2 Shubnikov–de Haas oscillations also predominate. However, at most values of φ, especially at values not too close to $\varphi=0$, the contribution of the oscillations at other frequencies is already significant and can even be comparable to the contribution of the fundamental frequency F_2 (see insert to Fig. 2).

The fact that under some conditions the fundamental frequency F_2 makes virtually the only contribution to the Shubnikov–de Haas oscillations makes it possible to evaluate the cyclotron mass of the carriers associated with oscillations at this frequency. The temperature dependence of the logarithm of the reduced amplitude of Shubnikov–de Haas

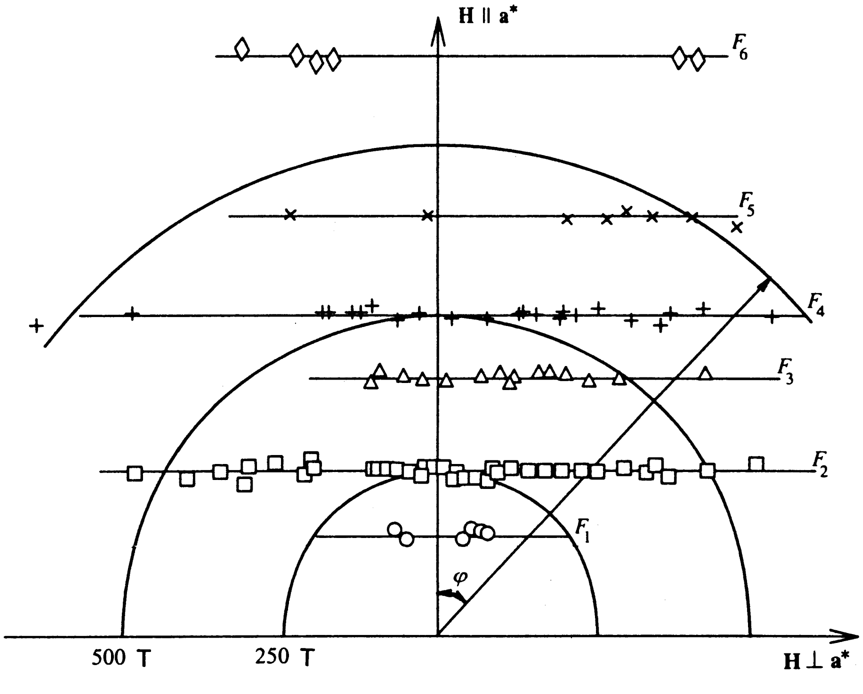

FIG. 3. Angular dependence of the frequencies of the Shubnikov–de Haas oscillations in polar coordinates.

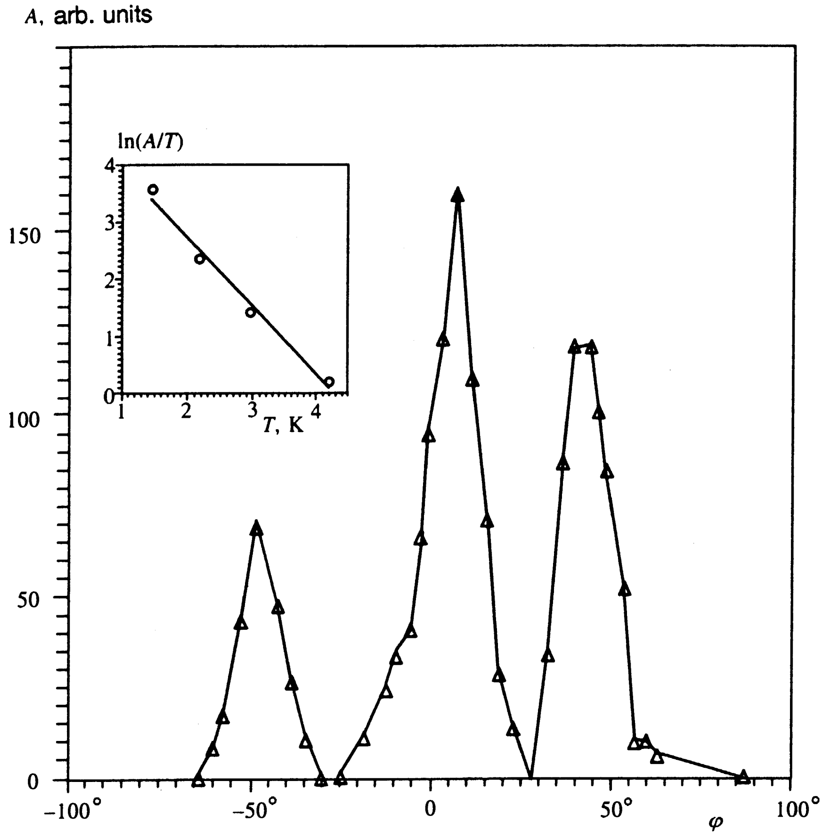

FIG. 4. Angular dependence of the amplitude of the Shubnikov–de Haas oscillations at the fundamental frequency F_2 when the current is parallel to the **bc** plane and $T=1.45$ K. Insert—temperature dependence of the reduced amplitude of the Shubnikov–de Haas oscillations at the fundamental frequency F_2.

oscillations when the current is parallel to **bc** and $\varphi=0$ is presented in the insert in Fig. 4. The dependence is approximated well by a straight line within the range of the permissible error. Thus, the cyclotron mass can be evaluated from the standard relation

$$\ln \frac{A}{T} = \text{const} - 2\pi^2 c k_B m^* (T - T_D)/e\hbar H, \quad (1)$$

where A is the amplitude of the oscillations, m^* is the cyclotron mass, and T_D is the Dingle temperature. The evaluation gives $m^* = 1.35 m_0$.

Figure 4 presents the angular dependence of the amplitude of the Shubnikov–de Haas oscillations at the fundamental frequency F_2 when the current is parallel to **bc**. The amplitude has a maximum, which does not coincide with **H**‖**a***, and differs only slightly from zero at $\varphi > \pm 60°$. In addition,

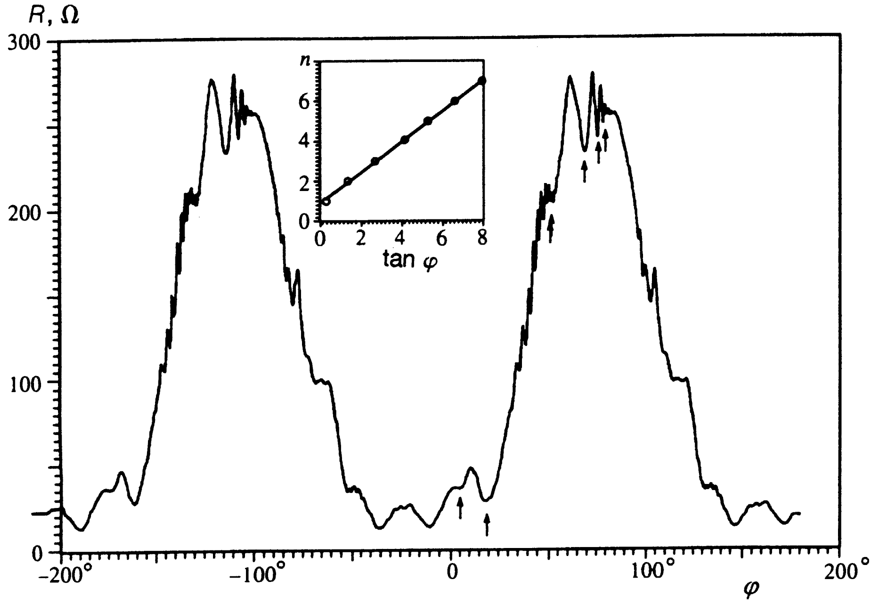

FIG. 5. Angular dependence of the resistance when $H=14$ T, the current is parallel to the **a*** axis, and $T=1.45$ K. The minima of the angular oscillations are marked by arrows. Insert—dependence of the number of a minimum on the tangent of the angle corresponding to it φ_n.

the intermediate zeros at $\varphi=\pm 28°$ are very significant. It should be noted that the analogous dependence for a current parallel to **a*** agrees qualitatively with the plot in Fig. 4.

Figure 5 shows the angular dependence of the magnetoresistance of a single crystal of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ when the current is parallel to **a***. The angle $\varphi=0$ corresponds to a field perpendicular to the conducting layers, and $\varphi=\pm 90°$ corresponds to a field parallel to these layers. The enormous anisotropy of the magnetoresistance observed here is noteworthy. While $[R(14T)-R(0)]/R(0)$ equals about 3 at the absolute minimum, this ratio reaches 90 at the absolute maximum. In addition, the angular dependence of the magnetoresistance exhibits both Shubnikov oscillations, which are especially prominent at $\varphi=40-55°$, and angular oscillations of the classical part of the magnetoresistance. The minima of the latter are marked with arrows in Fig. 5. The angles φ_n corresponding to these oscillations do not vary with the magnetic field, confirming their Shubnikov nature. At $\varphi>0$ the numbers of the minima of the angular oscillations closely correspond to the law $n \sim a \tan \varphi_n$ (see the insert in Fig. 5), while the numbers of the maxima of the corresponding oscillations poorly satisfy this relation.

4. DISCUSSION

Calculations of the band structure of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ were recently performed[9] on the basis of an analysis of the x-ray structural data in Ref. 7. The unit cell of this salt contains eight donor molecules of ET, and, therefore, the interaction between the eight highest occupied molecular orbitals results in the formation of eight energy bands. According to the stoichiometric formula, there are 1.5 electrons for each ET molecule in the unit cell; therefore, 12 electrons should accordingly be located in the eight energy levels. Depending on the degree of overlap or the presence of a gap between the sixth and seventh bands, the system under study can be either a two-dimensional semiconductor or a two-dimensional metal. The calculations in Ref. 9 showed that there is some slight overlap between these bands, which is responsible for the partial filling of these bands with electrons and, accordingly, the metallic character of the behavior of the conductivity of this salt down to helium temperatures. It was shown that the calculated Fermi surface consists of two cylinders, whose axes are parallel to **a***. The cross sections of the cylinders in the **bc** plane are shown in Fig. 6. According to the calculations, the cross sections of these cylinders are identical, and each amounts to 13% of the area of the corresponding cross section of the first Brillouin zone. However cylinder *A* corresponds to the carrier electrons, and cylinder *B* corresponds to the holes. It was asserted in Ref. 9 that these closed Fermi surfaces result from the hybridization of two latent one-dimensional Fermi surfaces. Quantum oscillations at a single frequency (if the possible contribution of harmonics and magnetic-breakdown orbits is disregarded) can be expected from a Fermi surface of such a form.

The study of the magnetoresistance in a single crystal of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ when the magnetic field was directed differently revealed that they have Shubnikov–de Haas oscillations at six different frequencies, which correspond to five closed orbits, since, in all likelihood, F_4 is the second harmonic of the fundamental frequency F_2, i.e., $F_4=2F_2$. The angular dependences of the frequencies of the oscillations let us to formally specify the overall Fermi surface as a set of five cylinders with axes parallel to **a***. The cross-sectional areas of these cylinders in the **bc** plane comprise the following percentages of the corresponding cross-sectional area of the Brillouin zone: 8% for F_1, 13% for F_2, 20% for F_3, 33% for F_5, and 46% for F_6. Thus, only the fundamental frequency F_2 corresponds to both theoretically calculated closed orbits. It is more difficult to ascertain whether the Shubnikov–de Haas oscillations at frequency F_2 are the result of the superposition of the oscillations of two orbits encircling identical areas or whether this fundamental frequency is specified by only one of them. If each of these orbits corresponded to carriers with different cyclotron masses, we would not expect relation (1) to hold when the amplitudes of the oscillations associated with these orbits are summed. However, according to the insert in Fig. 4, this relation holds well. Thus, either carriers with nearly identical cyclotron masses correspond to these two orbits, or only one orbit contributes to the Shubnikov–de Haas oscillations at the fundamental frequency F_2.

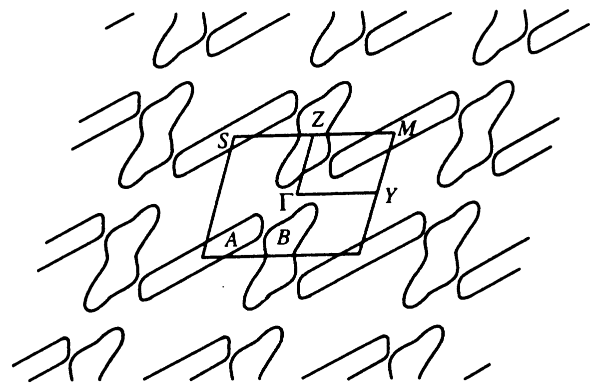

FIG. 6. Cross section of the Fermi surface in the **bc** plane in $ET_4[Hg_4Cl_{12}(C_6H_5Cl)_2]$ at room temperature.[9]

The reasons for the appearance of the remaining extreme orbits call for further detailed study. It is difficult to guess that all of them correspond to the real places of the Fermi surface. Some of them may have a magnetic-breakdown character. The calculated Fermi surface (Fig. 6) does not make it possible to imagine such orbits. However, the analogous picture at low temperatures can have a somewhat different form. Therefore, x-ray structural investigations of this compound at low temperatures followed by band calculations would be of interest.

The angular dependence of the amplitude of the Shubnikov–de Haas oscillations with the fundamental frequency (Fig. 4) is characterized by asymmetry relative to the **H**‖**a*** direction and by intermediate amplitude nulls at $\varphi=\pm 28°$. The first finding is evidently due to the low symmetry of the object under study. The other finding is most likely associated with the spin splitting of the Landau levels in the magnetic field.[10] Consideration of such splitting in the expression for the amplitude of the Shubnikov–de Haas oscillations results in the appearance of the diminishing factor

$$\cos(\pi g p m^*/2m_0),$$

where p is the number of the harmonic and g is the g factor. It vanishes under the condition

$$g p m^*/m_0 = 2n+1,$$

where n is an integer. Assuming that the cyclotron mass depends on φ, as does the area encircled by the respective orbit, i.e., $m^*(\varphi)=m^*(0)/\cos\varphi$, and taking into account the previously obtained result $m^*(0)=1.35m_0$, we find that when $g=2$, the amplitude of the first harmonic of the Shubnikov–de Haas oscillations vanishes for $n=1$ at $\varphi=\pm 28°$, in good agreement with the experimental results. The next pair of "spin zeros" for $n=2$ should exist at $\varphi=\pm 58°$. However, it was not detected experimentally, since oscillations are no longer observed at $\varphi > \pm 60°$.

Angular oscillations of the classical part of the magnetoresistance, which are periodic with respect to $\tan\varphi$ and similar to those discovered in $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$, were previously observed in several other organic metals. These can be of two types. The first is associated with motion of the electrons along closed orbits belonging to a Fermi cylinder corrugated along its axis, which is characteristic of quasi-two-dimensional electron systems. Oscillations of this type were observed, for example, in ET_2IBr_2 (Ref. 11). Angular oscillations of the second type are associated with the motion of electrons in open orbits belonging to corrugated Fermi quasiplanes, which are characteristic of quasi-one-dimensional electron systems. A striking example of such oscillations was discovered in $ET_2TlHg(SCN)_4$ (Ref. 12). The band calculations of $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ and the results already presented here indicate the presence of cylindrical sheets in the Fermi surface, and angular oscillations of the first type can therefore be expected. In this case, using the period $\Delta(\tan\varphi)$, we can roughly estimate[11] the area of the cross section of the cylinder responsible for the angular oscillations in the **bc** plane by approximating the orbit in this plane by a circle. The evaluation gives a value of the order of 40% of the area of the analogous cross section of the Brillouin zone. Taking into account the roughness of the approximation and the large set of cylindrical sheets comprising the Fermi surface, we can state that the area obtained lies within the expected range. At the same time, the fact that minima of the angular oscillations in $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$ closely correspond to the dependence $n \sim a \tan\varphi_n$ may attest to a connection between these oscillations and motion in quasiplanes, since in this case the characteristic points of the angular oscillations are the minimum points.[12] Conversely, when the electrons move along closed orbits, the characteristic points are the maximum points.[11] Thus, the available experimental material does not make it possible to unequivocally establish the nature of the angular oscillations discovered in $ET_8[Hg_4Cl_{12}(C_6H_5Cl)_2]$. A thorough study at various azimuthal angles is needed to clarify the situation.[11,12]

5. ACKNOWLEDGMENTS

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