Fermi surface in the organic superconductor $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$

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Information on part of the Fermi surface in the quasi-2D organic conductor $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$ at low temperatures has been found through a study of the amplitude and frequency of the Shubnikov–de Haas oscillations as a function of the direction of the magnetic field and the temperature. This part of the Fermi surface consists of two closed, essentially uncorrugated cylinders whose axes are oriented perpendicular to the conducting layers. The areas of the intersection of the cylinders with a plane parallel to the conducting layers are 0.8% and 1.7% of the area of the corresponding cross section of the Brillouin zone.

The molecule BEDT-TTF (ET) is a building block of many of the quasi-2D organic metals and superconductors which are presently known. Such molecules form well-conducting cation layers, which are separated by inorganic anion layers.[1,2] The high conductivity in the cation layers results from shortened bonds between sulfur atoms belonging to different ET molecules. It is thus clear that replacing sulfur atoms by atoms of the same group—selenium or oxygen—in some of the well-known ET complexes should have a strong effect on the conducting properties. Research on new compounds of this sort may prove extremely useful for solving the problem of constructing organic metals and superconductors with specified properties.

Several cation-radical salts based on the oxygen analog of the ET molecule, BEDO-TTF, have been produced in recent years. In this analog, the sulfur atoms of the peripheral rings are replaced by oxygen. Two salts, $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$ and $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$, have demonstrated superconducting properties.[3-5] In this letter we are reporting a study of the electronic structure of the quasi-2D superconductor $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$. The crystal structure of this compound, which is described in detail in Ref. 6, is typical of organic conductors based on ET: The

BEDO-TTF cations form conducting layers in the **ab** plane, which are separated by $ReO_4 \cdot H_2O$ anions along the **c** direction. The conductivity anisotropy is[5] $\sigma \mathbf{a}/\sigma \mathbf{c}^* \sim 10^3$–$10^4$. The resistance of $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$ along the conducting plane has a metallic temperature dependence between 300 and 30 K (Refs. 4 and 5). A first-order metal–metal phase transition has been detected near 200 K; it is seen as a jump in the resistance. Below 30 K at standard pressure, one observes an increase in the resistance with decreasing temperature. This resistance increase has been interpreted as a transition to a state with a spin density wave.[5] At $T=2.5$–3.5 K, this compound undergoes a superconducting transition.[4,5] An applied pressure shifts the first-order transition to a lower temperature and completely suppresses the transition to a spin density wave at a pressure as low as on the order of 1 kbar (Refs. 4 and 5).

It seems worthwhile to obtain information on the $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$ Fermi surface formed after these transitions. In the present letter we report a study of Shubnikov–de Haas oscillations, which gives us some idea of the shape of the Fermi surface in this compound at low temperatures and at standard pressure.

The magnetoresistance of single-crystal $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$ samples was studied as a function of the orientation and strength of the magnetic field in the temperature interval 1.5–4.2 K. The test samples were platelets with average dimensions of $1.5 \times 0.5 \times 0.02$ mm. The resistance was measured by the standard ac four-contact method at a frequency of 330 Hz. Measurements were taken in two regimes, which differed in the manner in which the measurement current flowed. In the first regime, the current flowed along the perpendicular to the conducting layers. In this case we used a module with platinum contacts, which were cemented to the crystal with graphite paste. In the second regime the current flowed along the conducting layers. In this case we used a module with platinum clamp contacts, which were clamped to gold stripes deposited on the crystal. The magnetic field was produced by a superconducting solenoid with a field up to 15 T and by a pulsed solenoid with a field up to 36 T. The results found in the measurements of the oscillating resistance were analyzed by means of fast Fourier transforms.

In a zero magnetic field, with the current flowing parallel to the conducting layers, the temperature dependence of the resistance of the test samples is qualitatively the same as that of Refs. 4 and 5. When the current instead flows along the perpendicular to the layers, the jump in the resistance associated with the first-order phase transition is less apparent. The onset of an insulating phase below 30 K is observed in all the test samples.

For the field directions $H \parallel \mathbf{c}^* \pm 55^\circ$ we observed Shubnikov–de Haas oscillations. The amplitude of these oscillations varied from sample to sample. The oscillations shown in Fig. 1 were observed in one sample as the measurement current flowed along the perpendicular to the conducting layers. We see from this figure that the amplitude of the Shubnikov–de Haas oscillations is so high that these oscillations are completely visible even at fields on the order of 2–3 T. The Shubnikov–de Haas oscillations are also clearly visible when the measurement current flows along the conducting layers. Figure 2 shows an example of the oscillations in this case; the regular part of the magnetoresistance has been subtracted here.

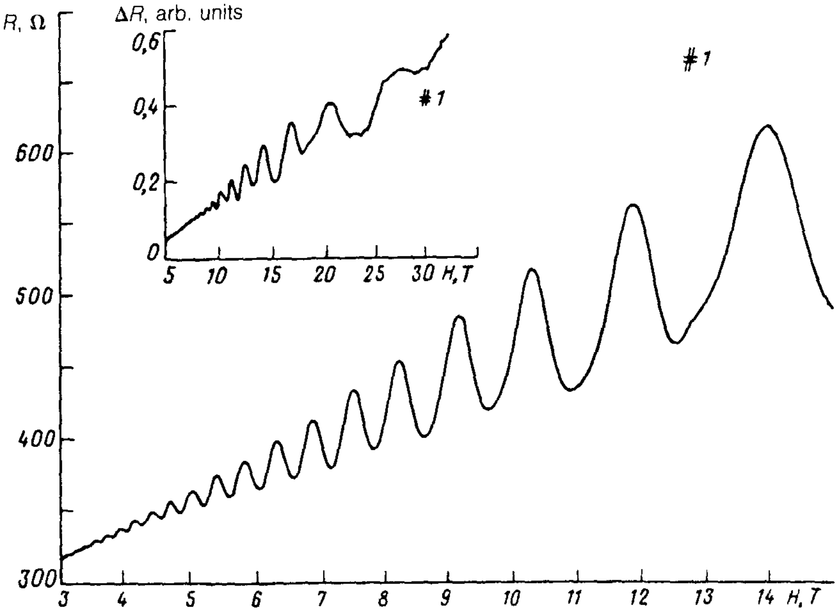

FIG. 1. Shubnikov–de Haas oscillations in sample 1 for a field direction near $H \| \mathbf{c}^*$ at $T=1.5$ K with $J \| \mathbf{c}^*$. The inset shows Shubnikov–de Haas oscillations in sample 1 in a pulsed solenoid at $T=1.5$ K with $J \| \mathbf{c}^*$ and $H \| \mathbf{c}^*$.

Shubnikov–de Haas oscillations are also seen on the angular variation of the resistance in a magnetic field; here they take the form of angular oscillations (Fig. 3). The changes in the phase of these oscillations as the magnetic field is weakened (Fig. 3) confirm that these oscillations are of a Shubnikov nature. The angular oscillations in the classical part of the magnetoresistance, which are characteristic of certain quasi-2D organic metals and which are associated with a motion of electrons along closed[7] and open[8] orbits, have not previously been seen in $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4 \cdot \mathrm{H}_2\mathrm{O}$ crystals.

Fourier analysis of the Shubnikov oscillations shows that these oscillations result from the superposition of at least two basic oscillations, with frequencies F_1 and F_2 which depend on the field direction. For the direction $H \| \mathbf{c}^*$, these frequencies are 38 and 81 T, respectively (see inset a in Fig. 2). The oscillations at the frequency F_2 are predominant for this field direction, for fields which are not too strong. The contribution from the oscillations at the frequency F_1 becomes noticeable only at strong magnetic fields (see the inset in Fig. 1 and also Fig. 2). The cyclotron carrier mass in the **ab** plane corresponding to the oscillations at F_2 is $m^*=1.1m_0$. With increasing value of the angle ϕ (this is the angle between the field direction and the $\mathbf{c}^*$ direction), the amplitude of the F_2 oscillations decreases considerably more rapidly than the amplitude of the F_1 oscillations. As a result, the F_1 oscillations dominate the picture almost completely at angles $\phi > 45°$.

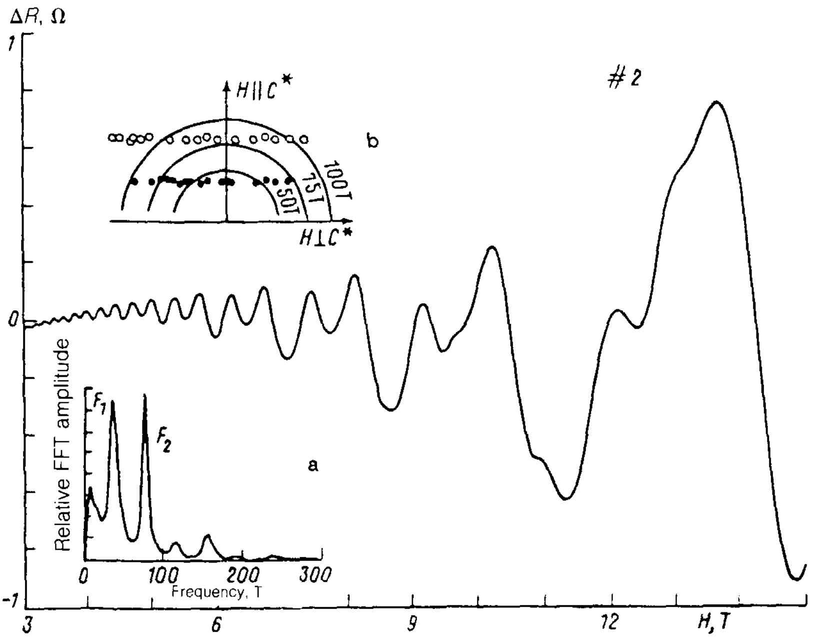

FIG. 2. Shubnikov–de Haas oscillations in sample 2 (the regular part of the magnetoresistance has been subtracted) for a field direction near $H\|\mathbf{c}^*$ at $T=1.5$ K with $J\|\mathbf{a}$. Inset a—Fast Fourier transform of the oscillations in the main part of the figure; inset b—angular variation of the Shubnikov–de Haas oscillation frequencies F_1 and F_2 in polar coordinates.

Inset b in Fig. 2 shows the Shubnikov–de Haas frequencies F_1 and F_2 versus the angle ϕ. By virtue of this dependence, the Fermi surface corresponding to the oscillations with frequencies F_1 and F_2 can be described fairly accurately as consisting of cylinders with axes directed along **c***. The areas of the intersection of the cylinders with the plane perpendicular to the **c*** axis are about 0.8% and 1.7% of the corresponding cross section of the Brillouin zone.

In summary, at least part of the Fermi surface in $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4 \cdot \mathrm{H_2O}$ consists of two cylinders with axes perpendicular to the conducting planes at low temperatures, with intersection areas which are very small in comparison with the Brillouin zone. The generatrices of the cylinders probably have only an extremely weak corrugation, since we do not see the well-known indications of a corrugation: beats in the Shubnikov–de Haas oscillations[9] and angular oscillations in the classical part of the magnetoresistance.[7]

While this study was being prepared for publication, we received information that S. Kahlich, D. Schweitzer, *et al.*[10] had found results close to those reported in this letter in a study of the magnetoresistance of $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4 \cdot \mathrm{H_2O}$.

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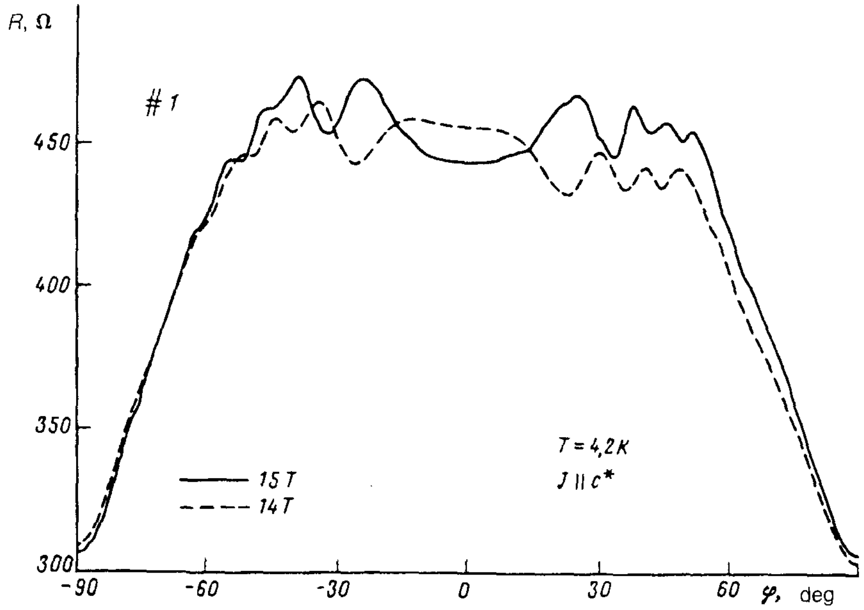

FIG. 3. Angular variation of the resistance of sample 1 in magnetic fields of 14 and 15 T with $J \| \mathbf{c}^*$ at $T=4.2$ K.

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