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M. V. Kartsovnik, V. N. Laukhin, and S. I. Pesotskiĭ. *Shubnikov–de Haas oscillations in organic metals.* The discovery of organic superconductivity in 1980 has engendered a great deal of interest in organic metals.[1] The many subsequent publications on the properties of such compounds led to the discovery of a number of properties which distinguish these compounds from most traditional metals. In particular, the question of the mechanism of superconductivity in these materials is itself still not entirely understood. In order to clarify the properties of both normal and superconducting states of organic metals, it is very important to know the electronic structure of the metals. A significant advance in this direction was the discovery of Shubnikov–de Haas (SdH) oscillations in a number of quasi-two-dimensional metals based on bis(ethylenedithio)tetrathiofulvalene (abbreviated as ET). This opened up the possibility of studying experimentally the Fermi surface (FS) of these materials.

Shubnikov–de Haas oscillations were first observed in the superconductor β-$(ET)_2IBr_2$.[2] A detailed investigation of high-quality samples of this compound revealed SdH oscillations with two very different characteristic frequencies.[3]

Oscillations of the first type—"fast" oscillations—were observed in a wide range of angles φ between the direction of the magnetic field **H** and the normal **c*** to the highly conducting ab plane of the crystals: $\pm$ (50–60)°. For $\mathbf{H}\|\mathbf{c}^*$ their frequency ($F \approx 3900$ T) corresponds to extremal closed sections of the Fermi surface $S_e \approx 3.7 \cdot 10^{15}$ cm^{-2}, which is $\approx 55\%$ of the area of the Brillouin zone. The cyclotron mass, determined from the temperature dependence of the amplitude of the oscillations, is quite large and constitutes $\approx 4.5 m_0$. The amplitude of the oscillations is a quite complicated function of the direction of the magnetic field. However, the dependence of the frequency of the oscillations on the angle φ is found to be very smooth and is described well by the relation $F \sim 1/\cos\varphi$. This result shows that the main motif of the Fermi surface of this compound is, at least, a not strongly corrugated cylinder whose axis is oriented along **c***. The degree of corrugation can be estimated from the beat frequency of the oscillations, the beats being especially pronounced at low angles φ. This frequency (≈ 30 T) is approximately 100 times lower than the fundamental frequency. Therefore, the Fermi momentum in the plane changes by $\sim 1\%$ along the **c*** axis.

Shubnikov–de Haas oscillations of the second type—"slow" oscillations—are clearly seen at low angles φ. Near the direction $\mathbf{H}\|\mathbf{c}^*$ their frequency ($F_S \approx 50$ T) corresponds to the extremal cross-sectional area of the Fermi surface equal to $\sim 0.6\%$ of the transverse cross section of the Brillouin zone; the cyclotron mass is $0.5 m_0$. The origin of the "slow" oscillations is still not entirely clear. The angular dependence of the frequency[4] indicates that these small sections of the Fermi surface are necks between the main cylinders or they are ellipsoidal pockets, flattened in the **c*** direction. The amplitude of the oscillations increases with the angle φ, but the amplitude of the "fast" oscillations as well as the classical part of the magnetoresistance increase even more rapidly. For this reason the "slow" oscillations are difficult to observe for large angles.

Thus, on the basis of observations of SdH oscillations in β-$(ET)_2IBr_2$, the following conclusions can be drawn concerning the properties of the Fermi surface of this compound.[5]

1. The main motif of the Fermi surface is a cylinder whose axis is oriented along **c*** (i.e., perpendicular to the highly conducting *ab* plane, in which layers of ET molecules form). An estimate of the degree of corrugation in the approximation of an isotropic FS in the plane gives $\Delta k_F / k_F \approx 10^{-2}$.

2. Besides the cyclotron mass, given above, analysis of the SdH oscillations makes it possible to estimate some other parameters of the electronic system. Thus, in the approximation of a quadratic dispersion law in the plane the Fermi energy is $\varepsilon_F \approx \hbar e H_n n / m^* c \approx 80$ meV, the transverse hopping integral is $2t_c \sim 1$ meV, the density of states is $N(\varepsilon_F) \approx 2c^* m^* / (2\pi\hbar)^2 \approx 9.6 \cdot 10^{33}$ (ergs·cm)$^{-1}$, the carrier density is $n \approx 2Sc^*/(2\pi)^3 \approx 1.3 \cdot 10^{21}$ cm^{-3}, and the average velocity in the *ab* plane is $\bar{v}_F \approx 0.8 \cdot 10^7$ cm/sec.

3. Besides the main slightly corrugated cylinder, the Fermi surface probably contains other, small sections in the form of necks or pockets flattened along **c***.

It is of interest to compare the data obtained for β-$(ET)_2IBr_2$ and for other representatives of the isostructural family β-$(ET)_2X$, where $X = I_3$, AuI_2 or I_2Br. At low temperatures the complex β-$(ET)_2I_3$ can exist in two modifications: β_L with $T_c \approx 1.5$ K and β_H with $T_c \approx 8$ K.[6] The only difference between the crystal structures is that a weak incommensurate superstructure, associated with orientational disordering of the terminal ethylene groups in the ET molecules, is present in the β_L phase and absent in the β_H phase.[7,8]

Jerome's group has observed SdH oscillations in the β_H phase,[9] and the parameters of these oscillations were virtually identical to those of the "fast" oscillations in β-$(ET)_2IBr_2$. We investigated the magnetoresistance of the β_L phase.[10] The "fast" SdH oscillations were not observed, probably because of the additional scattering associated with the presence of weak disorder in this modification due to the incommensurate superstructure. However, "slow" oscilla-

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tions were observed and it was found that they are appreciably different from those observed in β-$(ET)_2IBr_2$. Besides the fact that their frequency is approximately two times higher (here with $\mathbf{H}\|\mathbf{c}^*F\approx 100$ T), it was found that their dependence on the magnetic-field direction is completely different. In the complex with IBr_2 the frequency decreases rapidly away from the normal to the conducting plane, whereas in the present compound it increases; the amplitude, conversely, decreases. Assuming that the weak disorder caused by the terminal ethylene groups does not affect the form of the Fermi surface, it can be concluded that the specific form of the anion makes a significant contribution to the formation of definite sections of the Fermi surface of the β phase, though previously it was thought that the anions do not participate in the formation of the conduction band of these compounds, in any case, in calculations of the band structure[11] only the cationic layer was taken into account.

This effect was observed, virtually simultaneously with the discovery of SdH oscillations in β-$(ET)_2IBr_2$, in another organic superconductor $\varkappa$-$(ET)_2Cu(NCS)_2$.[12] This complex has one of the highest critical temperatures $T_c \approx 10.5$ K among the known organic superconductors.[13] The frequency of the SdH oscillations in a field perpendicular to the highly conducting plane ($F = 610$ T) corresponds to the extremal section of the Fermi surface, comprising $\sim 18\%$ of the cross section of the Brillouin zone. The angular dependence of the frequency of the oscillations is described ideally by the relation $F \sim 1/\cos\varphi$.[14] These results are in good agreement with band calculations.[12] According to these calculations the Fermi surface consists of two open sheets and a cylinder whose axis is perpendicular to the molecular layers. In addition, at certain points the open surfaces approach close to the cylinder. Recently, harmonics with frequencies corresponding to magnetic-breakdown orbits, agreeing with the indicated picture of the Fermi surface, were observed in fields $H > 20$ T.[15]

Representatives of a new family of layered conductors $(ET)_2MHg(SCN)_4$ with a massive anionic layer, containing the univalent cations $M^+ = K^+$, Rb^+, Tl^+, or NH_4^+, exhibit interesting properties in a magnetic field. A characteristic feature of these compounds is that, as band calculations show,[16] their Fermi surface should contain, besides the cylinder typical for quasi-two-dimensional metals, a pair of slightly corrugated open sheets, which are, rather, characteristic of quasi-one-dimensional systems. Existing experimental data[17–20] indicate an antiferromagnetic phase transition at $T \approx 10$ K in layers with K, Rb, and Tl. This transition leads to partial dielectrization and is probably associated with the instability of the quasi-one-dimensional subsystem with respect to the formation of a spin-density wave. Application of a magnetic field perpendicular to the highly conducting layers results in a gigantic magnetoresistance, which indicates an increased tendency toward dielectrization.[18,20] However, this dielectrization is not complete: In a field of 10 T the field dependence of the resistance becomes saturated and SdH oscillations become clearly visible.[20,21] The frequency of the oscillations correlates well with the computed area of the cylinder in Ref. 16. The flat sheets of the Fermi surface are now, most likely, closed by a dielectric gap. Thus, in this case, the metallic and semiconductor states exist simultaneously in the crystal.

An interesting feature of SdH oscillations in $(ET)_2MHg(SCN)_4$ layers with M = Tl, K is the appreciable anharmonicity in a field oriented near the normal to the molecular layers. In Ref. 21 this effect is attributed to the influence of spin splitting. In our opinion, however, this is doubtful, because we are far from the quantum limit: $\varepsilon_F/\hbar\omega_c \sim 10^2$. The spectrum of the SdH oscillations contains, besides the fundamental frequency (670 T), the second harmonic (1340 T) with anomalously high amplitude, sometimes exceeding the amplitude of the fundamental harmonic. Harmonics of higher order have not been observed. The reasons for this behavior are under investigation. They could be associated with effects of the magnetic-breakdown type.

In contrast to the ET-based layered metals discussed above, tetraselenotetracene chloride $(TSeT)_2Cl$ has a one-dimensional structure.[22] The stacks of TSeT molecules are aligned along the c axis and are separated from one another by Cl^- anions; maximum conductivity is observed in the **c** direction. It is known that a Peierls type instability with a metal-insulator transition is characteristic for such systems. In this compound, however, the existence of appreciable interstack interaction and the character of the temperature dependence suggest that a semimetallic state rather than a dielectric state is realized below the phase transition.[23] This proposition is confirmed by the observation of SdH oscillations at low temperatures in fields above 4 T.[24] Shubnikov–de Haas oscillations are more pronounced when $\mathbf{H}\perp\mathbf{c}$. For $H = 15$ T and $T = 15$ K the amplitude of the oscillations is $\approx 10\%$ of the resistance of the sample. The frequency of the oscillations with this orientation of the field ($F \approx 16$ T) corresponds to extremal sections of the Fermi surface $S_e \approx 1.6\cdot 10^{13}$ cm^{-1}, which is $\approx 1\%$ of the cross-sectional area of the Brillouin zone. As the angle between the field direction and the c axis decreases, the amplitude of the oscillations decreases and the frequency increases. This behavior permits representing the Fermi surface in the form of small disks compressed along the c axis.

Approximating the shape of the pockets in the Fermi surface by an ellipsoid of revolution with semiaxes $k_{F\perp}$ and $k_{F\|}$ across and along, respectively, the TSeT stacks and using the data on the resistance anisotropy,[25] we estimate (in the approximation of isotropic relaxation time) $k_{F\perp} \approx 5\cdot 10^{-2}$ Å^{-1} and $k_{F\|} \approx 10^{-2}$ Å^{-1}. Using these values for estimating the volume of the observed pockets, we obtain the carrier density $n \approx 2\cdot 10^{17}$ cm^{-3}, which is three to four orders of magnitude lower than the conjectured density in the high-temperature, metallic state of $(TSeT)_2Cl$. Estimation of the carrier density from the conductivity, using the cyclotron mass $m^* \approx 0.25m_0$ and the Dingle temperature $T_D \approx 1$ K, which are obtained from an analysis of the oscillations, also gives $n \approx 10^{17}$ cm^{-3}. Hence it can be concluded that the Fermi surface of $(TSeT)_2Cl$ is completely determined by the pockets revealed by the SdH oscillations.

It is worth noting that the oscillation in the field ≈ 15 T corresponds to quantum number $n = 1$, i.e., we are close to the quantum limit. It is of interest to investigate the behavior of this compound in stronger fields.

In conclusion we underscore the fact that the discovery of SdH oscillations played a significant role in the development of the physics of organic metals and superconductors. First of all, a new line of inquiry has been opened up and is developing rapidly—the fermiology of organic conductors. Reliable information about the shape of the Fermi surface

has now been obtained for a number of materials and estimates have been obtained for a number of very important parameters of the electronic system—the carrier density, the Fermi energy, the density of states, and the cyclotron mass. Second, the skepticism toward organic metals, as being dirty objects, which cannot be modeled, has been eliminated. On the contrary, the high degree of perfection of crystals of some layered organic metals has made it possible to observe in them a new galvanomagnetic effect, opening up new experimental possibilities for fermiology of quasi-two-dimensional systems: strong angular oscillations of magnetoresistance.[4,26]

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