RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Shubnikov–de Haas effect and the Fermi surface in an ambient-pressure organic superconductor [bis(ethylenedithiolo)tetrathiafulvalene]$_2$Cu(NCS)$_2$

K. Oshima
Cryogenic Center, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113, Japan

T. Mori and H. Inokuchi
Institute for Molecular Science, 38 Aza-nishigo-naka, Myodaiji-cho, Okazaki-shi, Aichi 444, Japan

H. Urayama, H. Yamochi, and G. Saito
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan
(Received 6 January 1988)

The Shubnikov–de Haas (SdH) effect has been observed in the recently discovered ambient-pressure organic superconductor [bis(ethylenedithiolo)tetrathiafulvalene]$_2$Cu(NCS)$_2$. This is the first unambiguous report on the SdH effect in organic compounds. The SdH signal is observed below 1 K, above 8 T, and at angles θ between the crystal a^*-axis and a magnetic field of less than 30°. The period $0.0015\cos\theta$ (T^{-1}) corresponds to the cylindrical closed Fermi surface obtained by the tight-binding method based on the extended Hückel approximation, which is critically dependent on the crystal symmetry. The temperature dependence of the oscillation amplitude gives the effective mass at the Fermi surface to be about $3.5m_0$.

Since the discovery of an organic superconductor in 1980 (Ref. 1), many studies have been devoted to magnetoresistance measurements. The first report on the Shubnikov–de Haas (SdH) effect in an organic compound was given by Kwak, Schirber, Greene, and Engler,[2] about $(TMTSF)_2PF_6$ under pressure (TMTSF is tetramethyltetraselenafulvalene). The observed frequency was 0.76 MG (period $\simeq 0.013\ T^{-1}$). Afterwards, Bando *et al.*, reported the SdH effect in $(TMTSF)_2ClO_4$.[3] They observed two types of oscillations with periods of 0.015 and 0.0036 T^{-1}. The longer one nearly corresponds to that of $(TMTSF)_2PF_6$. But later studies revealed the stepwise variation of the Hall field, indicating an abrupt change of carrier density at the fields corresponding to the longer-period oscillation.[4–6] Therefore, this branch of the oscillation is thought to occur due to a series of phase transitions among different spin-density-wave states rather than the SdH effect.[7–9] Meanwhile, the shorter period was considered as SdH for a while. But the oscillation amplitude decreases at sufficiently low temperature, which is different from the ordinary SdH behavior. A similar behavior has also been reported on the shorter-period branch found later in $(TMTSF)_2PF_6$.[10] Therefore, different origins are also proposed for this branch, and now the consensus is that this branch is not SdH, though the origin has not been identified.[11,12] Therefore the experimental results so far reported as SdH were apparently due to the SdH effect.

A different type of organic superconductor from TMTSF derivatives was discovered later: the bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) compounds.[13,14] The BEDT-TTF salts have a nearly two-dimensional character, in contrast to the TMTSF salts which have a pseudo-one-dimensional character. This was shown by Mori *et al.*[15] on the typical salt β-$(BEDT\text{-}TTF)_2I_3$. The Fermi surface obtained using tight-binding calculations based on the extended Hückel approximation was a round closed surface occupying a fairly large part of the first Brillouin zone. This model is very useful because it correctly describes the physical properties in spite of its simplicity. But recently, Kübler, Weger, and Sommers[16] have criticized this calculation and proposed a self-consistent band calculation. Their Fermi surface consists of an open sheet and comparatively small closed sheet. A significant contradiction exists between these two calculations.

An important key to judge the effectiveness of a model is a magnetic oscillation experiment related to the Fermi surface. We report in this paper the first unambiguous SdH oscillation observed in a new organic superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$.[17] This compound has a critical temperature higher than 10 K at ambient pressure. The crystal structure is analogous to that of the organic superconductor κ-$(BEDT\text{-}TTF)_2I_3$ obtained by Kobayashi *et al.*[18] The difference from the κ-$(BEDT\text{-}TTF)_2I_3$ crystal structure is the inequivalence of the two BEDT-TTF molecules which constitute a fundamental unit of the crystal structure, because of the different anion structure.[19] The lattice parameters are shown in Table I. The crystal has the shape of a hexagonal plate with the typical size of $2\times1\times0.05$ mm^3. The long direction corresponds to the crystal b axis and the c axis lies in the plate perpendicular to the b axis. It is known that the BEDT-TTF molecules constitute a two-dimensional conducting sheet in the crystal b-c plane (Fig. 1). The synthesis, crystal structure, and physical properties including superconducting properties were reported elsewhere.[17,20]

The temperature dependence of magnetoresistance where the external field is along the a^* axis is shown in Fig. 2. The measuring current is along the a^* axis, therefore the measurement is in the longitudinal condition. The sample is in the superconducting state at zero field.

TABLE I. Comparison of the lattice parameters and T_c for the BEDT-TTF-based organic superconductors with analogous structures.

	Structure	a (Å)	b (Å)	c (Å)	β (deg)	V (Å^3)	Z	T_c (K)
(BEDT-TTF)$_2$Cu(NCS)$_2$	Monoclinic, $P2_1$	16.248(5)	8.440(2)	13.124(5)	110.30(3)	1688.0	2	10.4
κ-(BEDT-TTF)$_2$I$_3$	Monoclinic, $P2_1/c$	16.387(4)	8.466(2)	12.832(8)	108.56(3)	1687.6	2	3.6

The normal resistance is recovered when the external field is increased above the superconducting upper critical field. The field dependence of the magnetoresistance has an anomalous shape above 1.25 K, showing a small peak just above the superconducting to normal transition. The origin is not clearly identified yet, but some part of this behavior may be ascribed to the current inhomogeneity, because this shape depends on sample and electrical-lead configurations.

The quantum oscillation is clearly visible below 1 K and above 8 T. The angular dependence of the oscillation period is described as $(0.0015 \pm 0.0001)\cos\theta$ (T^{-1}) where θ is the angle between the a^* axis and the external magnetic field H, and oscillations are observed at angles less than 30°. The SdH period $\Delta(1/H)$ is related to the extremal area S of the Fermi surface normal to the field direction by the equation $\Delta(1/H) = 2\pi e/\hbar cS$. Therefore, the observed oscillation corresponds to a cylindrical Fermi surface containing 18% of the first Brillouin zone, if we regard it as the SdH effect. The temperature dependence and the field dependence of the SdH oscillation amplitudes are expressed by the factors R_T and R_D, R_T showing the effect of finite temperature and R_D indicating the finite relaxation time.[21] [$R_T = \pi\lambda/\sinh\pi\lambda$, $R_D = \exp -\pi\lambda(x/T)$ where $\lambda = 2\pi kT/\beta H$, $\beta = e\hbar/mc$ for the fundamental frequency, and x is the Dingle temperature.] Experimental results are in accord with the above formulas, and we get an effective mass $m \simeq 3.5m_0$ and $x \simeq 1$ K. Thus our results show the behavior expected for SdH oscillations. The transverse condition where the measuring current is along the b axis gives essentially the same results for the SdH oscillation.

We have performed a tight-binding energy-band calculation on the basis of the extended Hückel approximation to reveal which part of the Fermi surface is experimentally observable. The band structure from the room-temperature crystal structure is shown in Fig. 3. The overlap integrals used in the calculation are indicated in Fig. 1. The results are similar to those for κ-(BEDT-TTF)$_2$I$_3$,[18] which shows a cylindrical Fermi surface in the b-c plane. The cross section is equal to the area of the first Brillouin zone. Though the Fermi surface crosses the zone boundary on Z-M, the Fermi surface of κ-(BEDT-TTF)$_2$I$_3$ becomes a cylinder, because of the degeneracy on this boundary arising from the c glide plane of the $P2_1/c$ space group.[22] In the case of the present salt, since the

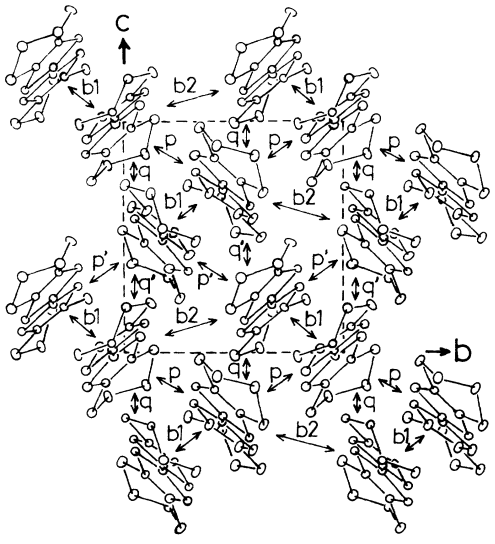

FIG. 1. The molecular arrangement of BEDT-TTF molecules. The adopted semiempirical parameters for the tight-binding band calculation are shown. The values of the overlap integrals are $b1 = 25.7$, $b2 = 10.5$, $p = 11.4$, $p' = 10.0$, $q = -1.7$, and $q' = -2.9$ $(\times 10^{-3})$.

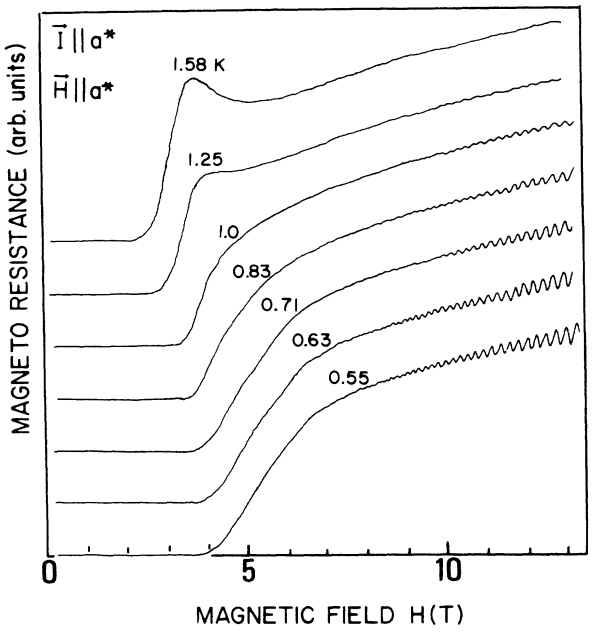

FIG. 2. The magnetoresistance as a function of magnetic field at temperatures from 1.58 to 0.55 K. The sample is in the superconducting state at zero field. Normal resistance returns above the upper critical field. Clear Shubnikov-de Haas oscillations are visible below 1 K.

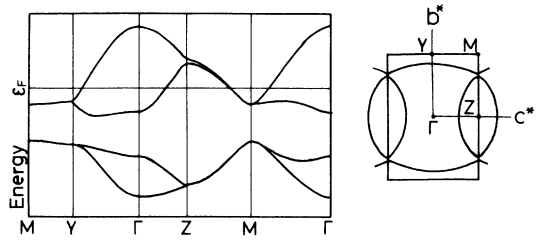

FIG. 3. The Fermi surface and band structure calculated by the tight-binding method based on the extended Hückel approximation.

asymmetrical arrangement of the anions reduces the crystal symmetry to $P2_1$, the degeneracy on Z-M is removed. As a result, the Fermi surface is separated into an open part which is normal to the b axis, and a closed part located around the Z point. As the closed part amounts to about 18% of the first Brillouin zone, it sufficiently corresponds to the experimental result.

Some problems in our calculation should be considered. First, the band calculation based on the lower-temperature crystal structure at 100 K gives a diminished gap, though the crystal symmetry is the same. It is necessary to check whether the lower-temperature crystal structure really supports the gap formation.

A second problem exists in the sign of the carrier. The preliminary result on the thermoelectric power is negative at all temperatures measured down to 10 K. Therefore the carrier should be electronlike. As the band scheme needs the positive carrier on the closed Fermi surface, we should ascribe the negative thermoelectric power to the open part of the Fermi surface. As can be seen in Fig. 3, the electronlike character is expected at the open part near the M point. Anyhow, it is necessary to check whether we can get a reasonable result from the band calculation.

As we have mentioned, there has been some criticism of such a simple calculation. The proposed Fermi surface by Kübler *et al.*[16] was completely different in the case of β-(BEDT-TTF)$_2$I$_3$. But if a small pocket in the Fermi surface does exist, as they propose, we should observe corresponding SdH oscillations. No experimental results have been reported yet. Indeed, the SdH oscillation will be difficult to observe for the Fermi surface calculated by Mori *et al.*,[15] because the expected frequency is high. We recommend further experimental confirmation of the Fermi surface using the SdH effect. There is a possibility of observing oscillations corresponding to the round Fermi surface in κ-(BEDT-TTF)$_2$I$_3$ at lower temperatures and at higher fields. The possibility of observing a magnetic-breakdown effect also exists in the case of our salt at higher fields. Physical insight can be given by the pressure effect on the SdH, if it can change the overlap integrals significantly. Reconfirmation of the SdH effect in the β-type salts is also necessary. We are now preparing for further study under extended conditions.

In conclusion, we have obtained unambiguous evidence of the SdH effect experimentally. The oscillation obtained corresponds to 18% of the first Brillouin zone of the crystal. The corresponding Fermi surface can be described using a simple tight-binding calculation based on the extended Hückel method. The effectiveness of the calculation can be tested by further experimental study at higher fields, lower temperatures, and under pressurized conditions.

We recommend that theorists further study the first-principle band calculations using the crystal structure of the compounds in this paper.

We would like to thank the members of the Cryogenic Center at the University of Tokyo for their support in this study. We would also like to thank Dr. K. Yamaji for his suggestions on the SdH experiment. This work was partly supported by a Grant in Aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control from the Japanese Ministry of Education, Science and Culture Grant No. 62604014.

[1]D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L95 (1980).

[2]J. F. Kwak, J. E. Schirber, R. L. Greene, and E. M. Engler, Phys. Rev. Lett. **46**, 1296 (1981).

[3]H. Bando, K. Oshima, M. Suzuki, H. Kobayashi, and G. Saito, J. Phys. Soc. Jpn. **51**, 2711 (1982).

[4]P. M. Chaikin, Mu-Yong Choi, J. F. Kwak, J. S. Brooks, K. P. Martin, M. J. Naughton, E. M. Engler, and R. L. Greene, Phys. Rev. Lett. **51**, 2333 (1983).

[5]M. Ribault, D. Jerome, J. Tuchendler, C. Weyl, and K. Bechgaard, J. Phys. (Paris) Lett. **44**, L953 (1983).

[6]K. Oshima, M. Suzuki, K. Kikuchi, H. Kuroda, I. Ikemoto, and K. Kobayashi, J. Phys. Soc. Jpn. **53**, 3295 (1984).

[7]L. P. Gor'kov and A. G. Lebed, J. Phys. (Paris) Lett. **45**, L433 (1984).

[8]K. Yamaji, J. Phys. Soc. Jpn. **54**, 1034 (1985).

[9]M. Heriter, G. Montambaux, and P. Lederer, J. Phys. (Paris) Lett. **45**, 943 (1984).

[10]J. P. Ulmet, A. Khmou, and L. Bachere, Physica B **143**, 400 (1986).

[11]K. Yamaji, J. Phys. Soc. Jpn. **56**, 1101 (1987).

[12]M. Ya.Azbel and P. M. Chaikin, Phys. Rev. Lett. **59**, 582 (1987).

[13]S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. Voiron, K. Carneiro, J. C. Scott, and R. L. Greene, Phys. Rev. Lett. **50**, 270 (1983).

[14]E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Konovich, M. B. Karatsovnik, A. V. Zvarykina, and L. J. Buravov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].

[15]T. Mori, A. Kobayashi, Y. Sasaki, R. Kato, H. Kobayashi, G. Saito, and H. Inokuchi, Bull Chem. Soc. Jpn. **57**, 627 (1986); T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett. 957 (1984).

[16]J. Kübler, M. Weger, and C. B. Sommers, Solid State Commun. **62**, 801 (1987).

[17]H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. 55 (1988).

[18]A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett. 459 (1987).

[19]H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Marayama, and H. Inokuchi, Chem. Lett. 463 (1988).

[20]K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 730 (1988); K. Nozawa, T. Sugano, H. Urayama, H. Yamochi, G. Saito, and M. Kinoshita, Chem. Lett. 617 (1988).

[21]D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge Univ. Press, Cambridge, 1984), Chap. 2.

[22]G. Burns, *Introduction to Group Theory with Applications* (Academic, New York, 1977), Chap. 12.