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Shubnikov–de Haas oscillations in the two-dimensional organic conductor τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim 0.75$)

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The quasi-two-dimensional organic τ-type conductor, τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim 0.75$), shows metallic temperature dependence of the resistivity down to $T_{min}\sim 50$ K, below which resistance upturn is observed. There has been no evidence of the phase transition through T_{min}. In this work, in pursuit of direct evidence for metal at low temperature by transport measurement, we show an observation of the Shubnikov–de Haas (SdH) oscillations for this salt. The observed frequencies of the oscillations are inconsistent with the previous band calculation. Further, it is remarkable that the amplitude of the oscillation was so giant ($|\Delta\rho/\rho_0|\sim 30\%$), and the oscillation above 20 T corresponds to a $N=2$ Landau state, i.e., next to a quantum limit. We also observed the SdH oscillations in other τ-type conductor, τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim 0.75$), which almost reproduced the previous report by Storr *et al.* [Phys. Rev. B **64**, 045107 (2001)].

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I. INTRODUCTION

The Fermi surface of the α-, β-, κ-, and τ-type quasi-two-dimensional organic conductors can be constructed by modifying a single round Fermi surface. Depending on the manner of which the two-dimensional Fermi surface crosses the first Brillouin-zone (FBZ) boundary, a large variety of reconstructed Fermi surfaces (FSs) appears.[1] Associated with the reconstructed FS, they show various ground states, such as superconductivity, antiferromagnetic ordering, a charge-density wave, and a metallic state at low temperature. Among these conductors, the ground state of τ conductors has not been clarified yet. These materials show remarkable properties such as large negative magnetoresistance, and switching of the symmetry of magnetoresistance by field and temperature.[2]

The chemical composition of τ conductors is nonstoichiometric. This is quite rare among the organic conductors. Namely, the ratio of donor to anion is $2:(1+y)$, where $y\sim 0.75$ from elemental analysis.[3] The calculated FS of the τ conductors is fourfold and star shaped (Fig. 1), which reminds us of a FS of a high-T_c superconductor, La$_{2-x}$Sr$_x$CuO$_4$. The resistivity ratio of $\rho_{\parallel c}/\rho_{\parallel ab}$ is about 10^3–10^4, where *ab* is parallel to the conducting plane. The donors of τ conductors in this report are EDO-S,S-DMEDT-TTF,[3] and P-S,S-DMEDT-TTF,[4] which are abbreviated below as O-O and N-N, respectively, since each donor has a six-membered ring that contains two oxygen or nitrogen atoms. The linear anions such as AuBr$_2^-$, I$_3^-$, and IBr$_2^-$ make crystals with these donors. The anions are located in the two crystallographically independent positions; one is inside the square lattice structure of donors that form the conducting layer, and the other is between the layers. The occupancy of the anion sites in the conducting layer is 100%, while those between layers are randomly occupied by about 75%. In addition to disorder in occupancy, another type of disorder is present. Bending disorder in the ethylenedioxy group (the edge of the ring containing two oxygen atoms) is observed in O-O salt, while the dimethylethylenedithio group (the edge of the ring containing two methyl groups) in N-N salt.[3]

The resistivity of τ-(O-O)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim 0.75$) shows metallic temperature dependence down to around $T_{min}=30$–50 K, below which a resistance upturn is observed. In the semiconducting region ($T<T_{min}$), large negative magnetoresistance appears, accompanying other remarkable features. Below 4 K, angular dependence of the interplane mag-

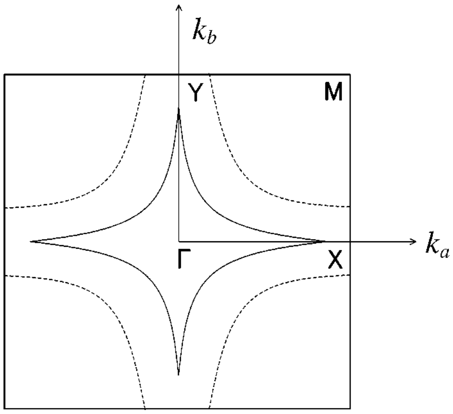

FIG. 1. Calculated Fermi surface of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ for $y=0.75$ (solid line) and $y=0$ (dotted line) (Ref. 3).

netoresistance for the magnetic field parallel to the conducting *ab* plane changes its periodicity between fourfold and twofold by the history of the application of magnetic field.[2] Such a phenomenon has never been observed at least in other organic conductors. Moreover, a large electronic specific-heat coefficient (60 mJ/mol K^2) was observed down to 0.1 K,[5] though the resistivity is semiconducting. The polarized reflectance spectra show Drude-like dispersion that also supports the metallic nature of this salt down to 22 K.[6] In spite of these accumulated works, direct evidence for metal by transport measurement was still absent.

Recently, Storr *et al.* reported the Shubnikov–de Haas (SdH) oscillations for the other τ conductor, τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y \sim 0.75$),[7] though the temperature dependence of its resistivity also becomes semiconducting as it does for the O-O salt.[4] Their result demonstrates that the Fermi-surface area is 6.8% of the FBZ. They also claimed the existence of a small FS pocket of 2.4% of the FBZ from the Fourier analysis. Two small FS's have not been presented in the previous calculation that gives a single FS of 12.5% of the FBZ. In any case, it is evident that the Fermi surface was proved to be present in the low-temperature ground state at least in magnetic field.

In this work, we study the low-temperature magnetoresistance of the two τ-type conductors, τ-(O-O)$_2$(AuBr$_2$)$_{1+y}$ and τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y \sim 0.75$), in high magnetic field. In the N-N salt, we reproduced almost the same result as that of Storr *et al*.[7] What is remarkable in our report is that we found the giant SdH oscillations ($|\Delta\rho/\rho_0| \sim 30\%$) in the O-O salt. The purposes of this paper are to show the giant oscillation of magnetoresistance and to discuss the low-temperature electronic properties, the ground state of τ conductors, and how the small FS pockets appear.

II. EXPERIMENT

The single crystals of τ-(O-O)$_2$(AuBr$_2$)$_{1+y}$ and τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y \sim 0.75$) were obtained by a usual electrochemical oxidation of EDO-*S*,*S*-DMEDT-TTF or P-*S*,*S*-DMEDT-TTF described elsewhere.[8] The crystals used in this measurement are black and square platelets with dimensions of $1.06 \times 0.76 \times 0.10$ mm^3 (sample 1), $0.94 \times 0.86 \times 0.09$ mm^3 (sample 2), and $0.76 \times 0.60 \times 0.04$ mm^3 (sample 3), respectively. The magnetoresistance was measured by a four-terminal method with ac current of 1 μA with frequencies of 28.2 Hz, 77.8 Hz, and 13.24 Hz for samples 1–3, respectively. The annealed gold wires (20 μm in diameter) were attached to the gold-evaporated surface by gold paint in the configuration for the electrical current perpendicular to the conducting ab plane (see the inset in Fig. 2). The magnetoresistance measurement was carried out using a hybrid magnet at the High Field Laboratory, Institute for Materials Research, Tohoku University. The measurement was performed at 0.48 K and 1.35 K in the magnetic field perpendicular to the conducting *ab* plane up to 27 T.

III. RESULTS

The temperature dependence of the resistivity ρ_c of the O-O salt is shown in Fig. 2 for the two samples (1 and 2) from the same batch. The room-temperature resistivity was 3.3×10^2 Ω cm and 3.6×10^2 Ω cm, respectively. The behavior of ρ_c is almost the same as was reported previously.[3] It shows a metallic nature down to 50 K, below which a resistance upturn is observed.

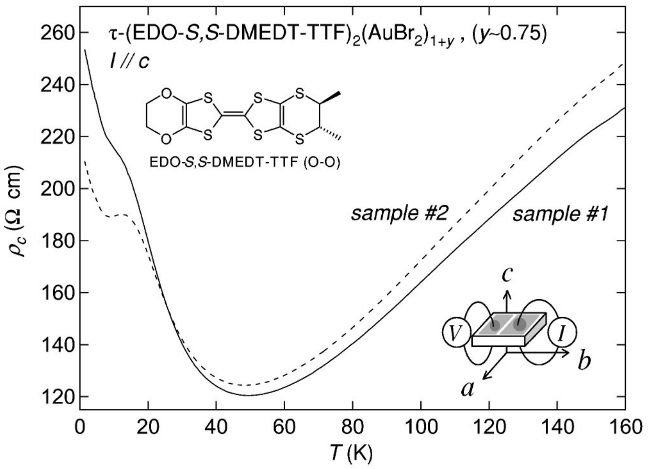

FIG. 2. Temperature dependence of interplane resistivity ρ_c of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y \sim 0.75$).

The field dependence of the magnetoresistance of the O-O salt for *I*, $B \| c$ at 0.48 K is shown in Fig. 3. Large negative magnetoresistance was also observed for $I \| c$ as well as for $B \| ab$.[2] Above 6 T, clear SdH oscillations were observed for both samples. The amplitude of the SdH oscillation is very large ($|\Delta\rho/\rho_0| \sim 30\%$ above 18 T) and the phase of the oscillation of both samples is reproducible. Furthermore, it is obvious that the weak oscillation is superimposed on the fundamental oscillation. Below 18 T, apparent hysteretic behavior is observed as was already reported for $B \| ab$.[2] However the range of the field, where the hysteresis is observed, is much wider for $B \| c$ than for $B \| ab$.[2]

Figure 4 shows the inverse field dependence of the SdH

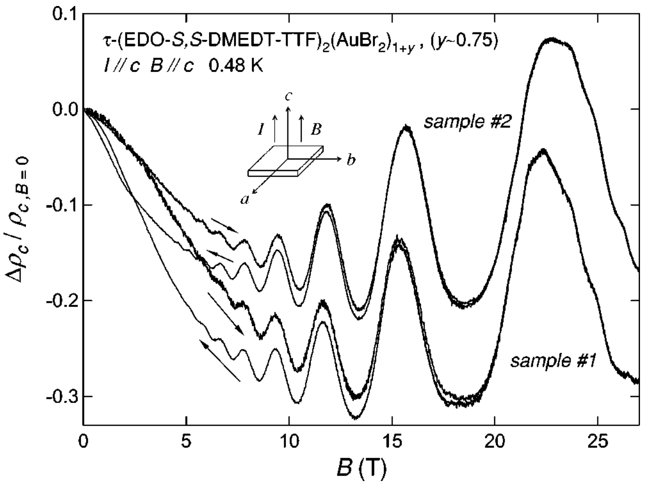

FIG. 3. Interplane resistivity ρ_c as a function of magnetic field *B*. The direction of the magnetic field is perpendicular to the conducting ab plane. The small oscillation ($F = 481$ T) is superimposed on the fundamental oscillation ($F = 50$ T).

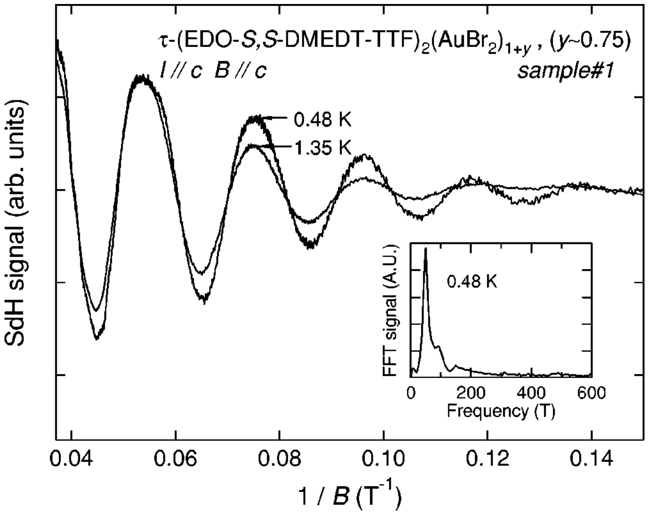

FIG. 4. The signal of Shubnikov–de Haas oscillations as a function of inverse magnetic field B^{-1} observed for τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$) at 0.48 K and 1.35 K. Inset shows the fast Fourier-transform spectrum for 0.48 K.

signals at 0.48 K and 1.35 K after subtracting each fitting function of a third degree polynomial. The frequency of SdH is found to be 50 T (fundamental) and 481 T from the data at 0.48 K for sample 1. These frequencies correspond to 0.66% and 6.1% of the FBZ, respectively. These values are inconsistent with the value of 12.5% calculated for $y\sim0.75$. From the data of the SdH signal amplitude, we can estimate the cyclotron effective mass m_c and the Dingle temperature T_D for the two-dimensional case.[9,10] These are estimated to be $m_c\sim1.6m_e$ for the 0.66% pocket and $3.5m_e$ for the 6.1% pocket, where m_e represents the free-electron mass, and $T_D=1.4$ K for sample 1. We measured the angular dependence of the SdH frequencies, and found the $\cos^{-1}\theta$ dependence (Fig. 5)

We examined the angular-dependent magnetoresistance (AMRO) for this salt (Fig. 6). The magnetic field was rotated in the ac plane. Some oscillations were observed, but these are not Kajita-Yamaji oscillations because the peak positions change with the field strength. These are SdH oscillations that change their frequency with the field rotation. For almost $B\|ab$, the peak effect was observed (see the inset of Fig. 6), which suggests the out-of-plane coherence.

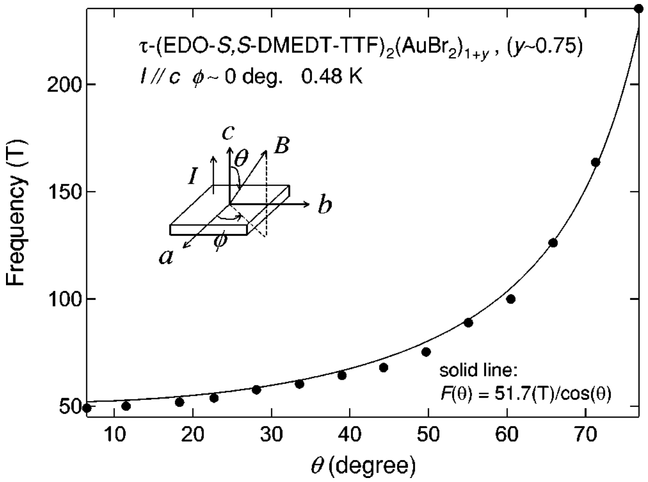

FIG. 5. The angular dependence of the frequencies of the Shubnikov–de Haas oscillations for τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$) at 0.48 K. It shows $\cos^{-1}\theta$ dependence that is expected for the cylindrical Fermi surface.

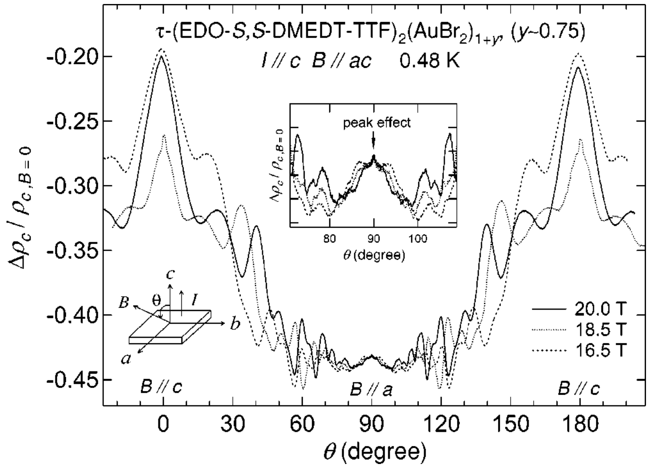

FIG. 6. The angular-dependent magnetoresistance (AMRO) of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$). There is no Kajita-Yamaji oscillation. For almost $B\|a$, the peak effect was observed.

We also studied the SdH effect for the other τ conductor, τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$) for $I,B\|c$ at 0.48 K (Fig. 7). The observed frequencies of the SdH were 175 T and 518 T, and almost the same as that reported by Storr *et al.* (186 T, 516 T).[7] The corresponding areas of the FS are 2.3% and 6.9% of the FBZ, which are compared with the value of 12.5% calculated for $y\sim0.75$.

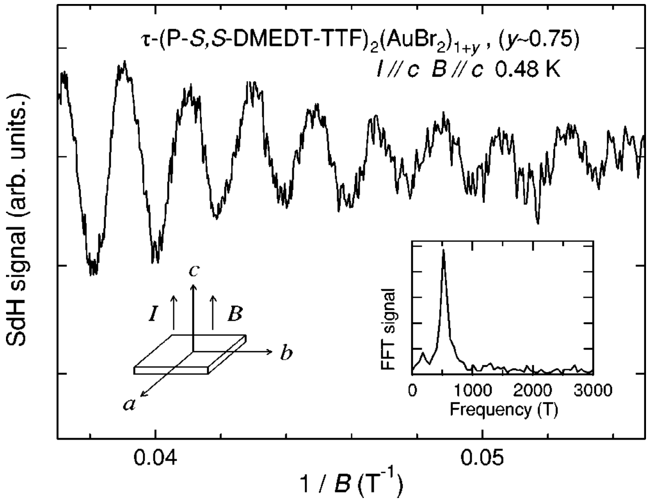

FIG. 7. The signal of Shubnikov–de Haas oscillations as a function of inverse magnetic field B^{-1} observed for τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$). Inset shows the fast Fourier-transform spectrum.

IV. DISCUSSION

We observed the giant SdH oscillations of τ-(O-O)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$) for $I,B\|c$ at 0.48 K and 1.35 K in high field above 6 T. The last peak ($\sim$25 T) is very close to the quantum limit that corresponds to the $N=2$ state. The reasons for such giant oscillations are high sample quality and the quasi-two dimensionality of the FS with extremely weak corrugation along the least conducting direction. Further, it is primarily due to the fact that the extremely small FS pocket is near the quantum limit. It seems that the conduction is mainly dominated by the carriers in a smaller FS pocket (0.66%) rather than that in a larger FS pocket (6.1%), probably because the cyclotron effective mass for a small FS pocket is $1.6m_e$ which is much smaller than $3.5m_e$ of the larger FS.

Though the ratio of in-plane and out-of-plane resistivity of this salt exceeds 10^4,[3] weak corrugation is non-negligible because we observed the peak effect in AMRO in this salt (Fig. 6). For simplicity, if we assume the FS's with the area of 0.66, 6.1% to be round, the ratio of the out-of-plane transfer integral t_c to the in-plane one t_a is $t_c/t_a=4.8\times10^{-4}$ and 1.3×10^{-3}, respectively. This estimation of the anisotropy is rather larger than that expected from the resistivity ratio. There is no Kajita-Yamaji oscillation in AMRO, so we could't get the information on the shape of the FS in the conducting plane. The angular dependence of the SdH frequencies obeys the $\cos^{-1}\theta$ dependence that proves the cylindrical two-dimensional FS (Fig. 5).

The estimated Dingle temperature is relatively low, which reveals unexpectedly good crystal quality, in spite of the fact that the disorder in anion layer and ethylenedioxy group is present,[3] that the resistance upturn takes place around 50 K, and that the residual resistivity ratio is around 1. The observed cyclotron effective mass is not as large as among other organic conductors. This result does not explain the large electronic specific-heat coefficient γ.

The observation of the SdH oscillations is evidence for the existence of the Fermi surface at low temperature, while the temperature dependence of the resistivity shows semiconducting behavior below 50 K. It is possible that the metallic state is realized only in magnetic field. However, at least above 22 K, the reflectance spectra show Drude-like dispersion which implies the metallic nature of this salt without external magnetic field.[6]

Arita *et al.* pointed out the importance of the almost zero dispersive regions in band structure near the Fermi energy in τ conductors, and proposed that the negative magnetoresistance is likely to occur from this flat band by ferromagnetic fluctuation.[11] Below 18 T, hysteretic behavior is obvious for $B\perp ab$ as well as for $B\|ab$ below 5 T.[2] This favors the ferromagnetic nature of the O-O salt. The magnetization curve also shows weak ferromagnetic behavior with small saturation magnetization ($1.0\times10^{-3}\mu_B$ / formula) below 20 K.[6]

The observed oscillations are composed of two independent frequencies, while the band calculation predicts a single FS. Both frequencies are different from the calculated FS area of 12.5% of the FBZ for $y\sim0.75$. If the anion composition y deviates from 0.75,[12] the area of the FS will change, and a small FS pocket may appear.[3] The fundamental oscillation corresponds to an extremely small FS with the area corresponding to only 0.66% of the FBZ. The other frequency of the SdH corresponding to 6.1% of the FBZ is clearly seen as an undulation in the fundamental oscillation. The idea to explain the coexistence of the two Fermi surfaces with different areas is the reconstruction of the FBZ at low temperature. If the FBZ is reconstructed by a kind of magnetic order or lattice modulation, the star-shaped Fermi surface is also reconstructed, and two Fermi surfaces might appear. However, the ^{1}H-NMR measurement[13] and the anisotropy of the static susceptibility do not show any clear evidence of the long-range magnetic order. Also, no crystal structural change in low temperature has been detected in the previous study.[14]

We also observed the SdH oscillations in the other τ-type conductor, τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$). The present result is almost the same as that previously reported by Storr *et al.*[7] The result shows the existence of two Fermi surfaces for this salt, while the band calculation predicts a single star-shaped FS almost the same as the O-O salt. Recently, we measured the static susceptibility using a large single crystal of τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ and observed clear anisotropy below $T_{M-I}=11$ K.[15] In ^{1}H-NMR measurement, the spin-lattice relaxation rate T_1^{-1} starts to decrease below about T_{M-I},[13] and the linewidth of ^{1}H-NMR of this salt increases rapidly below $\sim$30 K.[13] Furthermore, we confirmed that the linewidth of the ^{1}H-NMR in low temperature doesn't change with external field in preliminary study. It suggests the occurrence of the magnetic order below T_{M-I}. Therefore, the existence of the two FS's is expected to be explained by the reconstruction of the FS by the magnetic order for the N-N salt.

There are similarities between the O-O and N-N salts; at low temperature, the resistivity becomes semiconducting and large negative magnetoresistance appears, and then the SdH oscillations are observed. It is likely that the metallic ground state is achieved by applying the external magnetic field. On the other hand, the switching of magnetoresistance is observed only in the O-O salt,[2] and antiferromagnetic order is only in the N-N salt.

In conclusion, we observed SdH oscillations in two types of τ conductors, τ-(O-O)$_2$(AuBr$_2$)$_{1+y}$ and τ-(N-N)$_2$(AuBr$_2$)$_{1+y}$ ($y\sim0.75$). We have observed a large SdH oscillation in the O-O salt, which is associated with an extremely small FS (0.6% of the FBZ) and near the quantum limit. The observed frequencies of the SdH oscillations are inconsistent with the previous band calculation for both salts. This contradiction may be explained by the deviation of the anion composition y and/or the reconstruction of the FS.

ACKNOWLEDGMENTS

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