Symmetry Change in the Angular Dependence of Magnetoresistance of the Two-Dimensional Organic Conductor, τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75)$

Harukazu YOSHINO*, Koji IIMURA, Takahiko SASAKI[1], Akihiro ODA,
G. C. PAPAVASSILIOU[2] and Keizo MURATA

*Department of Material Science, Graduate School of Science, Osaka City University,
Sumiyoshi-ku, Osaka 558-8585*
[1] *Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577*
[2] *Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
Athens, Greece 116/35*

Angular dependence of magnetoresistivity, $\rho_c(\phi)$, of a quasi-two-dimensional organic conductor, τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75)$, where EDO-S,S-DMEDT-TTF is ethylenedioxy-S,S-dimethylethylenedithio-tetrathiafulvalene, was measured for the magnetic field and the electrical current parallel and perpendicular to the most conducting ab plane. The magnetoresistance is negative in the semiconducting range below about 50 K. It was found that the period of $\rho_c(\phi)$ changes from 90° at 5.0 T to 180° at 0.5 T and the principal axis of $\rho_c(\phi)$ at 0.5 T depends on the field-orientation at 5.0 T. The change in the period and the principal axis of $\rho_c(\phi)$ is discussed in terms of formation and reorientation of magnetic domains.

§1. Introduction

τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75)$ is an quasi-two-dimensional (Q2D) conducting salt which consists of an unsymmetrical organic donor, EDO-S, S-DMEDT-TTF (ethylenedioxy-S, S-dimethylethylenedithio-tetrathiafulvalene) and an
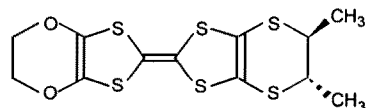
EDO-S, S-DMEDT-TTF

inorganic linear anion, AuBr$_2^-$. The salt is crystallized into the tetragonal system, space group I4$_1$22 and the packing of the donor molecules within the conducting layers ($\|ab$) has the four-fold symmetry.[1] Each conducting layer made of 2:1 mixed packing of donors and anions is sandwiched by insulating layers made of only anions which correspond to the composition, y. Elemental analysis gives that y is about 0.75.[1] Then this τ-type crystal structure gives cross-shaped 2D Fermi surface by tight-binding calculation.[1] This is consistent with metallic electrical resistivity measured within the ab plane.[1]

Recently, Murata *et al.*[2,3] reported the change in periodicity of the angular dependence of the c-axis magnetoresistance (MR), $\rho_c(\phi)$ for the magnetic field within the ab plane by varying the magnitude of the magnetic field and/or temperature[3] for the AuBr$_2$ salt. Namely, the $\rho_c(\phi)$ has the period of 180° at 1.1 K and 1.5 T, while

the period is 90° at higher temperature and/or at higher magnetic field as is expected from the four-fold symmetry of the molecular packing. This suggests that the AuBr$_2$ salt is in the two-fold symmetry state at least at 1.1 K and below 1.5 T. If the lowering of the symmetry is due to a kind of phase transition (i.e. the M-I transition at about 50 K), it is difficult to observe the two-fold symmetry by measuring macroscopic properties because, in general, the lowering of the crystal symmetry produces the domain/polycrystalline structure. In this paper the $\rho_c(\phi)$ is studied to elucidate the condition which enables us to detect the two-fold symmetry phase by measuring the MR at low temperature. The field and angular dependence of the MR is also studied up to 27 T to get more insight into the electronic state and origin of the negative MR.

§2. Experimental

The crystals were obtained by a usual electrochemical oxidation described elsewhere.[1] The appearance of the crystals is black square plate-like and the thinnest along the most resistive c-axis. The size of the crystals is $0.88 \times 0.63 \times 0.038$ and $0.75 \times 0.75 \times 0.18$ mm^3 for samples 1 and 2, respectively. The MR measurement up to 5 T was carried out at Osaka City University (OCU). The 23- and 27-T hybrid magnets were used for the measurement above 5 T at Institute for Materials Research (IMR) at Tohoku University. The MR was measured by a dc four-probe method for the electrical current parallel to the c-axis. Two pairs of annealed Au wires (10 μm in diameter) were attached, by using Au paste, to the opposite crystal surfaces parallel to the ab plane which

---

were previously evaporated by Au. The magnetic field was rotated within the *ab* plane. Thus the magnetic field was kept perpendicular to the electrical current and the angular dependence of the MR is considered to represent the anisotropy of the motion of carriers within the *ab* plane.

§3. Results and Discussion

Figure 1 shows the temperature dependence of the *c*-axis electrical resistivity, ρ_c measured for the samples 1 and 2. The magnitude of the electrical conductivity along the *c*-axis is about 3.1×10^{-3} and 3.9×10^{-3} S·cm^{-1} at 300 K for the samples, respectively. The magnitude of the conductivity is almost the same as that previously reported. [1] The temperature dependence of ρ_c is metallic but turns to semiconducting at about 50 K for both samples. The ρ_c curves in Fig. 1 are very similar to each other. Papavassiliou *et al.* [1] pointed out the occurrence of a weak localization as the origin of the semiconducting behavior of the electrical resistivity of the AuBr$_2$ salt. The overall temperature dependence of the ρ_c in Fig. 1 is similar to that of the ρ_{ab} in ref. 1. Thus, the ρ_c is considered to be a good probe into the motion of the carriers within the most conducting *ab* plane in spite of the strong 2D character of the electronic system.

The MR measurement at and below 5.0 T was carried out at 1.3 K in the semiconducting regime. Figure 2 shows the typical data obtained for the sample 1. The normalized angular dependence of the MR, $\Delta\rho_c(\phi)/\rho_{c,B=0}$ $(\rho_{c,B=0} = 2.5 \times 10^2\,\Omega\cdot\text{cm})$ at 5.0 T is shown in Fig. 2(a) and that at 0.5 T in Fig. 2(b), respectively. Negative magnetoresistivity previously reported was observed within the magnetic field range in the present study.

At 5.0 T, $\Delta\rho_c(\phi)/\rho_{c,B=0}$ shows no hysteretic behavior and has maxima at 0°, 90° and so on. The period of 90° is in accordance with the crystal symmetry within the *ab* plane examined at room temperature. The curve #1 in Fig. 2(b) shows the virgin data obtained before the field sweep above 0.5 T. The curves #2–4 in Fig. 2(b) were obtained after the field sweep from 5.0 to 0.5 T at 0°, 90° and 45°, respectively. The curves #2 and #3 have a period of 180°, though the phase between them is different from each other by 90°. The curve #4 is almost flat and very similar to #1. No distinct hysteresis for the angular sweep was observed for the curves in Fig. 2.

Figure 3 shows the $\Delta\rho_c(\phi)/\rho_{c,B=0}$ for the sample 1 at 1.3 K and 1.6 T. The curves #2–4 in Fig. 3 were obtained in the experimental conditions similar to those in Fig. 2(b), namely after the field sweep from 5.0 T to 1.6 T at 0°, 90° and 45°, respectively. One can find distinct hysteresis of the MR for the angular sweep in Fig. 3. This hysteresis suggests a kind of ferromagnetic nature of this material.

The 180° periodicity of the curves #2 and #3 in Fig. 2(b) implies that the band structure in the magnetic phase has a two-fold symmetry around the *c*-axis, while the crystal structure at room temperature has the four-fold symmetry. In general, a single crystal of a material becomes polycrystalline or a multidomain crystal if the crystal symmetry is broken when a phase transition occ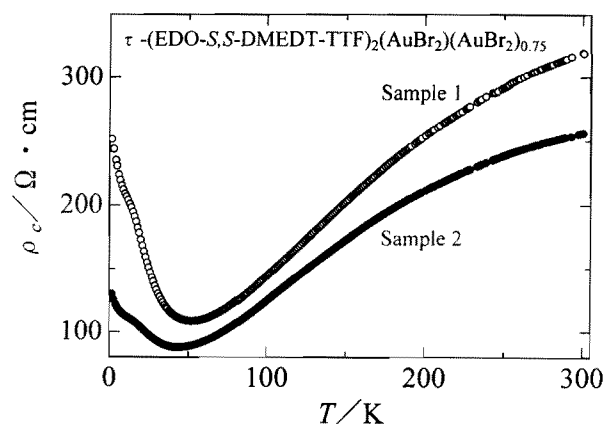urs and plural kinds of orientations of the low symmetry domains are expected. If this is the case with the AuBr$_2$ salt, namely, the salt undergoes a phase transition from the four-fold symmetry phase at higher temperature to the two-fold symmetry phase at lower temperature, do-

Fig. 1. Temperature dependence of the *c*-axis resistivity of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75$, samples 1 and 2).
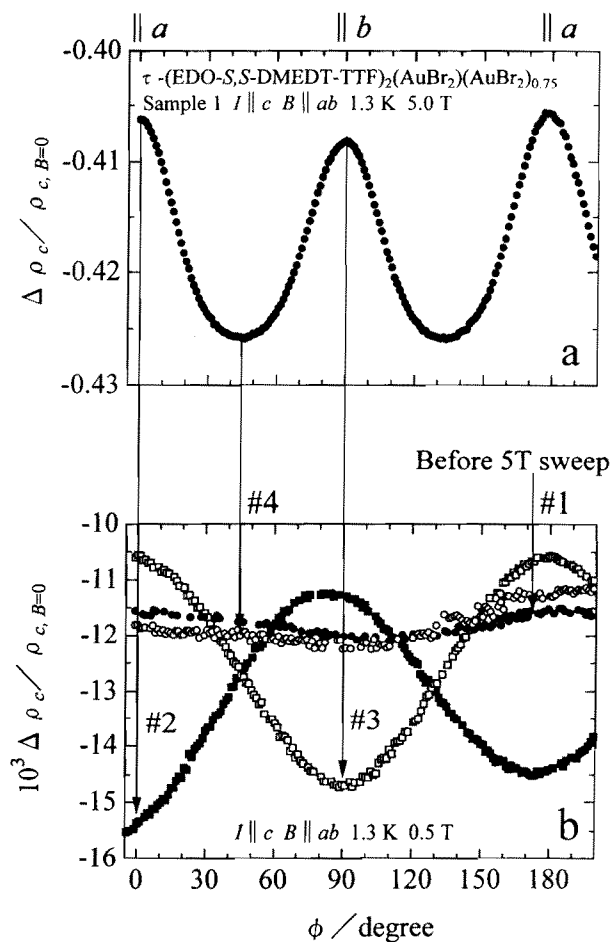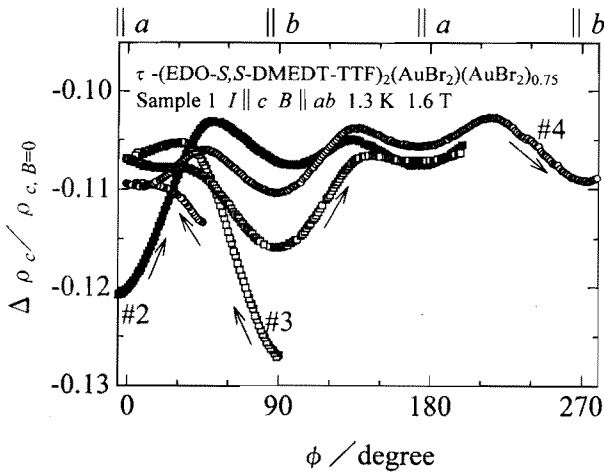

Fig. 2. Angular dependence of the magnetoresistance of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75$, sample 1) at 1.3 K for $I\|c$ and $B\|ab$ at 5.0 T (a) and at 0.5 T (b) before the field sweep above 0.5 T (#1) and after the field sweep from 5.0 T at 0° (#2), 90° (#3) and 45° (#4), respectively. The magnetoresistance is normalized by the resistivity $(2.5 \times 10^2\,\Omega\cdot\text{cm})$ at $B = 0\,\text{T}$.

Fig. 3. Angular dependence of the magnetoresistance of τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75$, sample 1) at 1.3 K for $I\|c$ and $B\|ab$ at 1.6 T after the field sweep from 5.0 T at 0° (#2), 90° (#3) and 45° (#4), respectively. The magnetoresistance is normalized by the resistivity $(2.5 \times 10^2\ \Omega\cdot\text{cm})$ at $B = 0$ T.

Fig. 4. Angular dependence of the magnetoresistance of τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75$, sample 1) for $I\|c$ and $B\|ab$ at 0.5 K and at 7.5 T (open circles), 11 T (closed circles), 15 T (open squares) and 20 T (closed squares), respectively. The magnetoresistance is normalized by the resistivity $(3.8 \times 10^2\ \Omega\cdot\text{cm})$ at $B = 0$ T.

main structure appears, since at least two kinds of orientations are possible for the lower symmetry domain. The hysteretic behavior of the MR suggests that the origin of the possible phase transition and, therefore, the lower symmetry domain are magnetic.

When the crystal of the AuBr$_2$ salt is cooled below the possible phase transition temperature without any magnetic field, the multidomain structure is considered to appear. The angular dependence of the MR measured for the polycrystalline sample with the field weak enough not to move domain walls is expected to be flat as is observed for the curve #1 in Fig. 2(b). On the other hand, the 180° period of the curves #2 and #3 suggests that the magnetic domains, each of which has the two-fold symmetry, are aligned along the a- and b-axes, respectively, by applying the magnetic field of 5.0 T. The 90° period of $\Delta\rho_c(\phi)/\rho_{c,B=0}$ at 5.0 T in Fig. 2(a) is the evidence that the magnetic field of 5.0 T is strong enough to align the magnetic domains along the crystallographically equivalent directions, $+a$, $+b$, $-a$ and $-b$, alternatively. Once the domains are aligned along these directions, they cannot be realigned by the low magnetic field such as 0.5 T. This explains the 180° period of the curves #2 and #3 without hysteretic behavior and suggests that the a- and b-axes are equivalently the easy axes for the magnetization within the ab plane. If it is the case, the same amount of two kinds of domains, whose spontaneous magnetization is parallel to the a- and b-axes, respectively, are considered to exist in the sample after the magnetic field of 5.0 T was applied along the $a + b$ direction (45° in Fig. 2(b)). This multidomain structure for #4 is artificial, while that for #1 is natural. Both the multidomain structures give almost the same flat angular dependence of the MR, because two kinds of MR components whose phases are shifted by 90° from each other are considered to contribute equally.

Figure 4 shows the $\Delta\rho_c(\phi)/\rho_{c,B=0}$ $(\rho_{c,B=0} = 2.6 \times 10^2\ \Omega\cdot\text{cm})$ of the AuBr$_2$ salt above 5 T measured for the sample 1 at 0.5 K at IMR. The 90° period at 5.0 T at
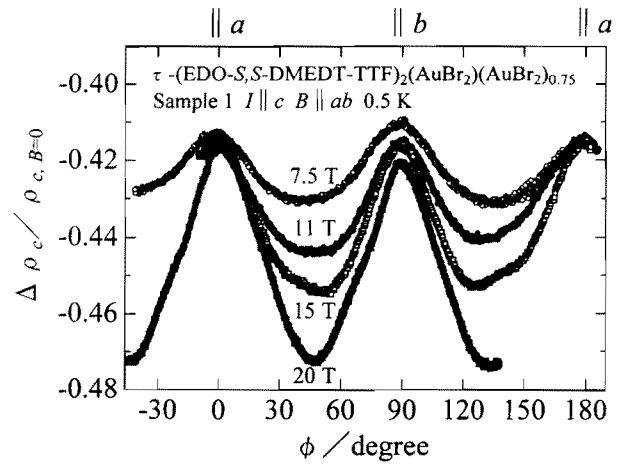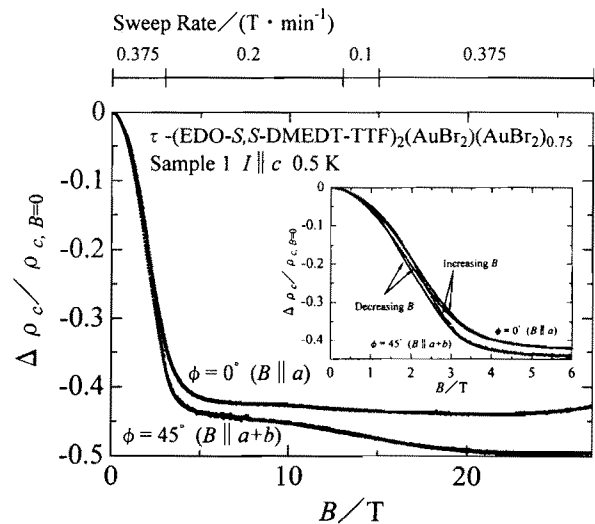

Fig. 5. Field dependence of the magnetoresistance of τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, $(y \sim 0.75$, sample 1) for $I\|c$ at 0.5 K with increasing and decreasing the magnetic field. The direction of the magnetic field is 0° ($\|a$) and 45° ($\|a + b$), respectively. The inset shows the same data in an enlarged scale to display the hysteresis clearly. The magnetoresistance is normalized by the resistivity $(3.8 \times 10^2\ \Omega\cdot\text{cm})$ at $B = 0$ T.

1.3 K is still observed. The MR is almost independent of the magnitude of the magnetic field at 0° ($\|a$) and 90° ($\|b$), while, at the angles off from the crystal axes, the MR continues to decrease with increasing the magnetic field. This is clearly shown as the field dependence of the MR in Fig. 5 obtained for the sample 1 but at another run at IMR. From 0 T, the MR rapidly decreases with increasing the magnetic field up to about 5 T at 0° ($\|a$) and 45° ($\|a + b$), respectively. Above 5 T, the MR is almost independent of the magnetic field at 0°, while gradually decreases at 45°. Finally above 25 T, the MR shows slight upturn both at 0° and 45°. With decreasing the magnetic field, the MR shows hysteretic behavior below 5 T as in the inset in Fig. 5. The zero field value of

ρ_c is, however, the same before and after the field sweep. Almost the same behavior of the MR was observed for the sample 2 (not shown).

The sweep rate of the magnetic field is presented at the top of Fig. 5 and that in the hysteresis region was 0.375 T/min. This hysteresis was also observed between 0 and 5 T at 1.3 K with the sweep rate of 0.167 T/min at OCU.

Since the AuBr$_2$ salt is considered to be weak ferromagnetic, the negative MR is probably due to the ordering of thermally fluctuating spins by the strong magnetic field as is often observed for the ferromagnets. It is, however, worth noting that two kinds of disorders, concerning the position of vacancy at the anion site and the orientation of the ethylenedioxy group of the donor molecule, are recognized at room temperature for the AuBr$_2$ salt.[1] Though the relation between these disorders and the negative MR as well as the semiconducting behavior of the resistivity is not clear, Papavassiliou *et al.*[4] pointed out the possibility of the weak localization in the AuBr$_2$ salt based on the similarity of the field dependence of the MR ($B \| c$ and $I \| ab$), which has negative slope at least up to 15 T at 2.1 K, to those of other organic compounds showing negative MR.

§4. Conclusion

The angular dependence of the MR of τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, ($y \sim 0.75$) was investigated for the electrical current along the c-axis and the magnetic field within the ab plane at 1.3 K ($B \leq 5.0$ T) and 0.5 K ($B \leq 27$ T). The period of $\Delta\rho_c(\phi)/\rho_{c,B=0}$ is 90° and no distinct hysteretic behavior was observed above 5 T. It was found that the shape of the data curves of $\Delta\rho_c(\phi)/\rho_{c,B=0}$ depends on the field treatment at higher magnetic field. It was suggested that the symmetry of the band structure around the k_c-axis is twofold from the 180° period of the $\Delta\rho_c(\phi)/\rho_{c,B=0}$ at 0.5 T. The AuBr$_2$ salt is considered to be in a kind of ferromagnetic state at least at low temperature. It was shown that the change in the periodicity of $\Delta\rho_c(\phi)/\rho_{c,B=0}$ at 0.5 T is explained by considering the realignment of the magnetic domains.

The magnetization is considered to be very small as is expected for weak ferromagnets, because the orientation of the samples, which were held by annealed soft Au wires, were not disturbed by the magnetic field even at 20 T at 0.5 K. The weak ferro-

magnetic phases have been reported for a few organic conductors which undergoes an antiferromagnetic transition at low temperature. Welp *et al.*[5] reported that a Q2D conductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene) undergoes an antiferromagnetic transition at about 45 K and shows the weak ferromagnetic behavior of dc magnetization curve below 22 K. Tamura *et al.* reported detailed studies on the weak ferromagnetic behavior of (DMe-DCNQI-d_8)$_2$Cu[6, 7] (T_N = 9.0 K) and (DBr-DCNQI)$_2$Cu[7] (T_N = 18.0 K) below the Néel temperature, T_N, where DMe-DCNQI-d_8 and DBr-DCNQI are fully deuterated 2,5-N, N'-dicyanoquinonediimine and 2,5-dibromo-N, N'-dicyanoquinonediimine, respectively. The present authors, however, could not find any MR studies on the BEDT-TTF and DCNQI salts similar to the present study. Thus τ-(EDO-S, S-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$, ($y \sim 0.75$) is probably the first example of the organic conductor whose magnetic domain structure was controlled by the field treatment and was detected by measuring the angular dependence of the MR.

Acknowledgements

1) G. C. Papavassiliou, D. J. Lagouvardos, J. S. Zambounis, A. Terzis, C. P. Raptopoulou, K. Murata, N. Shirakawa, L. Ducasse and P. Delhaes: Mol. Cryst. Liq. Cryst. **285** (1996) 83.
2) K. Murata, N. Shirakawa, H. Yoshino and Y. Tsubaki: Synth. Met. **86** (1997) 2021.
3) K. Murata, H. Yoshino, Y. Tsubaki and G. C. Papavassiliou: Synth. Met. **94/1** (1998) 69.
4) G. C. Papavassiliou, D. J. Lagouvardos, I. Koutselas, K. Murata, A. Graja, I. Olejniczak, J. S. Zambounis, L. Ducasse and J. P. Ulmet: Synth. Met. **86** (1997) 2043.
5) U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams and M. Hitsman: Phys. Rev. Lett. **69** (1992) 840.
6) M. Tamura, H. Sawa, S. Aonuma, R. Kato, M. Kinoshita and H. Kobayashi: J. Phys. Soc. Jpn. **63** (1993) 1470.
7) M. Tamura, H. Sawa, Y. Kashimura, S. Aonuma, R. Kato and M. Kinoshita: J. Phys. Soc. Jpn. **63** (1994) 425.