

Field-Induced Symmetry Change in the Magnetoresistance of Two-Dimensional τ -Type Organic Conductors

H. Yoshino^A, K. Murata^A, T. Konoike^A, T. Sasaki^B and G. C. Papavassiliou^C

^ADepartment of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

^BInstitute for Materials Research, Tohoku university, Aoba-ku, Sendai 980-8577, Japan

^CTheoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens 116-35, Greece

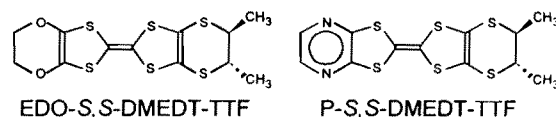
Magnetoresistance of two-dimensional organic conductors, τ -(EDO-S,S-DMEDT-TTF)₂(X)(X)_y and τ -(P-S,S-DMEDT-TTF)₂(X)(X)_y, (X=AuBr₂, I₃ and $y \sim 0.75$) is investigated. Tight-binding band calculation predicts crossed-shape Fermi surface with four-fold symmetry within the most conducting *ab* plane of these organic salts. All the salts undergo metal to semiconductor transition between 10 and 65 K, respectively. We measured angular dependence of the magnetoresistance, $\rho_c(\phi)$, for $I \parallel c$ and $B \parallel ab$ in the semiconducting region. It was found that the symmetry of $\rho_c(\phi)$ of τ -(EDO-S,S-DMEDT-TTF)₂(AuBr₂)(AuBr₂)_y, ($y \sim 0.75$) switches from four-fold at 5 T to two-fold at 0.5 T depending on field treatment. This novel phenomenon is interpreted by formation and alignment of magnetic domains with weak spontaneous magnetization. To reveal the low temperature state of the AuBr₂ salt, high field study up to 28 T and comparative ones for the other salts were carried out.

Key words: Organic conductor, magnetoresistance, weak ferromagnetism

Introduction

The most important character of a series of τ -type organic conductors is the packing pattern of donor molecules and anions within the conducting layer which is composed of 2:1 planer donors and linear anions[1]. Each anion is surrounded by four donors and neighboring donors contact with each other with dihedral angle of 90°. Each conducting layer is sandwiched by insulating anion layers corresponding to the composition $y \sim 0.75$. Almost 1/4 of the anion sites in the insulating layer are random vacancies. Tight-binding band calculation for the conducting layer gives *tetragonal* crossed shape Fermi surface for $y \sim 0.75$.

Among the τ -type conductors, the salts based on EDO-S,S-DMEDT-TTF and P-S,S-DMEDT-TTF have been studied extensively.



For simplicity these donors are denoted OO and NN, respectively, below. Temperature dependence of the electrical resistivity of τ -(OO)₂(AuBr₂)(AuBr₂)_y, (OO-AuBr₂), τ -(OO)₂(I₃)(I₃)_y, (OO-I₃) and τ -(NN)₂(AuBr₂)(AuBr₂)_y, (NN-AuBr₂) is metallic below room temperature, respectively, though some samples show semiconducting behavior[2-4]. This metallic

behavior is consistent with the band calculation but each salt undergoes metal-to-semiconductor "transition" well below the liquid N₂ temperature. The origin of the transition is unclear up to now. In this paper, angular dependence of the magnetoresistance of the salts is studied to get more insight into the mechanism of the phase transition.

Experimental

The angular and magnetic field dependence of magnetoresistance (MR) was measured for $I \perp ab$ and $B \parallel ab$ in the semiconducting phase of each salt. This is the best orientation of the fields to detect possible change in the band symmetry within the most conducting ab plane. Detail of experimental procedure is described in [5].

Results and discussion

Temperature dependence of c -axis resistivity which is normalized at 300 K is shown in Fig.1 for each salt.

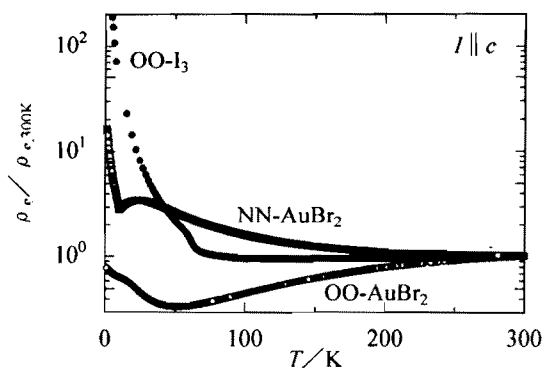


Fig.1 Temperature dependence of the electrical resistivity of OO-AuBr₂, OO-I₃ and NN-AuBr₂.

Below room temperature OO-AuBr₂ and OO-I₃ show metallic temperature dependence and, after having broad minimum, their resistivity shows rather rapid increase at about 40 and 60 K, respectively. On the other hand, the resistivity of NN-AuBr₂ is

semiconducting below room temperature and turns to metallic below 50 K. The M-I transition temperature of NN-AuBr₂ is about 10 K.

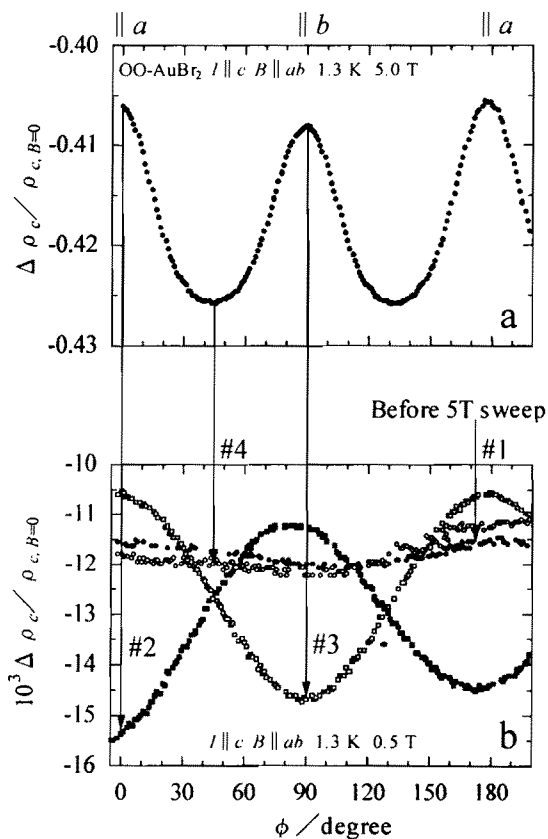


Fig. 2 Angular dependence of the normalized magnetoresistance of OO-AuBr₂ at 1.3 K at (a) 5.0 T and (b) 0.5 T.

The normalized angular dependence of the magnetoresistance, $\Delta\rho_c(\phi)/\rho_{c,B=0}$ ($\rho_{c,B=0} = 2.5 \times 10^2 \Omega \cdot \text{cm}$) at 1.3 K and 5.0 T is shown in Fig. 2(a) and that at 0.5 T in Fig. 2(b), respectively. 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.

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 occurs 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, domain 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.

The field dependence of ρ_c of OO- AuBr_2 is shown in Fig. 3. From 0 T, the MR rapidly decreases with

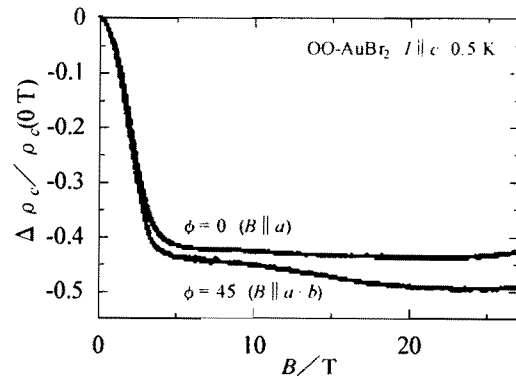


Fig. 3 Magnetic field dependence of the c -axis magnetoresistance of OO- AuBr_2 at 0.5 K.

increasing the magnetic field up to about 5 T at 0° ($\parallel a$) and 45° ($\parallel a+b$), 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. If the negative MR originates from the alignment of the possible magnetic domains, the saturation of the negative MR is consistent with the

explanation of the 90° period of $\Delta\rho_c(\phi)/\rho_{c, B=0}$ at 5.0 T in Fig. 2(a).

The angular dependence of the MR is also measured for OO-I₃ and NN-AuBr₂ to find whether the symmetry change occurs or not in the systems similar to OO-AuBr₂. The result obtained at 1.2 K and 5.0 T is shown

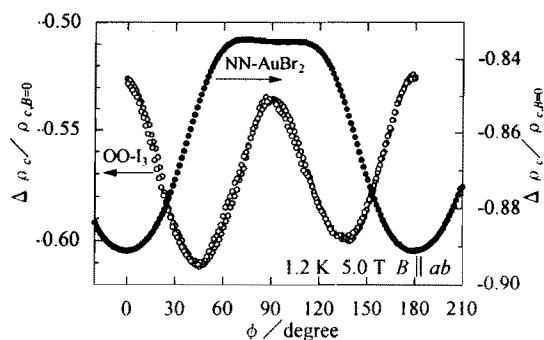


Fig. 4 The angular dependence of the magnetoresistance of OO-I₃ and NN-AuBr₂ at 1.2 K and 5.0 T. The angle, ϕ , is measured from a crystal edge.

in Fig. 4. The negative magnetoresistance was also observed for both the salts as well as OO-AuBr₂. This strongly suggests the close relation between the τ -type structure and negative MR. It must be also noted that weak localization due to one or both of the disorders concerning six-membered rings of the donors and anion vacancies may explain the metal to the semiconducting transition and the negative MR in the two-dimensional salts on the basis of two-dimensional weak localization[2].

The period of $\Delta\rho_c(\phi)/\rho_{c, B=0}$ of NN-AuBr₂ is 180° , while that of OO-I₃ is 90° . The space group of the OO-I₃ and NN-AuBr₂ is I4₁22 as same as OO-AuBr₂ at room temperature[1]. Thus the 180° periodicity for NN-AuBr₂ suggests that this salt is in a lower symmetry state in the semiconducting temperature region than that expected from the room temperature crystal structure. The negative MR as well as its 180° period remind us of the low-field state of OO-AuBr₂.

On the other hand, no clear 180° period has been

observed for OO-I₃ at lower fields at present and this is in contrast with the behavior of the MR of OO-AuBr₂ as noted above. The possible weak spontaneous magnetization of OO-I₃ is considered to be larger than that of OO-AuBr₂, because the metal to semiconducting transition temperature of the former (about 60 K) is higher than that of the latter (30-40 K).

In conclusion, a novel group of isostructural τ -type conductors, OO-AuBr₂, OO-I₃ and NN-AuBr₂ are investigated by measuring angular and magnetic field dependencies of magnetoresistance to reveal the nature of their semiconducting phase. Change in the period of the angular dependence of the MR from 90° at 5.0 T to 180° at 0.5 T has been found for OO-AuBr₂ at 1.3 K. This phenomenon is explained by assuming weak ferromagnetic domains with two-fold symmetry. Negative MR was also observed for OO-I₃ and NN-AuBr₂ but these salts show only 180° and 90° period of the angular dependence below 5.0 T, respectively.

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