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Is the Two Dimensional Organic Conductor, τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$ Clean or Dirty?

T. Nakanishi,[1] S. Yasuzuka,[1] M. Teramura,[1] L. Li,[1] T. Fujimoto,[1] T. Sasaki,[2] T. Konoike,[3] T. Terashima,[3] S. Uji,[3] Y. Nogami,[4] G. C. Anyfantis,[5] G. C. Papavassiliou,[5] and Keizo Murata[1]

[1]*Dep't. of Mat. Sci., Grad. School of Sci., Osaka City Univ., Osaka 558-8585, Japan*
[2] *Inst. for Mat. Res., Tohoku Univ., Sendai 980-8577, Japan*
[3] *National Inst. for Mat. Sci., Tsukuba, Ibaraki 305-0003, Japan*
[4] *Grad. School of Natural Science. & Tech., Okayama Univ., Okayama 700-8530, Japan*
[5]*Theor. and Phys., Chem. Inst., National Hellenic Res. Found., Athens, 116/35, Greece*

The transport properties of organic τ-type conductors seem to be very clean as well as very dirty depending on what we observe. To clarify this problem, we studied temperature and magnetic field dependence of resistivity, $\rho(T, B)$, in τ-(EDO-S,S-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$. The properties that favor "probably dirty" are: i) stepwise $\rho_a(T)$ increase below 20 K, which is suppressed by magnetic field, and ii) contrasted difference in $\rho(T)$ as well as magnetization $M(T)$ between field cooled (FC) and zero field cooled (ZFC). On the other hand, Shubnikov de Haas oscillations with very low Dingle temperature (T_D = 1.5 K) are typical of clean system. Based on these observations, we conclude this system changes from "dirty" to "clean" system by increase of magnetic field.
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1. INTRODUCTION

In the highly correlated system, the magnetic state is strongly concerned with their transport phenomena as seen in SDW, Mott insulator, high temperature superconductor and colossal magnetoresistance effect. A series of τ-type organic conductors such as τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$ (AuBr$_2$)$_{1+y}$ has provided remarkable features related to magnetism, where EDO-*S*,*S*-DMEDT-TTF is ethylenedioxy-*S*,*S*-dimethylethylenedithio-tetrathiaflcalene. Examples include huge negative magnetoresistance[1], memory effect in angular dependence of magnetoresistance[2], and weak ferromagnetic magnetization[3]. In the physics of τ-type conductors, the problems is the interplay between the transport and the spin structure, and how the spin and carriers responded to magnetic fields can vary from a system to another. However τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ has shown strong sample dependence in transport properties. The variation of y influencing the filling factor was small[4]. However, it was found that Cl, which is in the solvent during crystal growth as CH_2Cl_2, was introduced in to Br-site in AuBr$_2$-salt, the amount of which varies among samples. Here, we focus on the new τ-type conductor τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$ which is analogue to τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$. The AuCl$_2$-salt is free from halogen mixture from solvent and is expected to be much free from sample dependence observed in resistivity. In order to clarify the low temperature state of τ-type conductor and the effect of magnetism to transport properties, we measured resistance, magnetoresistance and magnetization. For the transport properties, we found that $\rho(T)$ shows a steep rise anomaly below T_C = 20 K and there is a difference in $\rho(T, B)$ between Field-Cool (FC) and Zero-Field-Cool (ZFC). Difference between FC and ZFC is also observed in the temperature dependence of magnetization, suggesting the occurrence of the spin-glass, which is associated with "dirty" nature. For magnetoresistance measurements, Shubnikov de Haas oscillations with very low Dingle temperature (T_D = 1.5 K), which favors "clean", are observed. These observations suggest that the present system changes from "dirty" to "clean" by the increase of magnetic field.

2. EXPERIMENT

The single crystals of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$ (y~0.75) were obtained by usual electrochemical oxidation method described elsewhere[5]. The electric contacts were made with Au wires, and carbon paste in the Au-evaporated surface on the crystal. For the in-plane (I // a) resistance and magnetoresistance study, four terminals were on the same side, and for the out-of-plane (I // c) study, the sample was sandwiched with pairs of voltage and current contacts. Magnetic field was applied perpendicular to the *a-b* plane up to 5 T and 27 T for magnetoresistance and Shubnikov de Haas measurements, respectively and the direction is tilted from normal to parallel to the plane. Dc magnetization for 10.8 mg of collected non-oriented crystals was measured by using SQUID magnetometer up to 5 T.

3. RESULTS AND DISCUSSION

Temperature dependence of in- and out-of-plane resistivities is shown in Fig. 1. The anisotropy estimated from these resistivity is about 10^2~10^3 at room temperature. In high temperature region, both curves show metallic feature and the out-of-plane resistivity gradually changes from metal to insulator around 50 K similarly to AuBr$_2$-salt. At T_C = 20 K these resistivities show the steep rise anomaly without hysteresis. Finally, this system becomes insulator with anomaly around 10 K. The abrupt increase of resistivities below 20 K may *not* be due to CDW transition, since the satellite spots were *not* observed in our X-ray diffraction experiment down to 9 K. However, non-linear transport is

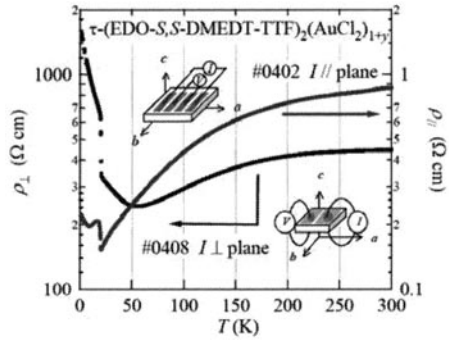

Fig. 1 Temperature dependence of resistivity of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$.

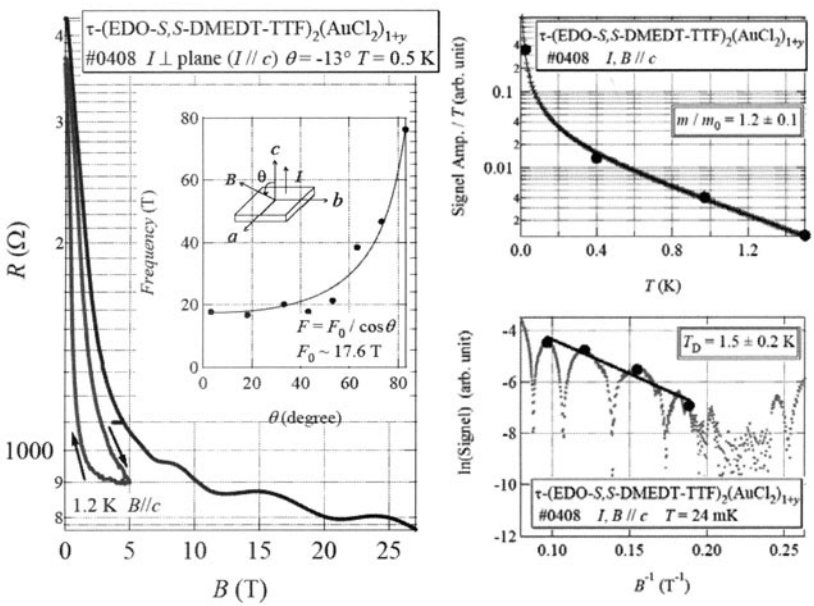

Fig. 2 (a) SdH oscillations of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$.
(b) mass plot. (c) Dingle plot.

observed below 1.13 K in the preliminary experiment.

Magnetoresistance up to 27 T is shown in Fig. 2 (a). Large negative magnetoresistance reaching about 80 % at high field with hysteresis is observed like $AuBr_2$-salt. The rapid decrease of resistance takes place under low field region and the rate of decrease becomes slow above 5 T. In higher field region only one and extremely slow frequency (17.6 T) of Shubnikov de Haas oscillations is observed, although $AuBr_2$-salt shows two Fermi pockets[6]. The frequency corresponds to 0.2 % of the First Brillouin Zone. The observation clarified that the ground state of this salt in high field region is metal nevertheless the temperature dependence of resistivity under zero field shows insulating behavior. The effective cyclotron mass and the Dingle temperature are shown in Fig. 2 (b) and (c), respectively. It is notable that the Dingle temperature is very low (T_D = 1.5 K) meaning that this system is very clean.

Temperature dependence of magnetoresistance at several fields is shown in Fig. 3 (a). The abrupt increase is suppressed by applying magnetic field and vanishes at 5 T. So the curve for 5 T has no anomaly around T_C that reflect in only intrinsic band structure. T_C slightly shifts to higher temperature by increasing field, which is also against CDW. In organic conductors it is the *first* observation that the irreversible behavior of magnetoresistance between FC and ZFC is discovered. The irreversible behavior suggests that the system has two metastable states related to cooling method as seen in magnetic domain in ferromagnetism or spin-glass.

In order to elucidate the origin of these phenomena we

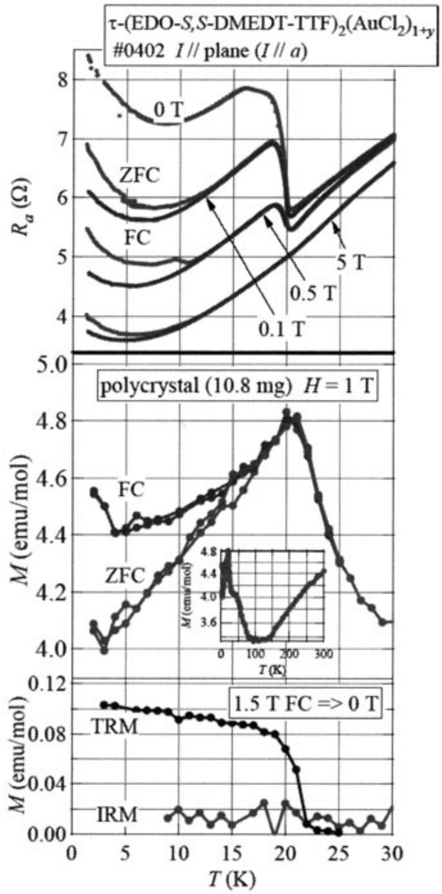

Fig.3 (a) Temperature dependence of magnetoresistance, (b) Magnetization and (c) remenant magnetization of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$($AuCl_2$)$_{1+y}$.

performed magnetization studies. The temperature dependence of magnetization is shown in Fig. 3 (b). The magnetization has peak (cusp) at 20 K and irreversible behavior below 15 K. These results are consistent with magnetoresistance phenomena. In this system the magnetic state strongly influences to the dynamics of the itinerant electrons.

Here the question is which kind of magnetism occurs, i.e. Antiferromagnetism (AF), Ferromagnetism (F), Ferrimagnetism (Ferri), Spin-glass (SG). At first, we consider as AF magnetism. AF is able to explain the peak at T_C in *M-T* curve. Typical AF behavior was observed in the analogue, τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$[7]. Because AF does not have remnant magnetization and irreversibility between FC and ZFC, simple AF state is unlikely. Second, F and Ferri allow the remnant magnetization. Moreover irreversibility is observable. On the other hand it is not reasonable that $M(T)$ for FC has the peak at T_C, because the simple ferromagnetic FC curve may increase by decreasing temperature below T_C. The magnetization of F or Ferri originates in very complex structure of magnetic domains and analogous material, τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, shows weak ferromagnetic feature[2, 3, 8]. The possibility of F or Ferri magnetization can not be completely discarded. If the canted antiferromagnetism, which has the characters both of F and AF, exists, these magnetization data can be explained. At last, we show possibility of SG state. SG has a cusp at T_C and remnant magnetization and irreversibility in difference of cooling method. Either canted ferromagnetic or SG like state or the coexistence of them is a candidate of the magnetic phase under 20 K.

Here it is an open question from where the spins originate. This salt contains no magnetic ions or radicals. For ferromagnetism of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ is explained by theory of flat band ferromagnetism. Conventional spin glass essentially requires magnetic impurity. However the macroscopic spin-glass like behavior allows several microscopic states, for example, the conventional spin from magnetic impurity, the ferromagnetic cluster. If the cluster is constructed, spin-glass behavior is able to occur.

Finally, we note about the relation between magnetization and transport phenomena. The steep rise anomaly of resistivity at T_C has magnetic instability. We expect that the disorder from the freezing spin or the magnetic domains can cause the anomaly. The large negative magnetoresistance may be the result of reduced disorder by applying magnetic field.

4. CONCLUSIONS

We have investigated the transport behaviors and magnetization of two dimensional organic conductor, τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$. The temperature dependence of resistivity shows an abrupt increase in resistivity at T_C = 20 K. Below T_C the irreversible behavior between FC and ZFC is discovered. Magnetization measurements also show irreversible behavior with cusp at T_C and remnant magnetization. The remarkable point is that the magnetic phase of this salt is strongly related to transport phenomena. These results suggest that the spin-glass state or weak ferromagnetic state with magnetic domain is the possible magnetic phase in ground state of this salt less than 5 T. The spin-glass like state or ferromagnetic state with domains supports the picture of random and dirty system. Nevertheless Shubnikov-de Haas oscillation in high magnetic field region favors very clean electron system (T_D = 1.5 K). These observations proves that the present system changes from "dirty" to "clean" in nature by the increase of magnetic field.

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