Magnetic ground state of quasi-two-dimensional organic conductor, \(\tau\)-(EDO-S,S-DMEDT-TTF)\(_2\)(AuCl\(_2\))\(_{1+y}\)

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Abstract. To understand the interplay between transport and magnetic properties, quasi-two-dimensional (Q2D) organic conductor \(\tau\)-(EDO-S,S-DMEDT-TTF)\(_2\)(AuCl\(_2\))\(_{1+y}\) was studied by measurements of electric resistivity (\(\rho_a, \rho_c\)), magnetoresistance (MR), susceptibility (\(\chi\)) and specific heat (\(C\)) in the temperature region between 1 K and 300 K. In spite of the fact that the drastic changes were observed in \(\rho_a, \rho_c\), MR and \(\chi\) at \(T_c = 20\) K, no anomaly was seen in \(C\). The concentration of spins estimated from \(M-H\) curve is about 360 ppm, which is difficult to detect anomaly in \(C\). These data suggest that the number of spins is very small in the ground state like spin-glass system.

1. Introduction

In the highly correlated system, the magnetism is of great interests with the transport phenomena as seen in SDW, Mott insulator, high temperature superconductor and colossal magnetoresistance effect. A series of \(\tau\)-type organic conductors such as \(\tau\)-(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-tetrathiafulvalene. Examples include huge negative magnetoresistance\(^1\), memory effect in angular dependence of magnetoresistance\(^2\), and weak ferromagnetic magnetization\(^3\). In the physics of \(\tau\)-type conductors, the problems is the interplay between the transport and the spin structure, and how the spin and carriers respond to magnetic fields can vary from a system to another. However \(\tau\)-(EDO-S,S-DMEDT-TTF)\(_2\)(AuBr\(_2\))\(_{1+y}\) and \(\tau\)-(EDO-S,S-DMEDT-TTF)\(_2\)(AuBr\(_2\))\(_{1+y}\) has shown strong sample dependence in transport properties. The effect of the variation of \(y\) influencing the filling factor was small. However, it was found that Cl, which is in the solvent during crystal growth as CH\(_2\)Cl\(_2\), was introduced into Br-site in AuBr\(_2\)-salt, the amount of which varies among samples. Here, we focus on the new \(\tau\)-type conductor \(\tau\)-(EDO-S,S-DMEDT-TTF)\(_2\)(AuCl\(_2\))\(_{1+y}\) which is an analogue of \(\tau\)-(EDO-S,S-
DMEDT-TTF)\textsubscript{2}(AuBr\textsubscript{2})\textsubscript{1+}. The AuCl\textsubscript{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 \(\tau\)-type conductor and the effect of magnetism to transport properties, we studied resistance, magnetoresistance, magnetization and specific heat. In the transport properties, we found that \(\rho(T)\) shows a steep rise anomaly below \(T_c = 20 K\) and 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 or weak ferromagnetic ground state. However the specific heat does not show any anomaly at 20 K. The spin concentration estimated from \(M-H\) curve is also small. These imply the spin-glass ground state.

2. Experiment
The single crystals of \(\tau-(EDO-S,S\text{-DMEDT-TTF})_2(AuCl_2)_{1+y}\) (\(y \sim 0.75\)) were obtained by usual electrochemical oxidation described elsewhere\[4\]. The electric contacts were made with Au wires, and carbon paste in the Au-evaporated surface on the crystal. For the in-plane (\(I \parallel a\)) resistance and magnetoresistance study, four terminals were on the same side, and for the out-of-plane (\(I \parallel c\)) 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. Dc magnetization for 10.8 mg of collected non-oriented single crystals was measured by using SQUID magnetometer up to 5 T. Specific heat was measured by differential thermal analysis method.

3. Results and Discussion
Temperature dependence of in- and out-of-plane resistivities is shown in figure 1. The anisotropy estimated from these resistivity is about \(10^2 \sim 10^3\) 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\textsubscript{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. Nevertheless, this material shows Shubnikov-de Haas oscillation suggesting a metallic state in magnetic field. It is also notable that the Dingle temperature is very low (\(T_D = 1.5 K\)) meaning that this system is very clean. The abrupt increase of resistivities below 20 K should not be due to CDW transition, since the satellite spots were not observed in our X-ray diffraction experiment down to 9 K.

Temperature dependence of magnetoresistance at several fields is shown in figure 2 (b). The abrupt increase is suppressed by applying magnetic field and vanishes in field of 5 T. So the curve for 5 T has no anomaly around \(T_c\) that reflects in only intrinsic band structure. The value of \(T_c\) slightly shifts to higher temperature by increasing field, which is also against CDW. Since the step-height did not coincide with \(T_c\), this change is not the transition described in the mean field theory. We speculate that the lifetime (\(\tau\)) of itinerant electrons becomes longer in magnetic field. 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 some 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 performed magnetization studies. The temperature dependence of magnetization is shown in figure 3 (a). The magnetization shows a peak...
(cusp) at 20 K and irreversible behavior below 15 K. We also confirmed residual magnetization in temperature dependence. These results are consistent with some phenomena observed in the magnetoresistance. In this system the magnetic state strongly influences to the dynamics of the itinerant electrons.

Here the question is what kind of magnetism occurs, i.e. antiferromagnetism (AF), ferromagnetism (F), ferrimagnetism (Ferri), spin-glass (SG). At first, we consider AF. AF is able to explain the peak at $T_C$ in $M$-$T$ curve. Similar AF behavior was observed in the analogue, $\tau$-(P-$S$,$S$-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+}$[5]. However simple AF state is unlikely because AF does not have remnant magnetization and irreversibility between FC and ZFC. Second, typical F and Ferri allow the remnant magnetization. Moreover irreversibility is observable. The analogous material, $\tau$-(EDO-$S$,$S$-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+}$, shows weak ferromagnetic feature[2, 3, 7]. If the canted antiferromagnetism, which has both of characters 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 residual 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 below 20 K.

Additional information is obtained from $M$-$H$ curve. Slight saturation is observed below $T_C$ (figure 3(a)). The saturating component subtracting linear component is very small (~2 emu/mol) as seen in figure 3(b). The value is corresponding to 360 ppm of 5580 emu, which is the value of $\mu_B \cdot N_A$ where $\mu_B$ and $N_A$ are Bohr magnetron and Avogadro number, respectively. Two cases might be possible, one is large number of spins with very small absolute value of “each spins” and the other is the case with very small number of spins for the case of canted-AF and SG, respectively. In the former case the

Figure 2. Temperature dependence of (a) magnetization and (b) magnetoresistance of $\tau$-(EDO-$S$,$S$-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+}$.

Figure 3. Field dependence of (a) magnetization, (b) saturating component and (c) magnetoresistance of $\tau$-(EDO-$S$,$S$-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+}$. 
small anomaly should be detectable by experiment of specific heat at $T_c$ as seen in SDW transition (18 K) of DMET-salt[6] although the heat capacity contains large phonon contribution at 20 K. Taking into account the result in the specific heat, which ignores the 20 K anomaly (figure 4), the latter case is more likely. Furthermore, the value of the concentration is in the region of diluted spin-glass system[7]. However, it must be noted that the data of heat capacity is not the evidence by large phonon contribution.

Here it is an open question from where the spins originate. This salt contains no magnetic ions or radicals. Arita et al. pointed out the importance of ferromagnetic fluctuation due to almost zero dispersive band structure in $\tau$-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$[8]. Conventional spin-glass essentially requires magnetic impurities. However the macroscopic spin-glass like behavior allows several microscopic states, for example, the conventional spin from magnetic impurities, the ferromagnetic cluster. If the cluster is constructed, spin-glass like behavior is possible to occur.

4. Conclusion
We have investigated the transport behaviors, magnetization and specific heat of $\tau$-(EDO-S,S-DMEDT-TTF)$_2$(AuCl$_2$)$_{1+y}$. The temperature dependence of resistivities shows the abrupt increase at $T_c$ = 20 K. Below $T_c$, the irreversible behavior between FC and ZFC is discovered in magnetoresistance and magnetization measurements. One of the remarkable points 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. Small saturating component in $M$-$H$ curve and no anomaly in specific heat imply the spin-glass ground state.

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