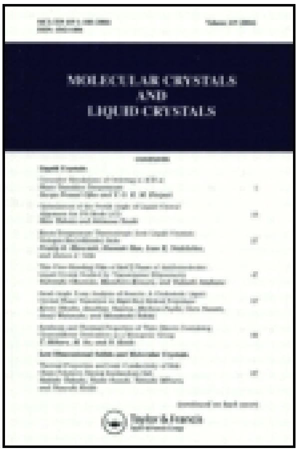

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Mysterious Thermal Properties of τ-(EDO-S,S-DMEDT-TTF) 2 (AuBr 2) 1+y and τ-(P-S,S-DMEDT-TTF) 2 (AuBr 2) 1+y (y⟊0.75)

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Mysterious Thermal Properties of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (y ~ 0.75)

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Thermal properties of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and its nitrogen analogue τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ systems were studied in the temperature region from 0.1K to 70K where the systems exhibit interesting features such as large negative magneto-resistance with large hysteresis and spin fluctuation. We found that in both systems, the component of the specific heat that depends linearly on temperature (γT term) is large. The magnitude of γ is several times larger than that of conventional organic metals. Below 10K, τ-(P-S, S-DMEDT- TTF)$_2$ (AuBr$_2$)$_{1+y}$ has the excess specific heat ΔC in addition to the lattice and electronic specific heat. Its excess entropy corresponds to 70% of two level system with Avogadro's number. Further investigation of this excess specific heat may provide us clues to clarify the origin of the spin fluctuation and the negative magneto-resistance.

Keywords: Specific heat; large γT term; Schottky anomaly; Negative magneto- resistance; Magnetic ordering

INTRODUCTION

τ-type organic conductors [1] are known to have unique (star-shaped) Fermi surfaces, the area and the shape of which can be varied by changing carrier density. In those systems, the band-filling can be rather easily controlled by changing the anion concentration "y" , by heat treatment and/or aging [2]. The conduction layers of these salts are composed of donors: ethylenedioxy-S,S-dimethylenedithio-tetrathiafulvalene (EDO-S,S-DMEDT-TTF), pyrazino-S, S-dimethylethylenedithio-tetrathiafulvalene (P-S,S-DMEDT-TTF), and anions: $AuBr_2$, AuI_2, $Au(CN)_2$, IBr_2, I_3 with the ratio 2:1. Each conducting layer is separated by the anion layer corresponding with the composition, y. Within the conducting layer, the packing pattern of the molecules has four - fold symmetry resulting in star-shaped Fermi surface in the metallic state [1].

Among τ- type organic conductors, τ-$(EDO\text{-}S,S\text{-}DMEDT\text{-}TTF)_2(AuBr_2)_{1+y}$, ($y$~0.75) has been most extensively studied. This crystal is known to exhibit interesting behaviors in magnetic properties [3] as well as electrical transport properties [2,4]. In the temperature region below 50K, there appears anomaly in the NMR signal such as the divergence in the line width and split of the signal into two components with different T_1. These observations suggest the existence of a large spin fluctuation [5]. Negative magneto-resistance with a mysterious angular dependence is also interesting [6]. When a magnetic field of 5T is rotated in the conducting plane, they observed magneto-resistance with the four-fold symmetry. As they reduced the field to 0.5T, on the other hand, the resistance was of 180 degree symmetry. This change in the magneto-resistance was discussed in terms of the formation and reorientation of magnetic domains. All of those experiments indicate that the origin of the negative magneto-resistance in this system is the spin scattering. Moreover, low residual resistivity ratio (about 1) suggests the magnetic scattering is strong. Recently, however, Shubnikov de Haas oscillation was observed in these systems that suggests the existence of carriers with high mobility. These contradictory experimental results attract our attention to these mysterious and new type of electronic states.

EXPERIMENTAL RESULTS AND DISCUSSION

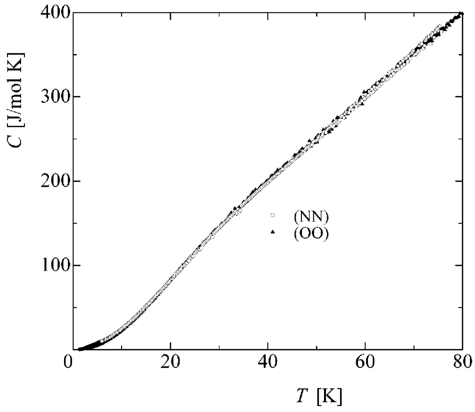

FIGURE 1 Specific heat of τ-(EDO-S,S-DMEDT-TTF)$_2$ (AuBr$_2$)$_{1+y}$, and τ-(P-S, S- DMEDT- TTF)$_2$ (AuBr$_2$)$_{1+y}$.

In this study, specific heat of τ-(EDO-S,S-DMEDT-TTF)$_2$ (AuBr$_2$)$_{1+y}$ and τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ were measured by a thermal relaxation method down to 0.1K up to 70K. Experiments were done both in a field cooling process and in a zero field cooling process. We used Cernox 1050 and 1030 as thermometer, stainless wire of ϕ15 mm diameter as electrical and thermal contact lead with thermal heat bath. Weights of samples are 0.4~0.6mg for both samples respectively. The measurements below 1.4K ware carried out by a ^{3}He-^{4}He dilution refrigerator.

Figure 1 illustrates raw data of specific heat for (OO) and (NN) systems. (Hereafter, we abbreviate τ-(EDO-S,S-DMEDT-TTF)$_2$ (AuBr$_2$)$_{1+y}$ and τ-(P-S,S-DMEDT- TTF)$_2$ (AuBr$_2$)$_{1+y}$ as (OO) and (NN) respectively.) In the region below 30K, we observe a specific heat that depends superlinearly on temperature. Above 30K, on the other hand, the specific heat does not obey the simple Debye model but is a linear function of the temperature. This feature is common to many charge transfer salts in which the vibrational modes are complex.

γT term at low temperatures

Figure 2 shows the C/T vs. T^2 plots for (NN) and (OO) systems. We see the slope of curves becomes steeper with decreasing temperature. The intersections of curves to the vertical axis give the coefficient γ of the specific heat components γT that is linearly dependent on temperature. They are 0.06J/molK^2 (OO) and 0.13J/molK^2 (NN) systems, respectively. These values are several times larger than those of conventional organic conductors, for examples, BEDT-TTF [7] and DCNQI-Cu system [8]. We believe the dominant part of this term comes from the electronic degree of freedom at the Fermi level. A band calculation based on the tight binding model indicates the existence of the large density of states at the Fermi level $N(E_F)$. Arita pointed out that the packing pattern of the conducing layer with four-fold symmetry possibly enhances the density of states [9]. He also conjectured that the electron-electron interaction leads to the magnetic fluctuation as well as negative magneto-resistance.

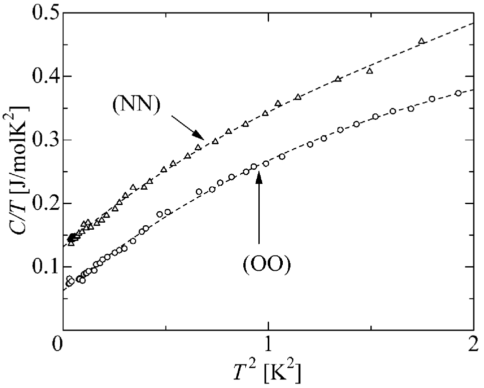

FIGURE 2 Low temperature C/T vs. T^2 for fτ-(EDO-S,S-DMEDT- TTF)$_2$ (AuBr$_2$)$_{1+y}$:(OO), and τ-(P-S, S- DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$:(NN).

However, we can not deny the possibility that γT terms are partly caused by magnetic origin. To examine the contribution of spins to the γT term, we have measured the specific heat in the magnetic field perpendicular to the conduction layer. Experiment was done in the field up to 7T and in the temperature region down to 1.5K. In this experiment, we could not observe any variation in the γT term under magnetic field. The fact that γT term remains invariant in the magnetic field excludes the possibility of the localized magnetic moments contributing to the γT term. Extensions of the experiments to lower temperatures down to 0.1K, however, are necessary.

Schottky Anomaly

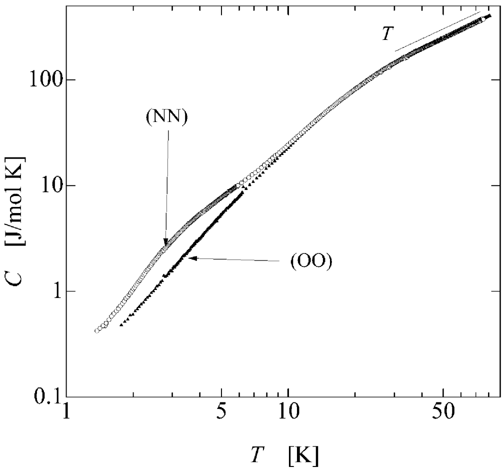

FIGURE 3 Log C vs. log T plots for τ-(EDO-S,S- DMEDT-TTF)$_2$ (AuBr$_2$)$_{1+y}$ (OO), and τ-(P-S, S- DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (NN).

In figure 3, we plotted log C vs. log T plots of the specific heat for (OO) and (NN) systems. At higher temperatures (T>30K), the specific heats of these systems are the same. Below 20K, the data of (NN) begin to deviate from those of (OO). The curve of (NN) looks to have a broad hump. Since specific heats of two systems are nearly equal in the temperature region above 20K and at the lowest temperatures below 1K, we expect that broad hump in the specific heat of (NN) is the appearance of some kind of freedom specific to (NN) system. In figure 4, we plot the excess specific heat, subtracting that of (OO) system.

At lowest temperatures, excess specific heat shows an exponential decay. In the intermediate temperatures, the specific heat has a maximum at 5K, and then monotonically decreases towards high temperatures. This temperature dependence is typical Schottky type. Schottky model fittings give us the information concerning the energy gap Δ, level degeneracy and the density N.

We can obtain the good fitting by the simple two level system, using the number of two level system $N(=0.78N_A)$ and level splitting $\Delta/k_B(=12.5\text{K})$ and ratio of the degeneracy between ground and first excited states $g_o/g_1(=1)$, as the fitting parameters.

At present, we have two candidates for the origin of this Schottky excess specific heat. One is the rotational freedom of the lattice. Methyl group leads to the Schottky anomalies in the case of deuterated system through the quantum tunneling [10]. (NN) and (OO) systems, however, have the same number of undeuterated methyl group and in the circumstances around the methyl groups there is no differences that cause the lower energy level splitting. The second is the spin freedom. In fact remarkable spin fluctuation in this temperature region are reported by the measurements of static magnetic susceptibility and spin relaxation. In specially around 10K (NN) system have sharp peak of inverse of the spin relaxation time T_1^{-1} and divergence of the line width [5], which we encounter in the case of magnetic ordering. We begin to focus on the spin fluctuation as the key information concerning the lowest mysterious electronic properties.

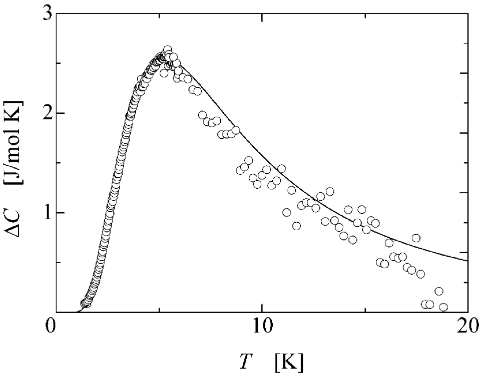

FIGURE 4 Excess specific heat of τ-(P-S, S- DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (NN).

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