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LOW-TEMPERATURE ELECTRONIC PHASES OF EDT-TTF BASED MOLECULAR CONDUCTORS

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Magnetic investigation was carried out for low temperatures electronic phases in (EDT-TTF)$_2$AuBr$_2$, which undergoes an SDW transition at 16 k. In the SDW phase, we observed an abrupt change of ^{1}H-NMR absorption line around 6 K where the ^{1}H-NMR spin-lattice relaxation rate shows an anomalous second peak. The electronic phase is discussed by microscopic point of view.

Keywords: organic conductor; ^{1}H-NMR; SDW

INTRODUCTION

EDT-TTF molecule is an organic donor that consists of half TTF and half BEDT-TTF units. One of the cation radical salts, (EDT-TTF)$_2$AuBr$_2$ is an organic donor with a quasi-one-dimensional electronic structure [1]. Its Fermi surface is very close to those of (TMT*C*F)$_2$*X* salts. There is no dimerization of donor molecules within the columns in (EDT-TTF)$_2$AuBr$_2$. Hence this salt is considered to be a quasi-one-dimensional 1/4-filled system. It shows metallic behavior down to about 30 k, and the resistivity increases abruptly below 16 K [1]. Recently we started magnetic investigation of this salt in order to clarify the low-temperature electronic phases. We found an SDW formation around 16 K, where the resistivity shows a minimum, by EPR, NMR and static spin susceptibility measurements [2]. In this paper, we focus on the SDW phase of (EDT-TTF)$_2$AuBr$_2$, and discuss a possible second phase transition by microscopic point of view.

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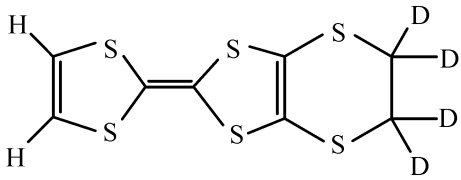

FIGURE 1 Molecular structure of partially deuterated EDT-TTF, d_4-EDT-TTF.

EXPERIMENTAL

Detailed analyses of the ^{1}H-NMR lineshape for the nuclei on the methyl groups enable us to determine the wave-number of the SDW phases of (TMT*C*F)$_2$*X* salt. For ^{1}H-NMR lineshape analyses, however, EDT-TTF molecule is disadvantageous because of the complicated line of the ethylene groups. Hence we synthesized a partially deuterated EDT-TTF molecule, d_4-EDT-TTF (Figure 1), according to the previous report [3]. The crystals of (d_4-EDT-TTF)$_2$AuBr$_2$ were prepared by the electrochemical oxidation of d_4-EDT-TTF using [CH$_3$(CH$_2$)$_3$]$_4$NAuBr$_2$ in a 1,1,2-trichloroethane solution under a constant current of 1.0 μA [1]. Static magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer for a mass of single crystals with the total amount of 1.70 mg at various magnetic fields. The SQUID measurements were carried out in the temperature range between 300 K and 1.8 K. The core diamagnetism was corrected by the Pascal's law. The ^{1}H-NMR measurements were performed by using a pulsed-NMR spectrometer operated at 86.4 MHz using a single crystal. The ^{1}H-NMR absorption lines obtained by fast Fourier transform (FFT) of spin-echo signals at different temperatures.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the spin susceptibility of (d_4-EDT-TTF)$_2$AuBr$_2$ for powdered samples determined by SQUID measurement at 3 kOe. Above 20 K, the spin susceptibility shows gradual decrease as temperature decreases, which is probably due to thermal contraction of the crystal. The spin susceptibility suddenly decreases below 18 K, indicating a magnetic phase transition. These observations are in excellent agreement with that of (h_6-EDT-TTF)$_2$AuBr$_2$. Hence the deuteration causes no significant effects in this system. Detailed discussion about the phase transition was described in the previous report [2]. Figure 3 shows the temperature dependence of the ^{1}H-NMR absorption lines of a single crystal at different temperatures. Since the ^{1}H sites are located only

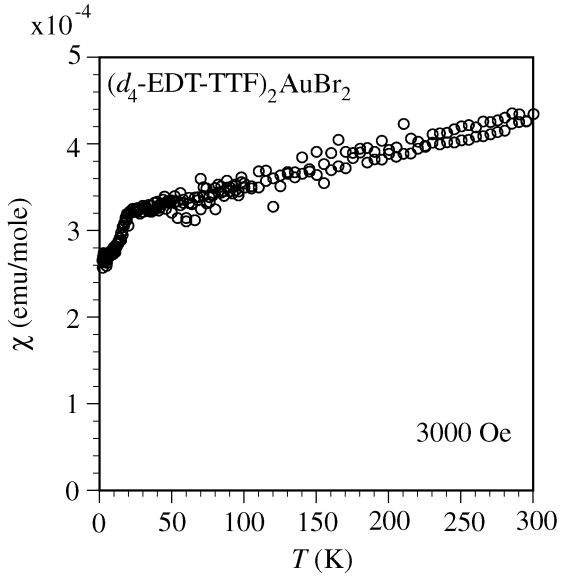

FIGURE 2 Temperature dependence of the spin susceptibility of (d_4-EDT-TTF)$_2$AuBr$_2$ for powdered samples determined by SQUID measurement at 3 KOe. The core dimagnetism was corrected.

on the vinylene group (Figure 1), the ^{1}H-NMR absorption lines are simple at paramagnetic state. Below 18 K, the ^{1}H-NMR absorption lines show significant broadening; there appeared broad satellites besides the main line. These observations are clear evidence of the onset of additional local field, indicating magnetic transition. The onset temperature agrees with the anomaly temperature of the spin susceptibility. However, when analyzing more precisely, it turns out that the lineshape shows an additional change below 6 K. In the previous report for the h_6-salt, we found another huge peak in the ^{1}H-NMR spin-lattice relaxation rate, ^{1}H-T_1^{-1}, at 6 K besides at the SDW transition temperature, T_{SDW} [2]. Below 6 K, the ^{1}H-T_1^{-1} starts to decrease rapidly. It reminds us so-called second peak in incommensurate SDW phases of (TMT*C*F)$_2$*X*. Hereafter we denote the second anomaly temperature as T^* after (TMT*C*F)$_2$*X* salts.

In (TMT*C*F)$_2$*X* salts, anomalous behaviors were observed at T^* in several physical properties; specific heat, electric threshold field and so on. But the origin of this anomalous behavior is far from clear. It is also debated whether this anomaly is a real thermodynamical transition or not. In the case of the (EDT-TTF)$_2$AuBr$_2$, the NMR lines change their shapes with broadening below T^*. The ^{1}H-NMR spin-spin relaxation rate, ^{1}H-T_2^{-1}, starts

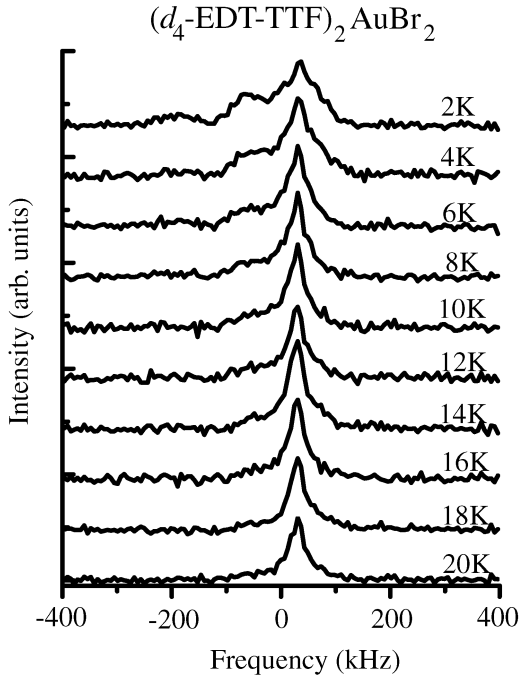

FIGURE 3 Temperature dependence of the ^{1}H-NMR absorption lines of the (d_4-EDT-TTF)$_2$AuBr$_2$ single crystal.

to decrease again below T^*. The additional increase of the NMR linewidth below T^* is consistent with the decrease of the ^{1}H-T_2^{-1}, considering a decoupling between nuclear spins. While we do not have a clear explanation of the ^{1}H-T_2^{-1} anomaly around T^*, possible reconstruction of the magnetic structure is very likely. As for (TMT*C*F)$_2$*X* salts, neither the linewidth nor the line-shift showed significant change upon cooling below T^* [4]. It is a remarkable difference between (EDT-TTF)$_2$AuBr$_2$ and (TMTSF)$_2$PF$_6$.

One of possible explanations is following: At T^*, (EDT-TTF)$_2$AuBr$_2$ may undergo a second transition of partial un-nested Fermi surface, resulting in the shift of the nesting-vector. (EDT-TTF)$_2$AuBr$_2$ is considered to have a significant two-dimensional feature according to the tight-binding band calculation. Because of the strongly warped Fermi surface of the present material, imperfect nesting is likely. In fact, the low temperature transport properties of (EDT-TTF)$_2$AuBr$_2$ suggest imperfect nesting below T_{SDW} [1]. The activation energy of the resistivity in the SDW phase seems to be small, assuming a full open gap.

Another explanation is a possible structural change; dimerization, charge disproportionation, coexistence of $2k_F$ SDW and $4k_F$ CDW and so on. We emphasize again that the present system is 1/4-filling if the donor maintains regular stack down to low temperatures. These structural change may actually reduce the system 1/4-filling to 1/2-filling, and affect significant influence on the magnetic structure. Recently a possible dimerization at T^* is pointed out by theoretical investigation [5]. In order to clarify the charge distribution, ^{13}C-NMR measurements are needed.

In conclusion, we investigated the low temperature electronic state of a quasi-one-dimensional system, (EDT-TTF)$_2$AuBr$_2$. We observed that ^{1}H-NMR lines change their shapes below 6 K. We proposed a possible explanation of the origin of the T^* anomaly in the SDW phase: It may be a second transition of partial un-nested Fermi surface, resulting in the change of the magnetic structure. Detailed analysis of the NMR results will be discussed elsewhere.

REFERENCES

[1] Mori, T., & Inokuchi, H. (1989). *Solid State Commun.*, *70*, 823.
[2] Nakamura, T. (2000). *J. Phys. Soc. Jpn.*, *69*, 4026.
[3] Kato, R. et al. (1989). *Chem. Lett.*, 781.
[4] Takahashi, T. et al. (1989). *J. Phys. Soc. Jpn.*, *58*, 703.
[5] Itakura, T., & Suzumura, Y. (2000). *J. Phys. Soc. Jpn.*, *69*, 320.