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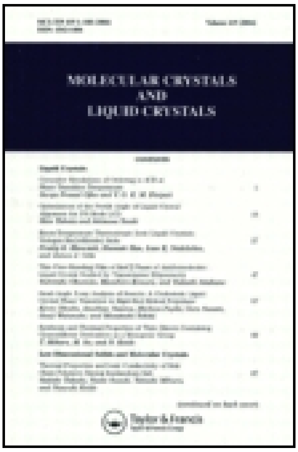

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Electronic and Magnetic Properties of π-d Interaction System: $(EDTDM)_2FeBr_4$

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$(EDTDM)_2FeBr_4$ based on π-d interaction system consists of quasi one-dimensional donor columns and square-lattice magnetic anion sheets (Fe^{3+}(s=5/2)). It behaves metallic at high temperatures and undergoes a metal-insulator transition at T_{MI}~15-20K, where the low temperature insulating phase is considered to be magnetic ordered state. The magnetic susceptibility, which is governed by Fe^{3+} d-spins, obeys the Curie-Weiss law in the high-temperature regime. Below 50K, the susceptibility deviates from the Curie-Weiss law and shows an antiferromagnetic transition at T_N~3K. The anomalous magnetization curves indicate an important role of π-d interaction in the magnetic behavior.

Keywords: TTF derivative; M-I transition; antiferromagnetic transition; π-d interaction

INTRODUCTION

Organic donor molecules, such as TTF derivatives, form a large variety of charge transfer complexes with acceptors, in which planar-shaped donor molecules form one- or two-dimesional arrangements through a face-to-face and/or side-by-side inter-molecular interactions. Consequently, the overlap of the π-electron wave functions between adjacent donors produce a low dimensional electronic structures, which are stabilized in a metallic or semiconducting phase depending on charge transfer rate, manner of molecular arrangement, Coulomb interactions, etc. When we employ transition metal anions that have localized d-electron spins as a constituent, the d-electron spins are expected to interact with donor π-electrons in the complexes. This π-d interaction will produce metal magnetism in the case of metallic π-electron system or π-d composite magnetism in the semiconducting phase [1, 2, 3].

Recently, Enomoto *et al.* [4] reported that $(DMET)_2FeBr_4$ shows the interesting interplay between magnetism and electron transport, which is associated with the interaction between the localized d-electrons and the conduction π-electrons. If the donor molecules of this system can be substituted for analogues with keeping the crystal structure unchanged, it is possible to investigate systematically the role of donor molecules in the π-d interaction system.

In this study, we focused on EDTDM (FIGURE 1) as a donor molecule where sulfur is substituted for selenium in DMET molecule, and the crystal structure and physical properties of $(EDTDM)_2FeBr_4$ and $(EDTDM)_2GaBr_4$ are investigated.

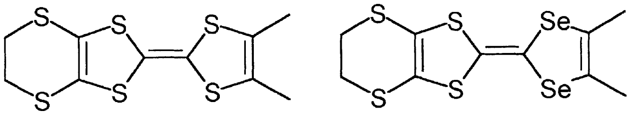

FIGURE 1: The molecular structures of EDTDM (left) and DMET (right) .

EXPERIMENTAL

Single crystals of $(EDTDM)_2FeBr_4$ were obtained by a galvanostatic anodic oxidation method (0.1-0.5 μA) for a synthetic period of 2 weeks using 9mg of EDTDM, 25mg of $TBAFeBr_4$ as a supporting electrolyte and 15cm^3 of chlorobenzene as a solvent. Single crystals of $(EDTDM)_2GaBr_4$ were obtained by using $TBAGaBr_4$ under the same condition. The crystal structures were determined by a single crystal X-ray diffraction method using RIGAKU AFC-7 four-circle diffractometer. The reflection data were collected in the range of 2θ=5 to 55°. Their structures were solved with the direct methods using SHELXS-86, and then refined with the full-matrix least-squares method using SHELXL-93. The coordinates of hydrogen atoms were calculated geometrically. The magnetic susceptibilities

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were measured using Quantum-Design MPMS-5 SQUID magnetometer up to a field of 5.5T in the temperature range 1.85-300K. Electrical resistivity was measured by constant current four-probe method (R≤10kΩ), or constant voltage two-probe method (R≥10kΩ). ESR measurements were performed with an ESR X-band spectrometer (JEOL JES-TE200) equipped with a continuous-flow cryostat (Oxford ESR910) in the temperature range 3.3K-300K.

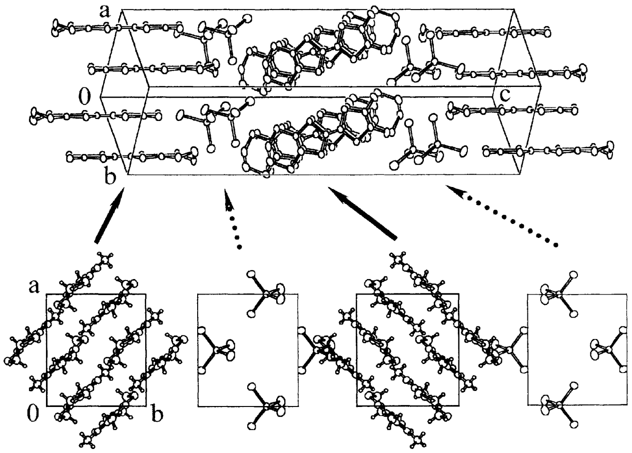

FIGURE 2: The crystal structure of (EDTDM)$_2$FeBr$_4$.

RESULTS AND DISCUSSION

Both of the obtained salts, (EDTDM)$_2$FeBr$_4$ and (EDTDM)$_2$GaBr$_4$, are isostructural to (DMET)$_2$FeBr$_4$ [4] with a 2:1 donor/anion composition. The crystal structure of (EDTDM)$_2$FeBr$_4$ is shown in FIGURE 2, which is characterized with an alternating stacking of EDTDM conducting sheets and FeBr$_4^-$ magnetic sheets. EDTDM columns are arranged in a face-to-face manner in the *ab*-plane where the columns on the adjacent layers are directed two different directions; one is along the *a*+*b* direction and the other is along the *a*-*b* direction. Two columns are crystallographycally equivalent, for the asymetric unit contains one molecule for donors and a half for anions.

From comparision of the intra-chain overlap integrals between (EDTDM)$_2$FeBr$_4$ and (DMET)$_2$FeBr$_4$ shown in FIGURE 3, it is re-

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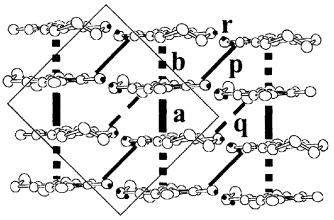

site	EDTDM	DMET
a(**a**/**b**)	24.92(1.12)	60.52(1.02)
b(**b**/**b**)	22.19(1)	59.55(1)
p(**p**/**b**)	1.502(0.0677)	10.81(0.182)
q(**q**/**b**)	2.787(0.126)	6.742(0.113)
r(**r**/**b**)	2.360(0.106)	6.237(0.105)

FIGURE 3: The intra-chain (**a**, **b**) and inter-chain (**p**, **q**, **r**) overlap integrals of $(EDTDM)_2FeBr_4$ and $(DMET)_2FeBr_4$ [4] calculated from extended Hückel approximation. The values of the overlap integrals that are normalized by the value of **b** are shown in parenthese.

vealed that the dimerization of donor molecules in $(EDTDM)_2FeBr_4$ is a little stronger than that in $(DMET)_2FeBr_4$. In addition, it is indicated that donor arrangement for $(EDTDM)_2FeBr_4$ is more one-dimensional than that for $(DMET)_2FeBr_4$. Actually, the intra-chain transfer integrals are five times larger than the inter-chain transfer integrals in $(EDTDM)_2FeBr_4$.

The anion molecules form two-dimensional square lattice in the *ab*-plane. The inter-anion Br-Br distance is estimated at 3.87Å for $(EDTDM)_2FeBr_4$ and 3.88Å for $(EDTDM)_2GaBr_4$, which is comparable with the sum of van der Waals radii (3.7Å), suggesting the presence of the inter-anion exchange interaction paths of the close inter-anion Br-Br distance. Moreover, there are close contacts between an anion and its neighboring donor molecules, whose intermolecular S-Br distance is estimated at 3.74Å for $(EDTDM)_2FeBr_4$ and 3.76Å for $(EDTDM)_2GaBr_4$, comparable to the sum of van der Waals radii (3.65Å). Therefore, we cannot ignore the interaction between adjacent two anion sheets, which are bridged by the donor columns.

For both $(EDTDM)_2FeBr_4$ and $(EDTDM)_2GaBr_4$ the in-plane resistivity shows metallic behavior above ~200K and apparently semiconducting behavior below ~200K. In contrast, the out-of-plane resistivity shows semiconducting behavior for both crystals. Therefore, both $(EDTDM)_2FeBr_4$ and $(EDTDM)_2GaBr_4$ have the similar transport property.

The magnetic susceptibility of $(EDTDM)_2GaBr_4$ shows Pauli paramagnetic behavior above ~20K, whose contribution gradually de-

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creases as the temperature decreases. Since the Pauli paramagnetic susceptibility is proportional to the conduction carrier density, the decrease in the density of states explains the apparent semiconductor-like behavior in the resistivity for $T \leq 200K$ even in the metallic phase though the presence of Fermi surface is predicted from band structure calculation at room temperature. Below ~20K the susceptibility decreases steeply as the temperature decreases, suggesting the appearance of an antiferromagnetic (AF) ordered state, taking into account NMR measurement [5].

The ESR signal of $(EDTDM)_2GaBr_4$ appears as one Lorentzian peak with line-width ΔH_{pp}~0.7mT and g-value g~2.01 at room temperature when the field is applied along the c^*-axis. In contrast, in the applied field along the a+b or the a-b direction, two Lorentzian peaks are observed with line-width ΔH_{pp}~0.65mT and 0.75mT and g-value g~2.0079 and 2.0025. The presence of two peaks is the consequence of 'double-column' structure. Since the long axes of donor molecules are nearly parallel to the c-axis, two donor columns are equivalent for $B//c^*$-axis. On the other hand, when the field is applied in the conducting plane, two columns are generally inequivalent, and giving double peaks in the ESR spectra. The ESR line-width ΔH_{pp} under the field along c^*-axis decreases with decreasing temperature and below ~15K the line-width abruptly diverges. The intensity has slight temperature dependence above ~15K and rapidly decreases below ~15K. The temperature dependence is consistent with the appearance of AF state below 15K, as the susceptibility and NMR suggest. SDW or Mott-like AF state is a plausible candidate of the ordered state below T_{MI}=15-20K.

FIGURE 4 show the temperature dependence of the magnetic susceptibility in an applied field of 1T (a) and the magnetization curves (b) for $(EDTDM)_2FeBr_4$. The susceptibility obeys the Curie-Weiss law in the high temperature region above ~50K, where the Curie constant C and the Weiss temperature Θ are estimated at C=4.74emu·K/mol and $\Theta=-2.8K$ ($200K<T<300K$), respectively. From the Curie constant, it is proved that Fe^{3+} spin (S=5/2) mainly serves as the origin of the magnetism of $(EDTDM)_2FeBr_4$. This salt shows antiferromagnetic transition at T_N~3K, below which the magnetic easy-axis is the a-axis. In addition, anisotropy appears in the susceptibility below ~50K, and it increases with decreasing the temperature. From the magnetization curves, a spin-flop transition

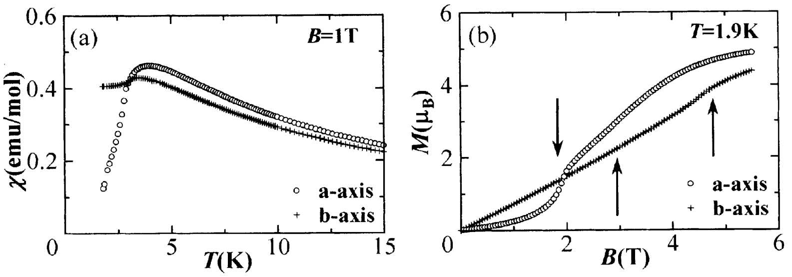

FIGURE 4: The temperature dependence of the magnetic susceptibility (a) and the magnetization curves (b) of $(EDTDM)_2FeBr_4$.

occurs at $B_{sf}\sim1.8T$ in addition to the appearance of an anomaly at ~2.9T when the magnetic field is applied along the a-axis. For $B//b$-axis, the magnetization curve has a shoulder around $B\sim4.5T$. A large difference emerges in the magnetizations between $B//a$-axis and $B//b$-axis. These unusual behaviors of the magnetization cannot be explained only by Fe^{3+} spins. The donor spins is considered to participate in the magnetization as in the case of $(DMET)_2FeBr_4$ [4].

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