High field magnetization of (Benzo-TTFVS)$_2$FeBr$_4$ and (Benzo-TTFVO)$_2$FeBr$_4$

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Abstract. We performed high field magnetization measurements up to 55 T for newly synthesized antiferromagnetic charge-transfer salts, (Benzo-TTFVS)$_2$FeBr$_4$ with $T_N = 5.8$ K and (Benzo-TTFVO)$_2$FeBr$_4$ with $T_N = 9.3$ K. A spin-flop behavior at 1.8 T and a saturation at 14.8 T were observed in the magnetization curve at 0.5 K for the (Benzo-TTFVS)$_2$FeBr$_4$ salt. For the (Benzo-TTFVO)$_2$FeBr$_4$ salt a spin-flop at 6.9 T and a saturation at 36.2 T were observed. We estimate the exchange interaction between d spins and the magnetic anisotropy for both salts from the magnetization data.

1. Introduction

Search for magnetic molecular conductors, especially ferromagnetic semiconductors and metals, has been a great issue for the development of molecular-type spintronics. We have extensively developed new charge-transfer salts composed of bent donor molecules and magnetic counter anions. We have found a ferromagnetic semiconductor based on a 2:1 salt (EDT-TTFVO)$_2$FeBr$_4$, in which the π electrons and the d spins significantly interact with each other, giving rise to a ferrimagnetic ordering at 1 K [1-3]. Subsequently we have synthesized a 1:1 salt (BEDT-TTFVS)FeBr$_4$, which exhibits a semiconducting behavior and a ferromagnetic ordering at 1.8 K [4,5]. These findings promoted us to search out FeBr$_4^{-}$ salts with other bent molecules.
(Benzo-TTFVS)$_2$FeBr$_4$ and (Benzo-TTFVO)$_2$FeBr$_4$ are recently developed by our group with bent donor molecules of benzotetrathiafulvalenothioquinone-1,3-dithiolemethide (Benzo-TTFVS) [6] and benzotetrathiafulvalenoquinone-1,3-dithiolemethide (Benzo-TTFVO) [7], respectively. The (Benzo-TTFVS)$_2$FeBr$_4$ salt shows a semiconducting behavior below 100 K with small activation energy of $< 30$ meV and an antiferromagnetic ordering at $T_N = 5.8$ K. The ESR experiment by Hayakawa et al. suggests that the strong fluctuation is coupled with the $\pi$-d correlation along the $b$-direction for which donor molecules and counter anions are stacked alternately [8]. The (Benzo-TTFVO)$_2$FeBr$_4$ salt, on the other hand, exhibits a clear metal-to-insulator transition at 166 K accompanied by a one-dimensional structural phase transition of the donor-stacked columns [7]. An antiferromagnetic ordering occurs at $T_N = 9.3$ K, which means that the exchange interaction between d spins for (Benzo-TTFVO)$_2$FeBr$_4$ is larger than that for (Benzo-TTFVS)$_2$FeBr$_4$.

The high field magnetization process towards the saturation of the magnetic moments for antiferromagnets provides us the information about the exchange interaction between d spins and the magnetic anisotropy energies. In this study, we performed the high field magnetization measurements up to 55 T to discuss the exchange interaction of the isostructural salts with the structural parameters and the band structure.

2. Experimental

The (Benzo-TTFVS)$_2$FeBr$_4$ and (Benzo-TTFVO)$_2$FeBr$_4$ salts were obtained by an electrochemical oxidation method [6,7]. The high field magnetization of (Benzo-TTFVS)$_2$FeBr$_4$ was measured up to 30 T using a homemade pulsed-magnet system combined with a $^3$He refrigerator by a conventional induction method. The high field magnetization measurements were performed up to 55 T for (Benzo-TTFVO)$_2$FeBr$_4$ at High Magnetic Field Laboratory of Osaka University.

3. Results and discussion

Figure 1 shows the magnetization curve of (Benzo-TTFVS)$_2$FeBr$_4$ measured at 0.5 K. Amount of the sample used in the measurements is 5.2 mg. The magnetization curve shows a positive curvature around 2 T, a linear increase with increasing field up to 14 T and a saturation at $H_c^2 = 14.8$ T. The saturation moment is 5.1 $\mu_B$ per formula unit, which means no contribution of the $\pi$ electrons to the magnetic moment. A clear spin-flop was observed at $H_{c1} = 1.8$ T as shown in the inset of Fig. 1.

Figure 2 shows the magnetization curve of (Benzo-TTFVO)$_2$FeBr$_4$ measured at 1.3 K. Amount of the sample used in the measurements is 2.6 mg. The magnetization curve shows a positive curvature around 7 T, a linear increase with increasing field up to 36 T and a saturation at $H_c^2 = 36.2$ T. In the high field region above 36 T a slight increase of the magnetization may be recognized. However, its origin is not clear at this stage of our experiment because of the small amount of the sample. A spin-flop is observed at $H_{c1} = 6.9$ T as shown in the inset of Fig. 2.

According to the mean-field theory [9], the $H_{c1}$’s and $H_{c2}$’s in the magnetization curves are given by relations of $H_{c1} = (2H_E H_A)^{1/2}$ and $H_{c2} = 2H_E$, where $H_E$ and $H_A$ are the exchange field and the anisotropy field, respectively. In the case of (Benzo-TTFVS)$_2$FeBr$_4$, $H_E$ is 7.4 T and $H_A$ is 0.22 T,
while \( H_E \) is 18.1 T and \( H_A \) is 1.32 T in the case of (Benzo-TTFVO)\(_2\)FeBr\(_4\). If we assume that the exchange interaction acts only on the nearest neighbor magnetic ions, the Hamiltonian of the exchange interaction on the \( S_i \) spin is given as \( H = -2zJ<S>S_i = g\mu_B H E S_i \), where \( J \) is the exchange integral, \( z \) being a number of the nearest neighbors, \( <S>=5/2 \), \( g=2 \), and \( \mu_B \) is the Bohr magneton. The values of \( zJ \) are
estimated to be -0.17 meV = -2.0 K for (Benzo-TTFVS)$_2$FeBr$_4$ and -0.41 meV = -4.7 K for (Benzo-
TTFVO)$_2$FeBr$_4$.

Structural analysis reveals that the Br-Br contact distance ($d_{Br-Br}$) between the FeBr$_4^-$ ions along the
intercolumn direction is very different between the salts. $d_{Br-Br}$ for (Benzo-TTFVS)$_2$FeBr$_4$ is 4.10 Å
comparable to the van der Waals one, while that for (Benzo-TTFVO)$_2$FeBr$_4$ is 4.01 Å shorter than the
van der Waals one. For (Benzo-TTFVS)$_2$FeBr$_4$, both the d-d superexchange interaction between the
FeBr$_4^-$ ions through the Br atoms and the $\pi$-d interaction play an important role. On the other hand, the
superexchange interaction may be strong for (Benzo-TTFVO)$_2$FeBr$_4$, which raises the $T_N$ as well as the
$H_{c2}$ in the magnetization curve compared to those for (Benzo-TTFVS)$_2$FeBr$_4$.

Finally, we point out the difference in the estimation of the exchange interaction from the $T_N$
and the $H_{c2}$. In the framework of mean field theory, both the $T_N$ and the $H_{c2}$ are proportional to the exchange
interaction. The ratio of the $T_N$ between (Benzo-TTFVS)$_2$FeBr$_4$ and (Benzo-TTFVO)$_2$FeBr$_4$ is
calculated to be 0.62, while the ratio of the $H_{c2}$ between (Benzo-TTFVS)$_2$FeBr$_4$ and (Benzo-
TTFVO)$_2$FeBr$_4$ is 0.40. There may exist key parameters in the different ratio so as to reveal the
mechanism of these antiferromagnetic ordering.

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