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2006 J. Phys.: Conf. Ser. 51 331

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## High field magnetization of (Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub> and (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub>

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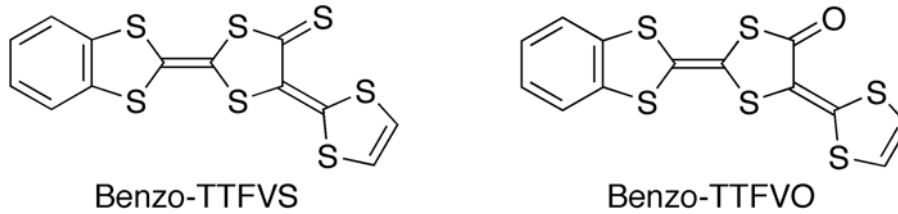
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**Abstract.** We performed high field magnetization measurements up to 55 T for newly synthesized antiferromagnetic charge-transfer salts, (Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub> with  $T_N = 5.8$  K and (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub> 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)<sub>2</sub>FeBr<sub>4</sub> salt. For the (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub> 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)<sub>2</sub>FeBr<sub>4</sub>, in which the  $\pi$  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<sub>4</sub>, which exhibits a semiconducting behavior and a ferromagnetic ordering at 1.8 K [4,5]. These findings promoted us to search out FeBr<sub>4</sub><sup>-</sup> salts with other bent molecules.



(Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub> and (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub> 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)<sub>2</sub>FeBr<sub>4</sub> 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)<sub>2</sub>FeBr<sub>4</sub> 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)<sub>2</sub>FeBr<sub>4</sub> is larger than that for (Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub>.

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)<sub>2</sub>FeBr<sub>4</sub> and (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub> salts were obtained by an electrochemical oxidation method [6,7]. The high field magnetization of (Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub> was measured up to 30 T using a homemade pulsed-magnet system combined with a <sup>3</sup>He refrigerator by a conventional induction method. The high field magnetization measurements were performed up to 55 T for (Benzo-TTFVO)<sub>2</sub>FeBr<sub>4</sub> at High Magnetic Field Laboratory of Osaka University.

## 3. Results and discussion

Figure 1 shows the magnetization curve of (Benzo-TTFVS)<sub>2</sub>FeBr<sub>4</sub> 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  $H_{c2} = 14.8$  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)<sub>2</sub>FeBr<sub>4</sub> 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  $H_{c2} = 36.2$  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)<sub>2</sub>FeBr<sub>4</sub>,  $H_E$  is 7.4 T and  $H_A$  is 0.22 T,

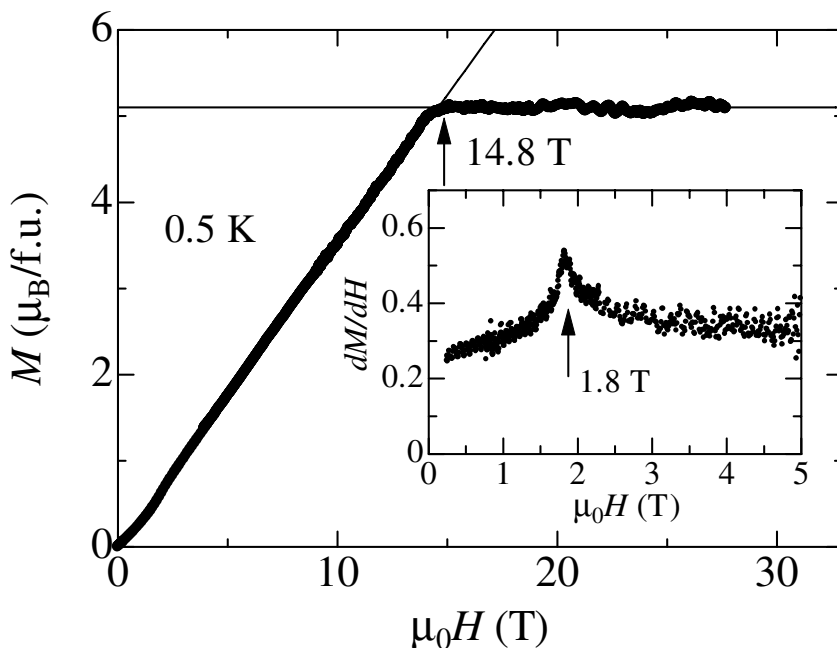


Figure 1. Magnetization curve of  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$  at 0.5 K. The saturation field of 14.8 T is indicated by an arrow. Inset shows the field dependence of the differential susceptibility in the lower field region. The peak indicated by an arrow corresponds to the spin-flop.

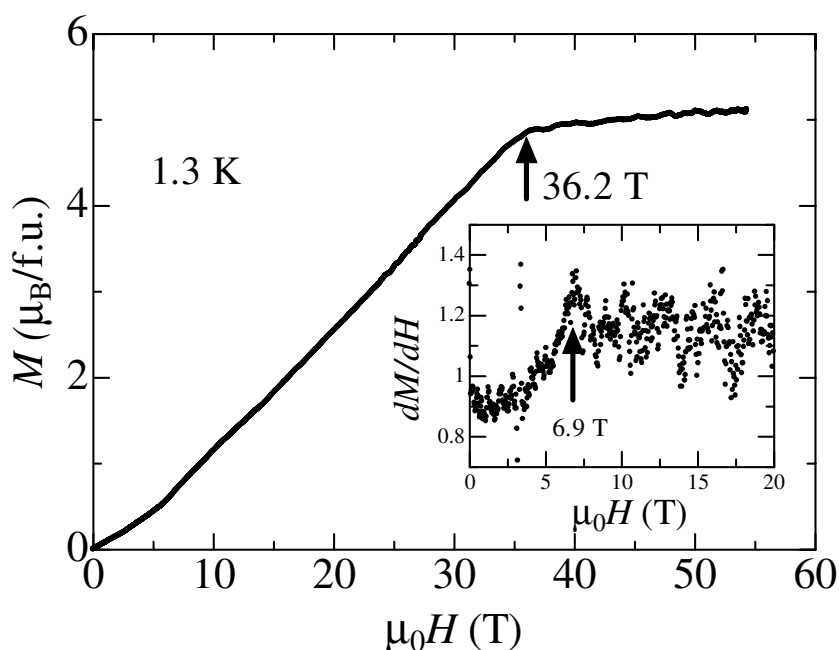


Figure 2. Magnetization curve of  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$  at 1.3 K. The saturation field of 36.2 T is indicated by an arrow. Inset shows the field dependence of the differential susceptibility in the lower field region. The peak indicated by an arrow corresponds to the spin-flop. while  $H_E$  is 18.1 T and  $H_A$  is 1.32 T in the case of  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$ . 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  $H = -2zJ\langle S \rangle S_i = g\mu_B H_E S_i$ , where  $J$  is the exchange integral,  $z$  being a number of the nearest neighbors,  $\langle S \rangle = 5/2$ ,  $g=2$ , and  $\mu_B$  is the Bohr magneton. The values of  $zJ$  are

estimated to be  $-0.17 \text{ meV} = -2.0 \text{ K}$  for  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$  and  $-0.41 \text{ meV} = -4.7 \text{ K}$  for  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$ .

Structural analysis reveals that the Br-Br contact distance ( $d_{\text{Br-Br}}$ ) between the  $\text{FeBr}_4^-$  ions along the intercolumn direction is very different between the salts.  $d_{\text{Br-Br}}$  for  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$  is  $4.10 \text{ \AA}$  comparable to the van der Waals one, while that for  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$  is  $4.01 \text{ \AA}$  shorter than the van der Waals one. For  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$ , both the d-d superexchange interaction between the  $\text{FeBr}_4^-$  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  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$ , which raises the  $T_N$  as well as the  $H_{c2}$  in the magnetization curve compared to those for  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$ .

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  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$  and  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$  is calculated to be 0.62, while the ratio of the  $H_{c2}$  between  $(\text{Benzo-TTFVS})_2\text{FeBr}_4$  and  $(\text{Benzo-TTFVO})_2\text{FeBr}_4$  is 0.40. There may exist key parameters in the different ratio so as to reveal the mechanism of these antiferromagnetic ordering.

### Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant No. 17540336).

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