Inorg. Chem. **2004**, *43*, 3780–3782

Inorganic Chemistry

Communication

Ferrimagnetic Ordering Due to Fe(III) d and Donor π Spins in (Ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide)$_2$·FeBr$_4$

Takuya Matsumoto,[†] Toyonari Sugimoto,*[,†,‡] Hiroko Aruga Katori,[‡,§] Satoru Noguchi,*[,‡,||] and Takekazu Ishida[‡,||]

*Research Institute for Advanced Science and Technology, Osaka Prefecture University,
Sakai, Osaka 599-8570, Japan, RIKEN (The Institute of Physical and Chemical Research),
Wako, Saitama 351-0198, Japan, Graduate School of Engineering, Osaka Prefecture University,
Sakai, Osaka 599-8531, Japan, and CREST, Japan Science and Technology Agency,
Kawaguchi, Saitama 332-0012, Japan*

Received February 5, 2004

Magnetization and heat capacity were measured down to 0.4 K in a 2:1 charge-transfer (CT) salt of a new donor molecule, ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide (**1**) with a magnetic FeBr$_4^-$ ion (**1**$_2$·FeBr$_4$). The Fe(III) d spins of FeBr$_4^-$ ions were subject to apparently ferromagnetic interaction with each other through the interaction with the π spins developed by localization of the conducting π electrons on the donor columns, eventually giving rise to ferrimagnetic ordering (FI) near 1 K, which provides the first example in a molecular π–d system.

To date, numerous charge-transfer (CT) salts have been prepared using several organic donor molecules and magnetic-metal anions, in which conducting π electrons and localized d (f) spins strongly interact and exhibit novel electrical conducting and magnetic properties.[1] Among them, FeCl$_4^-$, Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}^-$ ($0 < x < 1$, $0 < y < 0.5$), and Fe$_x$Ga$_{1-x}$Cl$_4^-$ ($0.35 < x < 0.5$) CT salts of bis(ethylenedithio)tetraselenafulvalene (BETS) were recognized as metal-to-insulator, superconductor-to-insulator, and superconductor-to-metal transitions, respectively, albeit at low temperatures as a result of the π−d interaction.[2−4] A ferromagnetic metal was achieved in the Mn/Cr oxalate-bridged CT salt of bis(ethylenedithio)tetrathiafulvalene,[5] but the ferromagnetism and metallic conductivity were based on each of the interactions between the conducting π electrons of donor molecules and between the localized d spins of Mn(II) and Cr(III) ions.

We recently synthesized a new CT salt, **1**$_2$·FeBr$_4$, which has a structure alternately stacked by layers of **1** molecules and FeBr$_4^-$ ions arranged in a square lattice.[6] Above 170 K, the electrical conductivity was metallic, but below 170 K the conductivity changed to a semiconductor with very small activation energy (<10 meV). The interaction between the Fe(III) d spins of FeBr$_4^-$ ions was very weak and antiferromagnetic (Weiss temperature, $\Theta = -3.9$ K) in such a higher temperature region than ca. 15 K that the conducting π electrons are supposed to survive, but the interaction apparently became ferromagnetic ($\Theta = +0.87$ K) below ca. 15 K and continued to 1.8 K, the lowest temperature used in this study. In correspondence to the change of this spin interaction, recent X-ray structure analyses of **1**$_2$·FeBr$_4$ in the temperature range of 6.5−300 K showed a marked increase in the contacts between **1** molecules and FeBr$_4^-$ ions and between the neighboring FeBr$_4^-$ ions in the crystal structure near 15 K.[7] The magnetization (M) curve approached saturation faster as the temperature decreased, but even at 1.8 K saturation was not accomplished at the magnetic field (H) of 5 T. The observed magnetization curve at 1.8 K showed a very good fit to the Brillouin function with $\Theta = +0.87$ K in the H's lower than 0.1 T, but above 0.1 T it approached saturation slower than the theoretical one as a result of the antiferromagnetic interaction of the π spins on the **1**-stacked columns with the Fe(III) d spins of FeBr$_4^-$ ions. In this communication we report that M and heat capacity (C) were measured down to 0.4 K for **1**$_2$·FeBr$_4$

---

* To whom correspondence should be addressed. E-mail:toyonari@riast.osakafu-u.ac.jp or noguchi@pe.osakafu-u.ac.jp.

[†] Research Institute, Osaka Prefecture University.

[‡] CREST, Japan Science and Technology Agency.

[§] RIKEN.

[||] Graduate School of Engineering, Osaka Prefecture University.

(1) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hurshouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209.

(2) Kobayashi, H.; Tomita, T.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368.

(3) Akutsu, H.; Arai, E.; Kobayashi, H.; Tanaka, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1997**, *119*, 12681.

(4) Kobayashi, H.; Saito, A.; Arai, E.; Akutsu, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1997**, *119*, 12392.

(5) Coronado, E.; Galán-Mascarós, J. R.; Gómez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447.

(6) Matsumoto, T.; Kominami, T.; Ueda, K.; Sugimoto, T.; Tada, T.; Noguchi, S.; Yoshino, H.; Murata, K.; Shiro, M.; Negishi, E.; Toyota, N.; Endo, S.; Takahashi, K. *Inorg. Chem.* **2002**, *41*, 4763.

(7) Matsumoto, T.; Sugimoto, T.; Inoue, K. Unpublished results.

10.1021/ic049851o CCC: $27.50

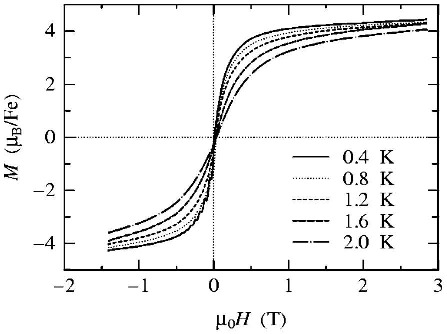

Figure 1. Magnetization (M) curves of $\mathbf{1}_2\cdot\mathrm{FeBr}_4$ at 0.4, 0.8, 1.2, 1.6, and 2.0 K. For clarity, the data is drawn one-way from +2.5 to −1.5 T.

and that the ferrimagnetic ordering (FI) due to Fe(III) d spins of FeBr_4^- ions and π spins of **1** molecules was accomplished near 1 K.

We measured the low-temperature M by an induction method down to 0.4 K using a pulse magnet system combined with a ^{3}He refrigerator. As Figure 1 shows, the M curve still reached saturation faster as the temperature decreased below 2 K. However, the degree of rapidity became very small between 1.2 and 0.4 K, suggesting that the M curve is completely saturated near the temperature range. A hysteresis was not observed in the M loop. To confirm the presence of FI and to determine the transition temperature (T_C), the data was analyzed using the Arrott method of M^2 vs H/M plot, which is advantageous especially for a high T_C. However, for FI with a low T_C and a small hysteresis loop, it is difficult to determine the T_C with the Arrott method since the Brillouin function shows a saturation behavior even for the paramagnetic state and the expansion of a magnetic free energy on M is only effective in very low H's. Thus, we developed a novel resonant circuit method to sensitively detect the M jump in a small hysteresis loop with ferromagnetic ordering or FI.[8] As shown in Figure 1, an oscillation initially appears below 1 K, when H changed from positive (negative) to negative (positive) and the magnitude of oscillation increased as the temperature decreased. A similar phenomenon was also observed in a sharp metamagnetic transition for $(\mathrm{Pr/Ca})\mathrm{MnO}_{3-\delta}$.[9] The oscillating behavior is clearer for bare signals induced in the M pickup coil. The inset of Figure 2 shows an example at 0.4 K. When H crosses zero, a sharp M jump occurs in a hysteresis loop, which causes a transient oscillation in the signal, and the corresponding frequency to the M jump crosses the resonant frequency of the circuit. Since the initial amplitude of the oscillation is proportional to the M jump, the amplitude was plotted against temperature and a steplike change was obtained (see Figure 2). This new method is more convenient than that of that of the Arrott plot to definitively determine T_C. If the T_C is defined as the midpoint of the steplike change, the value is determined to be 1.02 K.

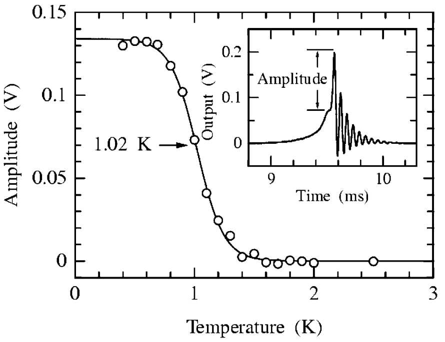

Figure 2. Temperature dependence of the oscillation amplitude. The solid curve is drawn by an empirically fitted function. Inset: Example of the signal voltage (amplitude = 0.13 V) measured at 0.4 K by the resonant circuit method.

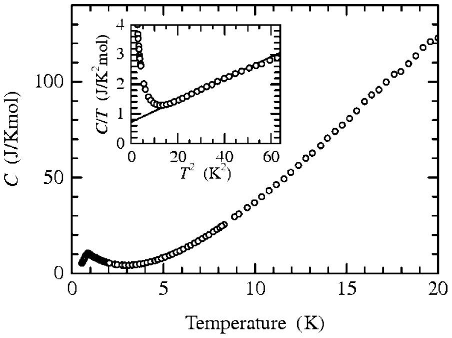

Figure 3. Temperature dependence of heat capacity (C) for $\mathbf{1}_2\cdot\mathrm{FeBr}_4$ under a zero magnetic field. Inset: C/T vs T^2 plot.

To confirm the T_C and to identify the type of FI, we measured the C by a thermal relaxation method down to 0.5 K using a ^{3}He cryostat (MagLab^{HC} microcalorimeter, Oxford Instruments). A clear peak was observed at 0.9 K, which is compatible with T_C determined from the M data. The lattice contribution was estimated from a linear relation in the C/T vs T^2 plot below 8 K, as shown in the inset of Figure 3. The parameters estimated from the slope and the intercept of the linear fitting are $\Theta_D = 145$ K and $\gamma = 724$ mJ K^{-2} mol^{-1}, respectively, where Θ_D is an averaged Debye temperature and γ is the heat capacity coefficient of the temperature-linear term, which gives the order of 1 mJ K^{-2} mol^{-1} in common metals due to the electronic contribution. However, under these conditions it is difficult to eliminate the electronic contribution from the data since the $\pi{-}$d interaction may form the strongly correlated electron system. By subtracting the lattice contribution from the experimental data, the magnetic heat capacity (C_{mag}) is obtained, but still includes the electronic contribution. Figure 4 shows this result. The shape of C_{mag} is not a λ-type anomaly as commonly observed in a second-order transition, but the cusp with a tail that extends to a high-temperature region, which is characteristic of the short-range or low-dimensional ordering in Heisenberg spin systems arranged in a two-dimensional square lattice.[10] Accordingly, the Fe(III) d spins of FeBr_4^- ions and the π spins of **1** molecules are in the two-dimensional FI state above T_C, but are converted to the three-dimensional FI below T_C. The magnetic entropy (S_{mag}) is calculated by integrating C_{mag}/T with respect to temperature (see also Figure 4). Compared to $R \ln 6$ and ($R \ln 6 + R \ln 2$) (R: gas constant), which correspond to the S_{mag}'s with $S = {}^5/_2$ of

---

(8) Noguchi, S.; Matsumoto, A.; Matsumoto, T.; Sugimoto, T.; Ishida, T. *Physica B* **2004**, *346−347*, 397.

(9) Noguchi, S.; Kawamata, S.; Ogomi, T.; Yamamoto, M.; Ishida, T. *J. Phys. Chem. Solids* **2003**, *64*, 2059.

(10) Bloembergen, P. *Physica B* **1977**, *85*, 51.

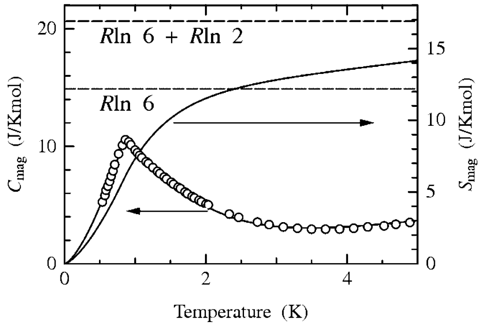

Figure 4. Magnetic heat capacity (C_{mag}) and magnetic entropy (S_{mag}) for $\mathbf{1}_2\cdot\mathrm{FeBr}_4$ as a function of temperature. A clear peak appears at 0.9 K. R ln 6 and (R ln 6 + R ln 2) correspond to S_{mag}'s with $S = {}^5/_2$ of Fe(III) d spins and with a total of $S = {}^5/_2$ and $S = 1/2$ of donor π spins, respectively.

Fe(III) d spins and with a total of $S = {}^5/_2$ and $S = {}^1/_2$ of donor π spins, respectively, the observed S_{mag} value is larger than R ln 6 but smaller than (R ln 6 + R ln 2) above 2.5 K, suggesting that the d spins coexist with the π spins of the donor columns, which provide an additional contribution to S_{mag}.

The temperature dependence of C under several H's of 0−1 T was also investigated (see Figure 5). H was perpendicularly applied to the plane of the FeBr_4^- square lattice. The C showed strong H dependence, i.e., a round peak that gradually shifted to the higher temperature side as H increased. This round peak is due to the magnetic Schottky anomaly caused by the Zeeman splitting of the degenerated ground state under the H's. This H dependence is very similar to that in other ferro- and ferrimagnetic materials such as *p*-nitrophenyl nitronyl nitroxide[11] and Cu(3-chloropyridine)$_2$-(N$_3$)$_2$,[12] but is in marked contrast to antiferromagnets such as a κ-type of CT salt of BETS with FeBr_4^- ion, which displays less H dependence.[13]

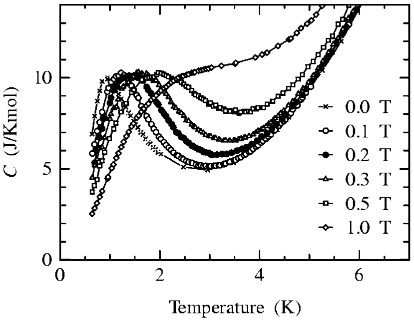

Figure 5. Temperature dependence of C for $\mathbf{1}_2\cdot\mathrm{FeBr}_4$ under several H's of 0.0, 0.1, 0.2, 0.3, 0.5, and 1.0 T.

In conclusion, this new CT salt of $\mathbf{1}_2\cdot\mathrm{FeBr}_4$ provides the first example of FI for the Fe(III) d spins of FeBr_4^- ions and the π spins of **1** molecules by virtue of π−d interactions, which typically prefer antiferromagnetic interactions or ordering. However, the mechanism of this FI still remains unclear, since there are open questions of (1) degree of localization of the conducting π electrons on the **1**-stacked column near 1 K, (2) distribution of localized charges and spins on the **1** molecules within each column and on each **1** molecule, and (3) parallel alignment of the Fe(III) d spins of FeBr_4^- ions through the interaction with the π spins of **1** molecules within each layer and between the layers. We are currently investigating the π−d interaction in this CT salt under high pressures, where the metallic conductivity might be maintained, and also in the CT salts of new donor molecules, which have magnetic-metal properties similar to **1**.

IC049851O

---

(11) Nakazawa, Y.; Tamura, M.; Shirakawa, N.; Shiomi, D.; Takahashi, M.; Kinoshita, M.; Ishikawa, M. *Phys. Rev. B* **1992**, *46*, 8906.

(12) Hagiwara, M.; Minami, K.; Katori, H. A. *Prog. Theor. Phys. Suppl.* **2002**, No. 145, 150.

(13) Fujiwara, H.; Fujiwara, E.; Nakazawa, Y.; Narymbetov, B. Zh.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **2001**, *123*, 306.