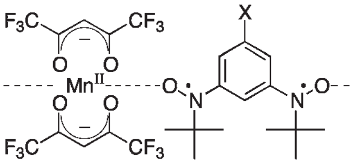
Pressure-induced Metamagnetic Behavior in a Quasi-One-Dimensional Molecule-based Ferrimagnet

Kentaro Suzuki, Yuko Hosokoshi,* and Katsuya Inoue*
School of Mathematical and Physical Science, The Graduate University for Advanced Studies, 38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585
Institute for Molecular Science, 38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585

(Received November 26, 2001; CL-011186)

Pressure effects on a molecule-based ferrimagnet of $[Mn(hfac)_2]\cdot(Br\text{-}BNO)$ (**1**) were studied, where hfac = hexafluoroacetylacetonate and Br-BNO = 5-bromo-1,3-bis(*N-tert*-butylaminoxyl)benzene. At ambient pressure, **1** is a ferrimagnet with $T_C = 5.4$ K. We observed the metamagnetic behavior of **1** under pressure.

The family of π-conjugated oligo(*N-t*-butylaminoxyl) radicals constructs the magnet by the complexation with $Mn(hfac)_2$ in a systematic way. We can obtain one-, two- and three-dimensional ferrimagnets with the antiferromagnetic exchange coupling on the Mn^{2+}–aminoxyl coordination.[1] In the case of 1,3-bis(*N-t*-butylaminoxyl)benzene (BNO), the complexation in 1 : 1 ratio with $Mn(hfac)_2$, yields a one-dimensional chain composed of the alternant alignment of BNO ($S = 1$) and Mn^{2+} ($S = 5/2$), that is, a one-dimensional ferrimagnetic chain.[2] Substitution of a halogen atom at 5-position of BNO results in the same chain structure with the same coordination geometry. The difference appears in the molecular packing between the chains. Due to the weak interchain interactions, three-dimensional magnetic phase transition occurs. In the complexes of $[Mn(hfac)_2]\cdot(BNO)$ (**2**) and $[Mn(hfac)_2]\cdot(F\text{-}BNO)$ (**3**), metamagnetic phase transitions occur at $T_N = 5.4$ and 5.2 K, respectively, due to the weak interchain antiferromagnetic interactions. On the other hand, the interchain interactions in $[Mn(hfac)_2]\cdot(Cl\text{-}BNO)$ (**4**) and $[Mn(hfac)_2]\cdot(Br\text{-}BNO)$ (**1**) are ferromagnetic. These complexes undergo ferrimagnetic phase transitions at $T_C = 4.8$ and 5.4 K, respectively. The different sign of the interchain interactions is attributed to the difference in the interchain molecular packing.



X = H; **2**, F; **3**, Cl; **4**, Br; **1**

We have recently started to study the pressure effects on the family of $[Mn(hfac)_2]\cdot(X\text{-}BNO)$, aiming to tune the interchain interactions. Continuous change of the lattice under pressure will provide us with the nature and path of the interchain magnetic exchange interactions. For the metamagnet of **2**, we briefly reported the enhancement of the interchain antiferromagnetic interactions with increasing pressure, which is proved by the higher T_N and the critical field (H_C).[3] In the same paper, we also noted the complicated results of the magnetism of **4** at 7 kbar. Both antiferromagnetic and ferromagnetic portions were observed as the interchain interactions in **4** under pressure. In the present paper, we will report the pressure effect on the magnetic properties of the quasi-one-dimensional ferrimagnet of **1**. In this compound, metamagnetic behavior is observed under pressure.

The complex of **1** is obtained by a conventional method.[2] Magnetic measurements were done using Quantum Design MPMS-2 and MPMS-5S SQUID magnetometers. For the measurements under pressure, sample is mounted in a small pressure-clamp cell made of Cu-Ti alloy with a pressure transmitting medium of fomblin oil (Montefluos, H-VAC140/13).[4] Ac magnetic susceptibility (χ_{ac}) was measured under an ac field of 1 Hz and 5 Oe.

Figure 1(a) shows the temperature dependence of χ_{ac} of **1** at ambient pressure ($p = 0$). The divergence of the real component (χ') at 5.4 K is noticeable. The imaginary component (χ'') appears at 5.4 K and increases as temperature decreases. In the magnetization isotherms, rapid saturation is observed as is shown in Figure 1(b). From these, ferrimagnetism of **1** with $T_C = 5.4$ K is evident at $p = 0$. The behavior under 2 kbar ($p = 2$) is similar to that at $p = 0$. The divergence of χ' at 5.8 K is seen. When we apply the pressure larger than 3 kbar ($p \geq 3$), the magnetic behavior changes. The temperature dependence of χ_{ac} and the magnetization isotherms under pressure are shown in Figure 1(c)–(f). The remarkable difference is the maximum in the temperature dependence of χ' and χ''. In the temperature dependence of χ_{ac} at $p = 3.5$, both χ' and χ'' show peaks at 5.3 K (Figure 1(c)). At $p = 7$, the values of χ' and χ'' take maxima at 4.5 K (Figure 1(e)). The observed maximum in χ_{ac} is understood as the metamagnetic phase transition when the magnetization isotherms are taken into account. The shape of the magnetization isotherms at $p \geq 3$ is different from the one at $p = 0$. The characteristic is the concave shaped curve which is clearly seen in the magnetization isotherm at 1.8 K at $p = 7$ (Figure 1(f)). The bending of the magnetization isotherms at $p = 7$ is seen below 4.5 K, at which χ_{ac} takes a maximum. This bending in magnetization is related to the spin-flip in a metamagnet. At $p = 3.5$, the slope of the magnetization curve below 20 mT at 1.8 K is smaller than the one at 4.5 K. This behavior is also related to the small critical field of metamagnetism, H_C. As increasing p, the enhancement of H_C is observed.

Now, let's look back to Figure 1(e). In the temperature dependence of χ' at $p = 7$, there is a shoulder at 5.8 K, in addition to the peak at 4.5 K. It must be noted that χ'' appears at 7.2 K. At $p = 3.5$ also, χ'' appears at considerably higher temperature (6.8 K) than the maximum of 5.3 K, as is shown in Figure 1(c). The shoulder of χ' at $p = 7$ and the non-zero value of χ'' is related to the formation of the ferro/ferrimagnetic domains by the short-range magnetic correlation. Field depen-

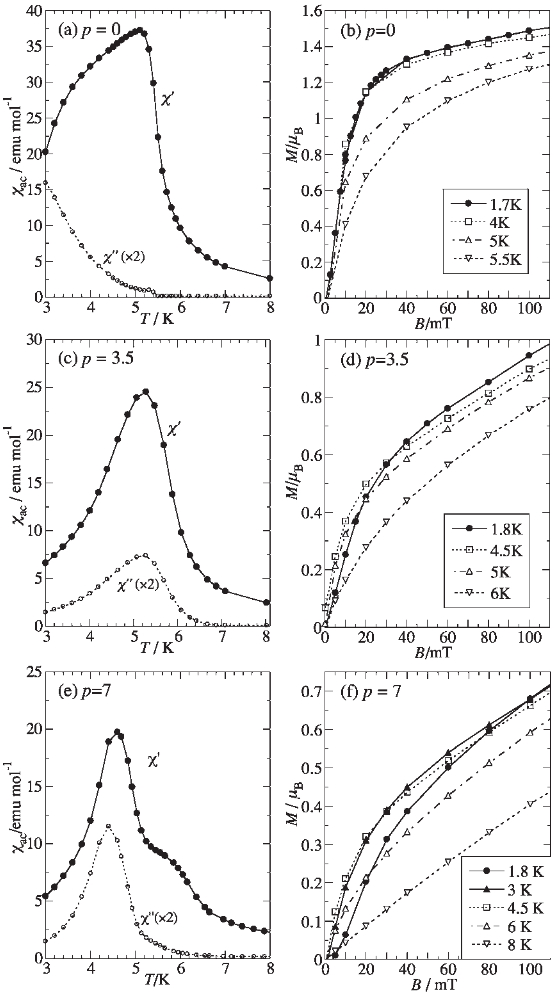


Figure 1. Temperature dependences of the ac magnetic susceptibility and magnetization isotherms of **1** at several pressures: (a); (b) at ambient pressure, (c); (d) at 3.5 kbar, (e); (f) at 7 kbar.

dent behavior of χ_{ac} is observed below this temperature. The temperature at which χ'' appears is slightly elevated as increasing p.

Here, we discuss the pressure effects on the magnetic interactions in **1**. In the family of [Mn(hfac)$_2$]·(X-BNO), ferrimagnetic chains elongate along the b-axis with a two-fold screw symmetry. (The space group is $P2_1/n$.) The nearest neighboring chains are seen along the a-axis. In this direction, F···F contacts between hfac molecules exist in **2**, whereas Br···F contacts between Br-BNO and hfac are noticeable in **1**. Substitution of halogen atoms affects also the molecular arrangements along the c-axis: the Mn···Mn and/or BNO···B-NO sequence is seen in **2**, whereas the alternate arrangement of Mn and Br-BNO is realized in **1**. At ambient pressure, the interchain magnetic exchange couplings in **1** are both ferromagnetic along the a- and c-axes. We guess that one of the magnetic exchanges is reduced in magnitude and is transformed to antiferromagnetic one with increasing p. This change causes the metamagnetic behavior of **1** at $p \geq 3$. The formation of ferro/ferrimagnetic domains is probably due to another interchain ferromagnetic exchange, which is unchanged or slightly enhanced under pressure. In the complex **4** under pressure, the ferromagnetic and antiferromagnetic interchain interactions are much competing with each other. This is probably due to the different size of the halogen atoms.

In conclusion, we observed the pressure-induced crossover between ferrimagnetic and metamagnetic states of **1** at $p \geq 3$. The change of the ground state properties is attributed to the change of the relative molecular arrangement of the chain structures under pressure. The pressure-induced change from ferromagnetic to antiferromagnetic states, is also reported in genuine organic ferromagnets, β-p-NPNN and p-Cl-C_6H_4-CH=N-TEMPO.[5] The present case is ferrimagnetic one and the situation would be more complicated. However, in the present case, we have a series of compounds with similar structures. In the family of [Mn(hfac)$_2$]·(X-BNO), the crystal structure in the extreme limit of ferrimagnet or metamagnet is known. By a systematic study on the family with making reference to one another, we can get insight into magneto-structural correlations and mechanism of the magnetic exchange interactions in molecule-based magnets. The detailed pressure dependence study on the family is now under way.

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (B) of Field-Induced New Quantum Phenomena in Magnetic Systems (No. 13130202) and for Encouragement of Young Scientists (No. 12740389) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 K. Inoue, in "π-Electron Magnetism: From Molecules to Magnetic Materials," ed. by J. Veciana, Springer, Berlin (2001), Structure and Bonding, Vol. 100, p 61; H. Iwamura and K. Inoue, in "Magnetism: Molecules to Materials II," ed. by J. S. Miller and M. Drillon, Wiley-VCH, Weinheim (2001), p 61.

2 K. Inoue and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, **1994**, 2273; K. Inoue, F. Iwahori, A. S. Markosyan, and H. Iwamura, *Coord. Chem. Rev.*, **198**, 219 (2000).

3 Y. Hosokoshi, K. Suzuki, K. Inoue, and H. Iwamura, *Mol. Cryst. Liq. Cryst.*, **334**, 511 (1999).

4 Y. Hosokoshi, M. Tamura, and M. Kinoshita, *Mol. Cryst. Liq. Cryst.*, **306**, 423 (1997); Y. Hosokoshi, M. Mito, M. Tamura, K. Takeda, K. Inoue, and M. Kinoshita, *Rev. High Pressure Sci. Tech.*, **7**, 620 (1998).

5 K. Takeda, M. Mito, T. Kawae, M. Takumi, K. Nagata, M. Tamura, and M. Kinoshita, *J. Phys. Chem. B*, **102**, 671 (1998); M. Mito, T. Kawae, M. Hitaka, K. Takeda, T. Ishida, and T. Nogami, *Chem. Phys. Lett.*, **333**, 69 (2001).