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FERROMAGNETIC AND ANTIFERROMAGNETIC BEHAVIOR OF 4-METHACRYLOYLOXY- AND 4-ACRYLOYLOXY-2,2,6,6-TETRAMETHYLPIPERIDINE-1-OXYL

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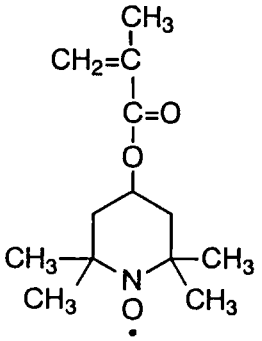
Abstract The magnetic properties of 4-methacryloyloxy- and 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MOTMP and AOTMP, respectively) were studied. The magnetic susceptibility, magnetization, and molar heat capacity of MOTMP show that the crystal has one-dimensional ferromagnetic coupling, and that the coupling between the one-dimensional coupling chains was antiferromagnetic, resulting in a metamagnet below 0.16 K. On the other hand, AOTMP, where hydrogen atom is substituted for a methyl group at α-position, shows an antiferromagnetic coupling between the nitroxyl radicals.

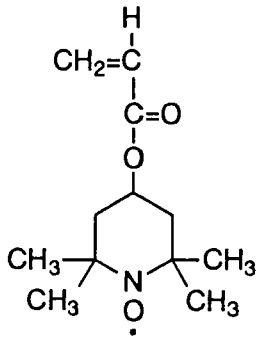
INTRODUCTION

In our earlier work on the magnetic behavior of polymers of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MOTMP) and 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (AOTMP), antiferromagnetic interaction was found to be operative between the pendant radicals.[1-2] The reciprocal magnetic susceptibilities of these polymers followed the Curie-Weiss law, whose Weiss constants θ were -2- -3 K. The comparison of the magnetic behavior between polymers and the corresponding monomers suggested a possibility of ferromagnetic

interaction below 20 K in the case of MOTMP. However, we did not investigated the origin of the ferromagnetic interaction, because the magnetic interaction was much weaker than that of MOTMP-polymer.



MOTMP



AOTMP

The existence of ferromagnetic interaction of electron spins in organic free radicals has been confirmed by several groups. About ten years ago, bis(2,2,6,6-tetramethyl-piperidine-4-yl-1-oxyl)suberate (TANOL suberate) was found to have two-dimensional ferromagnetic coupling, and the coupling between the planes was antiferromagnetic, resulting in a metamagnet below 0.39 K.[3-4] Recently, Kinoshita *et al.* investigated the magnetic properties of 2-(4'-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-N-oxide (p-NPNN), and showed that ferromagnetic interaction was operative between the adjacent radicals.[5-7] More recently, β- and γ-phase crystals of p-NPNN were reported to be bulk ferromagnets.

We reinvestigated the magnetic properties for MOTMP and AOTMP. The measurements of magnetic susceptibility, magnetization, and molar heat capacity indicated that MOTMP had one-dimensional ferromagnetic coupling J_F (J_F/k_B = 0.45 K, k_B: Boltzmann constant), and the coupling between the one-dimensional ferromagnetic chains was antiferromagnetic, resulting in a metamagnet below about 0.16 K. On the other hand, AOTMP, which has no methyl group, showed antiferromagnetic interaction. Intermolecular magnetic coupling in these radicals changed from antiferromagnetic to ferromagnetic by substituting hydrogen at α-position with a methyl group.

In this paper, we describe the magnetic properties of MOTMP and AOTMP. Furthermore, their magnetostructural correlations are discussed on the basis of results of the X-ray structure analysis.

EXPERIMENTAL

MOTMP and AOTMP were synthesized by the same method as shown previously.[1,8] The gram magnetic susceptibility χ_g for MOTMP and AOTMP was determined by the Gouy method at room temperature using distilled water as a standard. The temperature dependence of χ_g was determined by the Faraday method, using a Cahn 1000 electrobalance in the temperature range between 2.5 and 300 K. The molar magnetic susceptibility χ_p of the materials was calculated by the following equation.

$$\chi_p = \chi_g \cdot M - \chi_{dia} \quad (1)$$

where M is the molecular weight of the material. Magnetic susceptibility at very low temperature was determined by the a.c. method in the range from 0.07 to 1.2 K.

Heat capacity measurements were carried out for MOTMP in the temperature range from 0.07 to 25 K by use of an adiabatic calorimeter working with a $^3He/^4He$ dilution refrigerator.[9]

X-ray structure analyses for MOTMP and AOTMP at room temperature were made on a Rigaku AFC5R diffractometer using graphite monochromated Mo K_α radiation and a 12 kW rotating anode generator. The dimensions for the analyzed crystals were 0.2 x 0.1 x 0.5 mm for MOTMP and 0.2 x 0.2 x 0.3 mm for AOTMP. All calculations were performed using TEXAN crystallographic software package of Molecular Structure Corporation.

RESULTS AND DISCUSSION

Magnetic susceptibility

The molar paramagnetic susceptibility χ_p followed the Curie-Weiss law, with the Weiss constant +0.2 K and -1.2 K for MOTMP and AOTMP, respectively.[10]

Fig. 1 shows the temperature dependence of χ_pT as a function of temperature. The values χ_pT for MOTMP are fairly constant above about 50 K, but they gradually increase with lowering the temperature, indicating the presence of a weak ferromagnetic interaction. The temperature dependence of AOTMP was quite different from that of MOTMP. The values χ_pT for AOTMP decrease monotonously with lowering the temperature, indicating the existence of an antiferro-

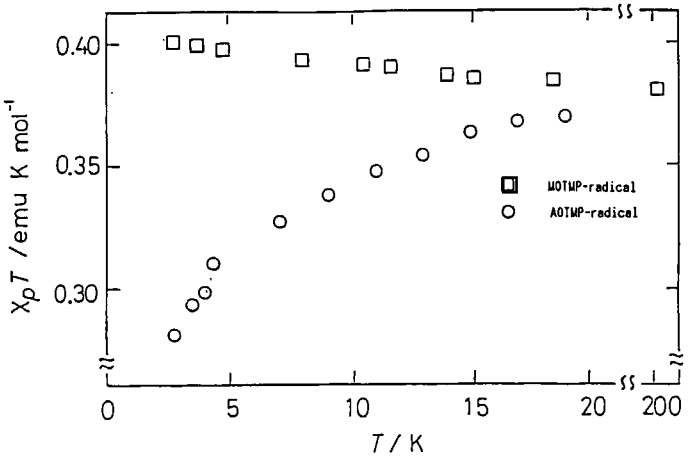


FIGURE 1 Temperature dependence of $\chi_p T$ for MOTMP and AOTMP as a function of temperature.

magnetic interaction. Fig. 2 shows the temperature dependence of χ_p and its reciprocal in the range from 0.07 K to 1.2 K.

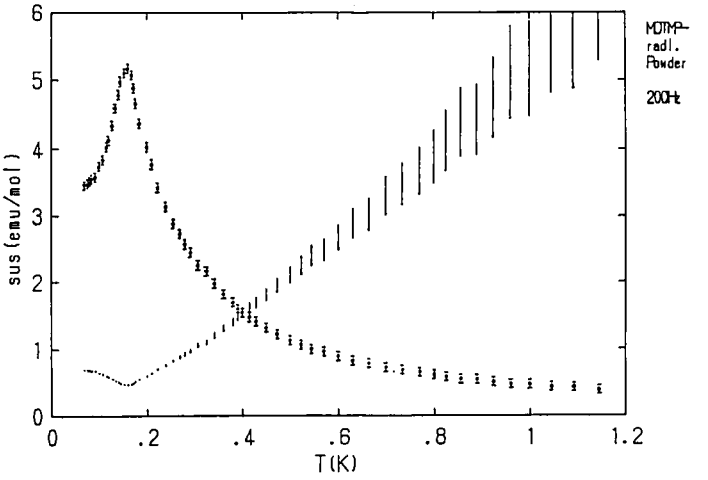


FIGURE 2 Temperature dependence of χ_p and its reciprocal for MOTMP at very low temperature.

The Weiss constant θ was determined to be +0.16 K by extrapolation in the latter. This finding shows the existence of ferromagnetic interaction. In the former, however, χ_p shows a maximum at 0.16 K, which is Néel point, and converges to the 2/3 of the maximum with lowering the temperature below this temperature. No magnetic hysterisis was observed at 0.07 K. These findings show that MOTMP is

probably metamagnet below 0.16 K. Fig. 3 shows the magnetization curve as a function of the external field H_{ext}. At the temperature higher than 0.16 K, magnetization increased as H_{ext} increased. Below the transition temperature, however, the magnetization curve has the

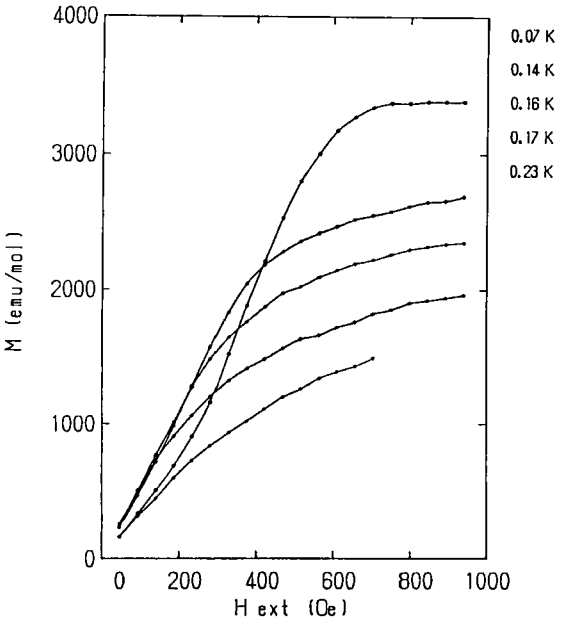


FIGURE 3 Magnetization curve as a function of the external field for MOTMP at very low temperature.

S-shape characteristic of metamagnets. This behavior is similar to that found in the metamagnet.[3,11] The critical field, where the magnetization increases abruptly, is relatively small(H_{ext} ~330 Oe), indicating that the antiferromagnetic interaction is quite weak.

Molar Heat Capacity for MOTMP

In order to understand the magnetic behavior of MOTMP more precisely, the molar heat capacity was measured. Fig. 4 shows the temperature dependence of the molar heat capacity C_p. A sharp peak due to the magnetic transition is observed at about 0.14 K. This temperature is reasonable, as it is almost consistent with the Weiss temperature estimated on Fig. 2. Furthermore, there is a broad hump centered around 0.4 K. Fig. 5 shows the temperature dependence of the molar heat capacity C_p on a double-logarithmic scale. The hump was clearly observed by subtracting the lattice heat capacity estimated by curve 1. This hump fits well with the high-temperature expansion of

the S = 1/2 one-dimensional Heisenberg model using Pade approximation.[12] And the exchange interaction in the one-dimensional chain J_F was estimated to be J_F/k_B = 0.45 K (k_B: Boltzmann constant).

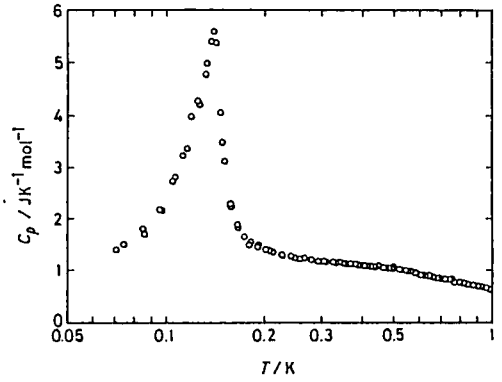


FIGURE 4 Temperature dependence of the molar heat capacity of MOTMP.

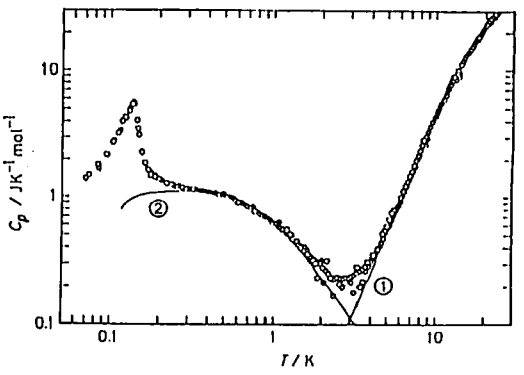
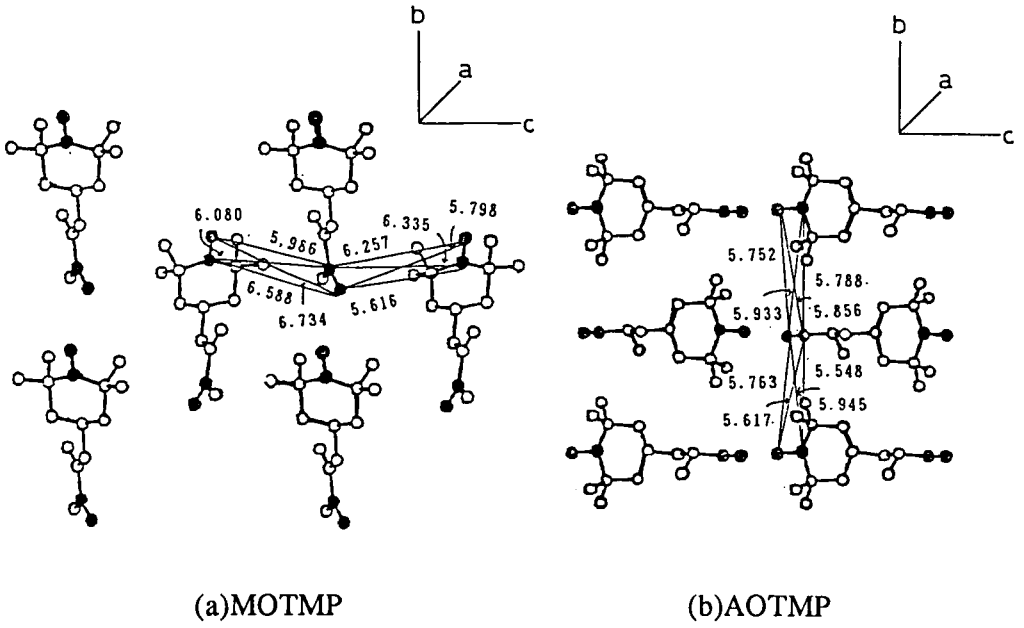


FIGURE 5 Molar heat capacity for MOTMP at very low temperature. Curve① Lattice heat capacity, and curve② one-dimentional Heisenberg ferromagnet.



(a)MOTMP (b)AOTMP

FIGURE 6 The projections of the crystal structure of the *bc*-plane for (a)MOTMP and (b)AOTMP.

X-ray Structure Analyses

In order to understand the origin of the one-dimensional ferromagnetic coupling of MOTMP, X-ray structure analysis was performed. For comparison, structure analysis was also performed for AOTMP. Crystal data for MOTMP and AOTMP are shown in Table I. Both crystals were monoclinic and had $P2_1$ symmetry. Lengths of *a*-axis are almost the same in both crystals. Since lengths of *b*-axis and *c*-axis of MOTMP are almost the same as those of *c*-axis and *b*-axis of AOTMP, respectively, unit cells of both monomers seem to have quite similar structure. Fig. 6 shows the projection of the crystal structure of MOTMP and AOTMP on the *bc* plane.

Table I Selected Crystallographic Parameters for MOTMP and AOTMP.

	MOTMP	AOTMP
space group	monoclinic, $P2_1$	monoclinic, $P2_1$
a, Å	6.071(2)	5.965(2)
b, Å	9.770(2)	11.254(2)
c, Å	11.828(1)	9.677(2)
β, deg	101.82	98.93
Z	2	2
R/R_W value	0.056/0.058	0.072/0.094

The difference in crystal structure between AOTMP and MOTMP was observed in their relative orientation. In MOTMP, all monomers are parallel to *b*-axis, while AOTMP is antiparallel to *c*-axis. The difference in magnetic behavior between AOTMP and MOTMP might be ascribed to the difference in the mutual orientation of both monomers.

CONCLUSION

The measurements of magnetic susceptibility, magnetization and heat capacity, are summarized as follows.

(1) Ferromagnetic interaction J_F is operative in a one-dimensional chain, and J_F/k_B = 0.45 K (k_B: Boltzmann constant).

(2) χ_p shows a maximum at 0.16 K. If MOTMP is a bulk ferromagnet, such a peak should not be observed. This fact shows that the magnetic interactions between the one-dimensional chains are antiferromagnetic. From the measurement of molar heat capacity, these antiferromagnetic

interactions seem to be weaker than J_F. Therefore, MOTMP can be concluded to be a metamagnet below 0.16 K.

The X-ray structure analysis of single crystals of MOTMP and AOTMP suggests that the intermolecular exchange interaction changed from antiferromagnetic to ferromagnetic by changing the relative orientation of the nitroxyl radicals.

ACKNOWLEDGMENTS

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