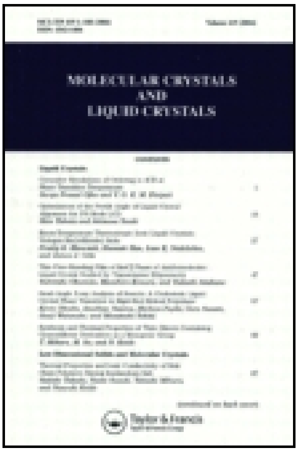

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Magnetic Properties of 1,5-Dimethylverdazyl Radical Crystals. Finding of New Organic Ferromagnet, p-CDTV

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MAGNETIC PROPERTIES OF 1,5-DIMETHYLVERDAZYL RADICAL CRYSTALS. FINDING OF NEW ORGANIC FERROMAGNET, *p*-CDTV

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Abstract Magnetic properties of organic radical crystal, 3-(4-chlorophenyl)-1,5-dimethyl-6-thioxoverdazyl (*p*-CDTV), have been studied by measuring heat capacity and ac susceptibility above 0.13 K in external magnetic fields of 0-30 kOe. The *p*-CDTV has been found to be a new and bulk ferromagnet with the second highest Curie temperature T_C=0.68 ± 0.02 K of genuine organic ferromagnet. The *p*-CDTV behaves as a quasi-one-dimensional Heisenberg ferromagnet with the intrachain exchange interaction of $2J/k_B$=+12.0±0.6 K above the transition temperature T_c. The interchain exchange interaction zJ'/k_B was estimated to be +0.21±0.02 K, where z is the number of interchain bonds per spin.

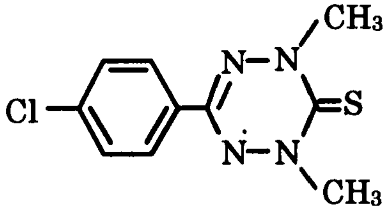
INTRODUCTION

The search for ferromagnetic organic radical crystals has been one of the most challenging problems in the field of material science.[2-4] Recently, several examples of organic bulk ferromagnets composed only of light elements such as H, C, N, and O have been reported, e.g. the *p*-nitrophenylnitronyl nitroxide radical (T_C=0.60 K),[5] a nitroxide biradical (T_C=1.48 K),[6] two nitroxide monoradicals (T_C=0.18 K and 0.4 K),[7] and a nitronyl nitroxide radical with a hydroquinone moiety (T_C=0.5 K).[8] The Curie (transition) temperatures (T_C) observed, however, are very low as compared to those of typical transition metals (T_C=1043 K for Fe, T_C=1388 K for Co, and T_C=627 K for Ni). Further, the examples of organic ferromagnets are limited to nitroxide and nitronyl nitroxide radicals. Therefore, the search for new kinds of organic ferromagnets with a high Curie temperature remains to be a matter of high interest.

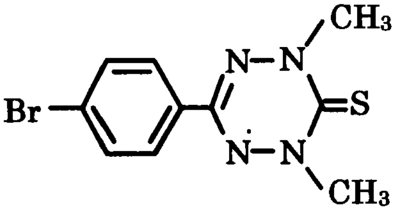
The synthesis and ESR study of a series of 1,5-dimethyl-6-oxo- and thioxoverdazyl radicals have been performed by Neugebauer et al.[9] These verdazyl radicals have a delocalized π-electron system, differing from nitroxide and nitronyl nitroxide radicals with a π-electron system localized in the part of NO group. Further, these verdazyl radicals have comparatively small molecular weight. Consequently, we can expect a strong intermolecular exchange interaction between neighboring radical molecules.

In a previous paper, we measured the static magnetic susceptibilities, χ_M, of 3-(4-chlorophenyl)-1,5-dimethyl-6-thioxoverdazyl (*p*-CDTV) and 3-(4-bromophenyl)-1,5-dimethyl-6-thioxoverdazyl (*p*-BDTV), which have similar molecular structure to each other, in the temperature range of 4-300 K, using a SQUID magnetometer[10]. The χ_M of *p*-CDTV follows the Curie-Weiss law with a Curie constant of 0.381 K emu/mol and a positive Weiss constant of $\theta = +3.2 \pm 0.2$ K, suggesting intermolecular ferromagnetic exchange interaction between neighboring radicals. On the other hand, the χ_M of *p*-BDTV follows the Curie-Weiss law with a Curie constant of 0.381 K emu/mol and a negative Weiss constant of $\theta = -25 \pm 2$ K above 80 K. At lower temperatures, the susceptibility deviates from the Curie-Weiss law and exhibits a broad maximum at 26.5 ± 0.5 K. This susceptibility can be explained by the one-dimensional (1D) Heisenberg model with negative exchange interaction of $2J/k_B = -41.3$ K.

In the present work, in order to clear the low temperature magnetic property of *p*-CDTV, the simultaneous measurements of heat capacity and ac magnetic susceptibility of *p*-CDTV radical crystal have been performed above 0.13 K under the external field of 0-30 kOe.



p-CDTV



p-BDTV

EXPERIMENTAL

Measurement of heat capacity.

Heat capacities, C_p, were measured above 0.2 K in the external magnetic field of 0-30 kOe, using the usual type of adiabatic calorimeter, whose detailed description was previously reported.[11] The data were taken on a 0.3136 g powder sample of *p*-CDTV, and have been corrected for the heat capacity of the addenda.

Measurement of ac magnetic susceptibility.

In the temperature range of 1.7-300 K, the ac susceptibility (χ) measurements were performed using the Lake Shore 7110 ac susceptometer. The relaxation effects of the susceptibility were checked under various ac fields H(ν) and frequencies (ν), as will be discussed later. On the other hand, in the temperature range between 0.13 and 2.0 K, the ac susceptibility measurements were also performed by the use of a handmade Hartshorn bridge in the ac field of about 100 mOe at 164 Hz. The field dependence of the ac susceptibility was also studied under the external magnetic field of 0-2 kOe applied parallel to the ac field.

RESULTS

The ac susceptibility of *p*-CDTV was measured in the temperature region between 1.7 and 300 K, using the Lake Shore 7110 ac susceptometer. For the check of the relaxation

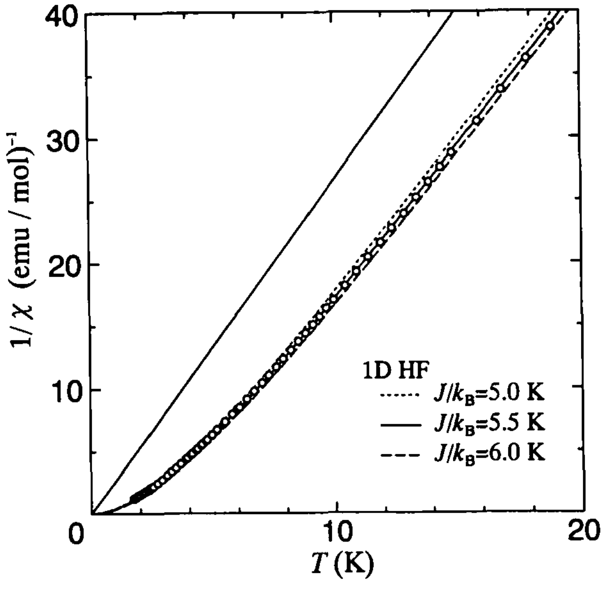


FIGURE 1 Inverse magnetic susceptibility, $1/\chi$, of *p*-CDTV at low temperatures. Above 5 K, the observed values (open circles) obey the theoretical results for the 1D isotropic Heisenberg ferromagnet (HF) with J/k_B=+5.5 ± 0.5K.[12] The straight line corresponds to χ of the paramagnet with g=2.00 and S=1/2.

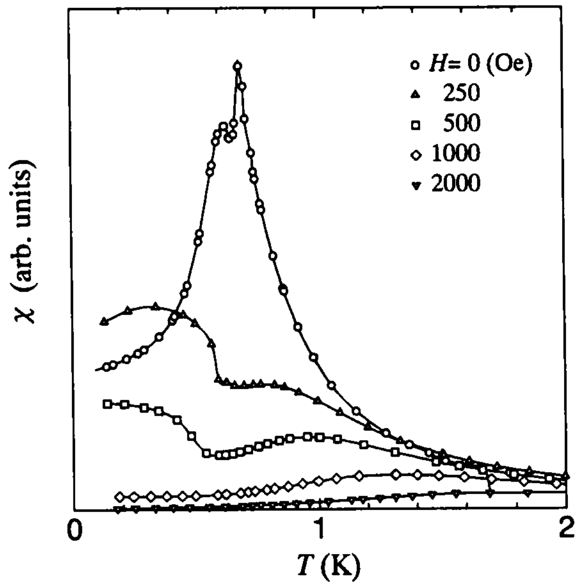


FIGURE 2 External field dependence of the ac magnetic susceptibility, χ, of *p*-CDTV.

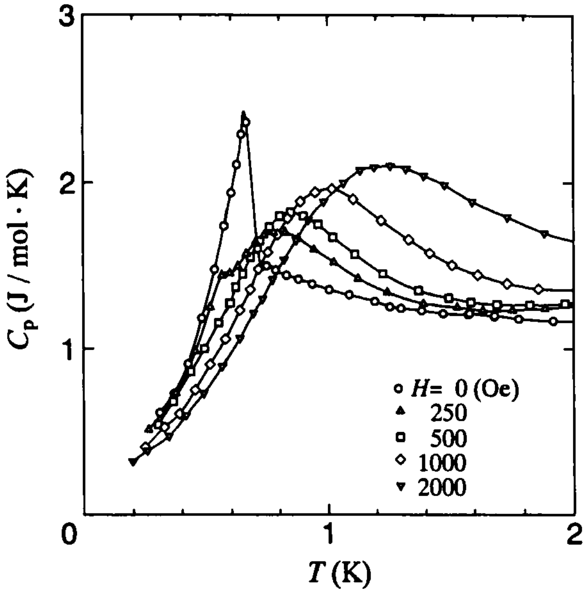


FIGURE 3 External field dependence of the heat capacity, C_p, of *p*-CDTV.

effects on the magnetic susceptibility, the measurements were performed by varying the ac fields H(ν)=0.1, 0.5, 2, 4, and 10 Oe (peak to peak) and frequencies ν =5, 25, 125, 500 and 1000 Hz. No relaxation effects were observed in the present experimental condition down to 1.7 K. The data have been corrected for the diamagnetic contribution of $\chi_{\text{dia}}=-0.133\times10^{-3}$ emu/mol, calculated by Pascal›s method. Above 20 K, the ac susceptibility of *p*-CDTV follows the Curie-Weiss law with a positive Weiss constant of +3.0 ± 0.2 K, indicating dominant ferromagnetic exchange interaction between neighboring radical molecules. A plot of $1/\chi$ against T is no longer linear at lower temperature (<20 K), as shown in Fig. 1. Such a magnetic behavior is characteristic of a ferromagnetic substance.

The low temperature ac susceptibility, χ, of the *p*-CDTV was also measured down to about 0.1 K at $H(\nu)<10$ Oe (ν =164 Hz), using the Hartshorn bridge method. As shown in Fig. 2, the susceptibility of *p*-CDTV increases rapidly below 1 K and reaches a maximum at T=0.68 K under zero external field. The appearance of the peak of the susceptibility may be due to the time-dependent effects of the ac method.[6] At low temperatures, the susceptibility seems to reach a limitting value which corresponds to the inverse of demagnetization field factor for a ferromagnet. As is seen in Fig. 2, the fluctuation of the magnetic moments is supressed by the external fields and the peak becomes smaller. Below 0.5 K, the susceptibility shows a plateau which seems to be a character in the ferromagnetically ordered state, as demonstratively seen in the results for the field 500 Oe. The small hump around 1 K is due to the one-dimensional short range ordering effects in the paramagnetic region. The susceptibility for the higher fields than 1000 Oe is almost supressed as observed in the case of the ferromagnetic *p*-nitrophenylnitronyl nitroxide (*p*-NPNN) (β -phase).[5b] The result suggests that the *p*-CDTV crystal undergoes a bulk ferromagnetic transition at 0.68 K.

Heat capacity measurement of *p*-CDTV has been performed between about 0.2 K and 10 K under the external fields of H=0, 0.25, 0.50, 1, 2, 5, 10, 20 and 30 kOe. As shown in Fig. 3, C_p of *p*-CDTV exhibits a sharp λ -like peak at 0.67±0.02 K in zero external field, corresponding to a three-dimensional magnetic phase transition. From these facts, we may conclude that the *p*-CDTV is a new and bulk ferromagnet with the second highest Curie temperature T_c=0.68±0.02 K of genuine organic ferromagnets.

It is clear that a wide plateau of the heat capacity follows a sharp peak at T_c, as shown in Fig. 3. The value of heat capacity, C_p, around this plateau is comparable with the theoretical value (C_m(max)=0.134R=1.12 J/mol K, R: gas constant) for the 1D ferromagnet with S=1/2.[12] The lattice contribution is considered to be small in this temperature region, as observed for the *p*-BDTV radical with similar molecular structure.[13]

The application of external field gives a sensitive effect on the heat capacity; even in the small field H=0.25 kOe, the sharp peak is crushed down to leave a vague trace of it nearly at T_c, and another broad hump of the heat capacity appears above T_c. This hump grows up toward higher temperatures as the field is increased. Such a field dependence in the heat capacity of *p*-CDTV is well explained as a characteristic feature of the 1D Heisenberg ferromagnet,[14] as will be described later. These results indicate that *p*-CDTV behaves as a quasi-one-dimensional (quasi-1D) ferromagnet above the transition temperature T_c.

DISCUSSION

Generally, the organic free radicals have the g-value very close to the free electron one (g=2.0023). In fact, the g-value of *p*-CDTV is 2.0037 in benzene at room temperature as determined by an ESR measurement.[9] From this fact we can presume a small spin-orbit interaction and consequently an isotropic exchange interaction.[15,16] Thus, the S=1/2 isotropic Heisenberg model is most suitable to describe the present system.

As described in a previous section, the *p*-CDTV has a character of quasi-1D ferromagnet above T_c. Therefore, the low temperature behavior of the ac susceptibility, χ , of *p*-CDTV will be analyzed based on the quasi-1D ferromagnetic Heisenberg model. The Hamiltonian is given by

$$\mathcal{H} = -2J\sum_{i}\mathbf{S}_i\cdot\mathbf{S}_{i+1} - g\mu_B H\sum_{i} S_i^z - 2J'\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1}$$

where J and J' are the intra- and inter-chain exchange integrals, respectively, and H is the applied field.

First we consider the case for J'=0 as the first approximation, in order to explain the magnetic susceptibility of *p*-CDTV above 1.7 K (Fig. 1). In such a case, the susceptibility of 1D ferromagnet with S=1/2, χ_{1D}, is given by

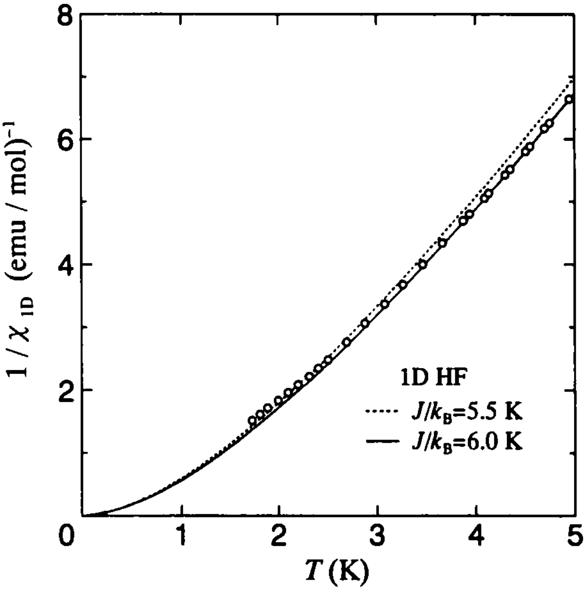


FIGURE 4 Inverse susceptibility of *p*-CDTV corrected for the isolated 1D system (open circle). Theoretical results for the isotropic 1D Heisenberg ferromagnet[20,21] are drawn for J/k_B=5.5 and 6.0 K.

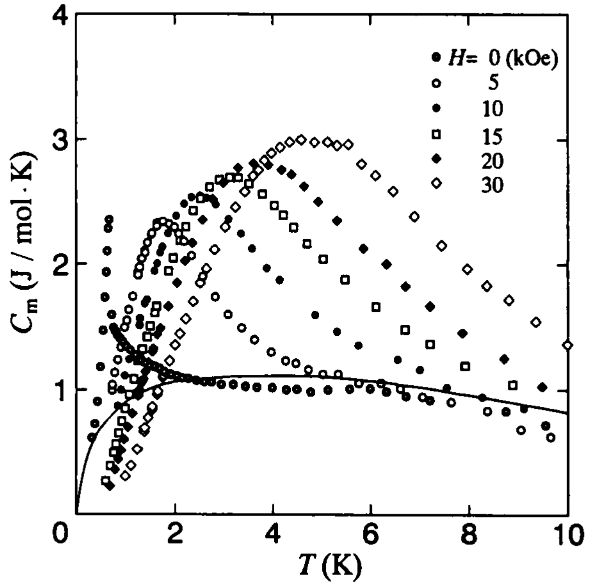


FIGURE 5 Field dependence of magnetic heat capacity, C_m, of *p*-CDTV. The solid line is the results of theoretical calculation for the isotropic 1D Heisenberg ferromagnet with J/k_B=6.0 K.

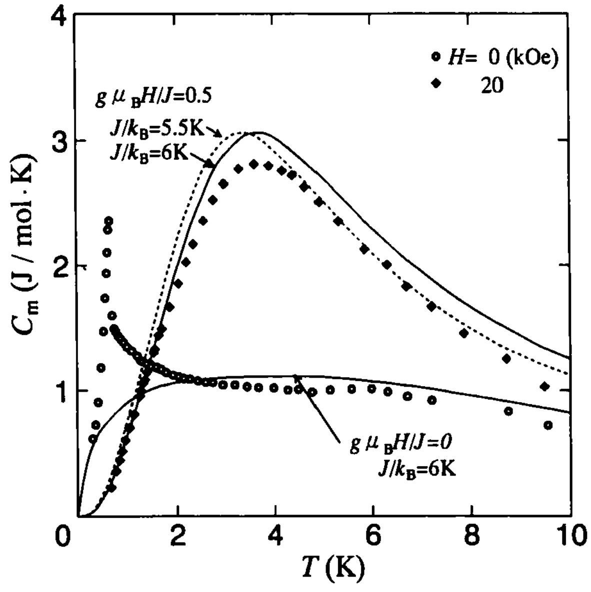


FIGURE 6 Magnetic heat capacities of *p*-CDTV in the external fields H=0 and 20 kOe. The results of theoretical calculation for the isotropic 1D Heisenberg ferromagnet are given for $g\mu_BH/J$=0 (H=0, J/k_B=6.0 K) and $g\mu_BH/J$=0.5 (···;H=20.5 kOe, J/k_B=5.5 K. —;H=22.3 kOe, J/k_B=6.0 K).

$$\chi_{1D} = \frac{Ng^2\mu_B^2}{4k_BT}\left[1+\left(\frac{J}{k_BT}\right)^a\right] \qquad (2)$$

with a=1 for $k_BT/J>1$.[12] For lower temperatures ($k_BT/J<1$), however, a depends on T ($a \to 4/5$ for $T \to 0$). In fact, above 5K our data are well reproduced by Eq. (2) with J/k_B=+5.5±0.5 K and g=2.00 as shown in Fig. 1. At lower temperatures below 5 K, we have to consider the effects from the interchain interaction (J') which induces the three-dimensional ordering at T_c=0.68 K. By the mean-field theory, the susceptibility of the quasi-one-dimensional (q-1D) system, $\chi_{q\text{-}1D}$, is given by Eq. (3)[17-19]

$$\chi_{q\text{-}1D} = \frac{\chi_{1D}}{1-\dfrac{2zJ'}{Ng^2\mu_B^2}\chi_{1D}}, \qquad (3)$$

where χ_{1D} is the susceptibility of pure 1D Heisenberg model and z is the number of interchain bonds per spin. The three-dimensional transition temperature T_c is approximated as the temperature at which the denominator of Eq. (3) becomes zero. In order to estimate J' at low temperatures ($k_BT/J<1$), we need to use more accurate χ_{1D} than Eq. (2) which is valid for $k_BT/J>1$. The thermodynamical quantities, including χ_{1D}, for the isotropic 1D Heisenberg ferromagnet with $S=1/2$ are studied on the basis of the modified spin wave theory and also of the Bethe-Ansats integral-equation method by Takahashi and Yamada {TY},[20,21] where the susceptibility is expressed as

$$\chi_{1D}^{TY} = \frac{Ng^2\mu_B^2}{8J}\left[0.1667\left(\frac{2J}{k_BT}\right)^2 + 0.581\left(\frac{2J}{k_BT}\right)^{1.5} + 0.68\left(\frac{2J}{k_BT}\right)^1 + O\left(\frac{2J}{k_BT}\right)^{0.5}\right] \quad (4)$$

Using χ_{1D}^{TY} for χ_{1D} in the denominator of Eq. (3), we can estimate the interchain interaction, zJ'/k_B. The value obtained is $zJ'/k_B=+0.21\pm0.02$ K (or $zJ'/J=3.8\times10^{-2}$). Using the value of zJ' obtained, we can evaluate the experimental χ_{1D} corrected for the isolated chains again from Eq. (3) by using the value of zJ' and the observed value of $\chi_{q\text{-}1D}$, as shown in Fig. 4. Due to this correction, χ_{1D} becomes smaller than $\chi_{q\text{-}1D}$ as T becomes lower; although the correction is less than 1% at 5 K ($k_BT/J\fallingdotseq1$), it amounts to more than 20% at 1.7 K ($k_BT/J\sim0.3$). As shown in Fig. 4, the value of χ_{1D} estimated from experimental value is well reproduced by the TY thoery with $g=2.00$ and $J/k_B=+6.0\pm0.3$ K.

The low temperature heat capacity, C_p, of p-CDTV radical was measured in the external fields of 0-30 kOe. The magnetic heat capacity, C_m, was obtained by subtracting the lattice contribution which was evaluated by referring to the lattice heat capacity of the p-BDTV radical crystal[13] with correction for the difference in the mass of Br and Cl atoms.[22,23] C_m is larger than the lattice contribution below 5 K in zero field. The field dependence of the heat capacity (Fig. 5) is qualitatively similar to that of the 1D ferromagnetic Ising system, $(CH_3)_3NHCoCl_3{\cdot}2H_2O$.[11] In zero field and in the paramagnetic state, C_m of p-CDTV keeps the values comparable to C_m(max) $=0.134R=1.12$ J/mol K above 2 K, which is a characteristic feature of the isotropic 1D

Heisenberg ferromagnet.[12] This is ascertained by a theoretical calculation of the magnetic heat capacity of a 1D ferromagnetic Heisenberg chain with J/k_B=6.0 and J'/k_B=0. The calculated heat capacity is shown by the solid curve in Figs. 5 and 6. There is a small discrepancy between the observed values of C_m and the theoretical ones for J/k_B=6.0 K and J'/k_B=0 K. This may be explained by the entropy consumption due to the three-dimensional ordering at low temperatures. The critical entropy $S_m(T_c)$ up to T_c is only 25% of the total entropy $R\ln 2$, as described later.

Another evidence for the one-dimensional interaction in this *p*-CDTV is more clearly disclosed in the heat capacity curve in high magnetic fields as discussed in the following (see Figs. 5 and 6). In Fig. 5 is shown the temperature dependence of the magnetic heat capacity of the *p*-CDTV as a function of applied field. In the external field of 5 kOe, which is much larger than the interchain exchange field $H_{ex}=2zJ'\langle S\rangle/g\mu_B\sim$ 1.5 kOe, the sharp λ-like peak observed in zero field disappears completely and the broad hump (rounded peak) appears at around 1.8 K. The hump grows gradually and shifts to the higher temperatures as the external field is increased, as shown in Fig. 5. The field dependence of C_m of this kind has not been reported because of the lack of real 1D Heisenberg ferromagnets with S=1/2.

The theoretical calculation of the field dependence of the magnetic heat capacity, C_m, has been performed for the ideal 1D Heisenberg ferromagnet by Bonner[14] for some discrete fields $g\mu_BH/J$=0.5, 1.0, 1.5 and 2.0. In Fig. 6, we compare the C_m of *p*-CDTV for H=20 kOe, which corresponds to $g\mu_BH/J$=0.45, with that obtained by theoretical calculation ($g\mu_BH/J$=0.5). It can be seen that the calculated curve reproduces satisfactorily the experimental curve (Fig. 6).

The temperature dependence of the magnetic entropy $S_m(T)$ was obtained from the relation

$$S_m(T) = \int_0^T \frac{C_m}{T} dT \tag{5}$$

The low-temperature part of $S_m(T)$ is determined by extraporating the experimental value of C_m down to 0 K with the three-dimensional spin-wave approximation, namely, with a series expansion starting from $T^{3/2}$ terms. At any rate, $S_m(T_0)$ at the lowest T_0 for the present data points is fairly small for $S_m(\infty)$=Rln2. About 80% of the magnetic

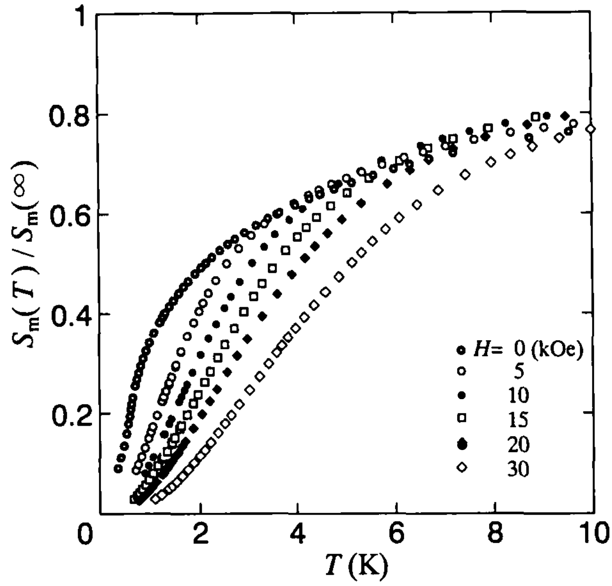


FIGURE 7 Temperature dependence of the magnetic entropy, S_m, of *p*-CDTV.

entropy (*R*ln2 for $S=1/2$) is consumed up to 10 K, and the remaining 20% is expected at higher temperatures, as shown in Fig. 7. This implies that there is one unpaired electron in each of *p*-CDTV molecules in the crystal. The critical entropy $S_m(T_c)$ up to T_c is about 25% of the total entropy Rln2. This is another reflection of the low-dimensionality of the magnetic interaction in *p*-CDTV: the value of $S_m(T_c)$ is nearly 50% for the two-dimensional localized spin systems and, in the usual three-dimensional systems, $S_m(T_c)$ is rather close to *R*ln2.[24,25]

One-dimensional (1D) magnet with localized spins is one of the most simple systems of many-body problem from which exact or correct physical quantities have been derived. For 1D Heisenberg antiferromagnets with $S=1/2$, the exact ground state energy, energy dispersion relation, various thermodynamical quantities are obtained.[26] The physical properties expected of these antiferromagnets have been experimentally checked with abundant real magnetic compounds. The magnetic properties of *p*-BDTV studied in a previous work, belong to this group, and can be explained by the one-dimensional Heisenberg model with negative exchange interaction of $2J/k_B=-41.3$K.[10,13]

However, for 1D ferromagnetic systems, the situation rather differs from the case of antiferromagnets, because we can rarely get the 1D quantum ferromagnetic substances. Consequently, only a few examples of 1D Heisenberg ferromagnet, such as $(C_6H_{11}NH_3)CuC_{13}$ (CHAC),[27] $K_2Cu_{0.59}Zn_{0.41}F_4$,[28] and γ -phase of *p*-NPNN,[5b] have been reported. As described above, the present experiments have given prototype thermodynamical behavior expected of the most isotropic Heisenberg ferromagnet in one dimension, including the magnetic susceptibility and the field dependence of magnetic heat capacity.

1,3,5-Triphenylverdazyl (TPV) radical is well known as one of the stable organic free radicals. Consequently, the magnetic properties of TPV radical and its derivatives have been studied extensively, indicating the antiferromagnetic intermolecular interaction in these radicals, as observed for usual organic free radical solids.[29-32] Positive Weiss constant (θ=+1.6 K) was observed for one of the verdazyl radicals (1,5-diphenyl-3-(4-nitrophenyl)-6-phenylverdazyl).[33] However, the presence of antiferromagnetic coupling between ferromagnetic chains has been suggested, because the magnetic susceptibility, χ_M, exhibits a maximum at 2.15 K. Further, X-ray structure analyses have been performed for these verdazyl radicals, in order to find a relation between crystal structure and observed spin-spin exchange interactions, e.g. antiferromagnetic and ferromagnetic behavior at low temperature.[31-34]

As described above, *p*-BDTV behaves as one-dimensional Heisenberg antiferromagnet with negative exchange interaction of $2J/k_B$=-41.3 K. The *p*-CDTV, on the other hand, has been found to be a new and bulk ferromagnet with the Curie temperature of T_c=0.68 K. Further, the *p*-CDTV behaves as a quasi-one-dimensional Heisenberg ferromagnet with the intrachain exchange interaction of $2J/k_B$=+12.0 K above T_c. Therefore, X-ray structure analyses of *p*-BDTV and *p*-CDTV are interesting, in order to clear how replacement of the bromo atom in *p*-BDTV by chloro one affects the crystal structure and thus the magnetic behavior of the radicals. However, to our regret, we have not succeeded in obtaining single crystals suitable for X-ray structure analyses to date. 1,5-Dimethyl-6-thioxo-verdazyl radicals show lower chemical and thermal stability in organic solvent than that of 1,3,5-triphenyl-verdazyl radicals, although these verdazyl radicals can be isolated as solvent-free pure radical solids.

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