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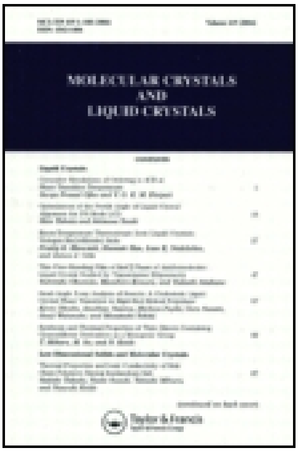

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Pulsed and CW ESR Study of Exchange Interaction, Spin Relaxation and Spin Dynamics on Low-Dimensional Organic Magnetic Materials

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PULSED AND CW ESR STUDY OF EXCHANGE INTERACTION, SPIN RELAXATION AND SPIN DYNAMICS ON LOW-DIMENSIONAL ORGANIC MAGNETIC MATERIALS

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Abstract In order to clarify the spin dynamics of the stable radical crystals, we have investigated the magnetic behavior and spin relaxation of low-dimensional antiferromagnetic organic materials, *N*-[(3-Nitrophenyl)thio]-2,4,6-triphenylphenylaminyl radical crystals, by cw and pulsed ESR. With decreasing temperature from 298 to 20 K, the line width of the cw ESR spectrum increases. Upon further decrease of temperature, significant exchange narrowing occurs below 10 K. The line broadening is more prominent in the direction of $g_{//}$ than that of $g_{\perp}$. The temperature dependence of the inverse of the transverse relaxation time, T_2, for the $g_{//}$ direction shows a divergence at ca. 20 K as determined by the FID analysis. This temperature is consistent with the magnitude of an antiferromagnetic interaction of J/k = −26 K. These findings indicate that the spin relaxation and spin dynamics in this system are governed by low-dimensional antiferromagnetic interactions among the radical species.

INTRODUCTION

Purely organic molecular crystals have attracted increasing interests in the field of molecular based magnetism.[1] They are expected to exhibit various macroscopic magnetic behaviors, *i.e.*, ferro- or ferrimagnetism, antiferromagnetism, etc. depending on their crystal structures. The dimensionality of the exchange interaction is important for

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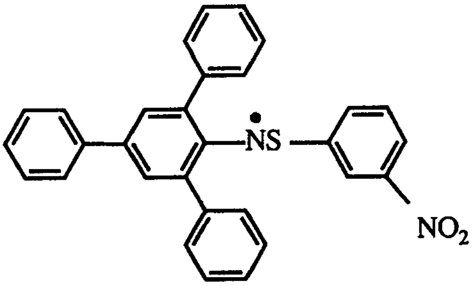
magnetic phase transitions. In the case of a pure one-dimensional system, it is well-known that the magnetic phase transition to the ferro- or antiferromagnets never occurs. However, the low-dimensional systems are interesting from the theoretical view point.[2] In a low-dimensional magnetic system, short-range ordering of spins and spin fluctuation are expected to occur in a wide range of temperatures which are higher than that corresponding to the intra-chain exchange integral, J/k. Therefore, the spin dynamics and spin relaxation of low-dimensional magnetic systems are attractive from both the theoretical and experimental view points.

Recently, we have found that the *N*-[(3-Nitrophenyl)thio]-2,4,6-triphenylphenylaminyl radical, **1**, which is a new class of stable free radicals, can be isolated as pure crystals.[3] In the radical the unpaired π-electron in SOMO is extensively delocalized over the whole molecule. The magnetic properties of the radical crystals with a delocalized unpaired π-electron are interesting, because most of the known organic radicals exhibiting long-range intermolecular magnetic interactions are those with a localized unpaired spin. The magnetic behavior of the radical crystals of **1** has been analyzed in terms of a Heisenberg alternating linear-chain model.[4] The magnetic behavior has shown quasi one-dimensional properties, and the spin fluctuations are therefore very interesting. We report



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herein a cw- and pulsed ESR study of the spin relaxation and spin dynamics for the radical crystal of **1**.

EXPERIMENTAL

The synthesis and isolation of the *N*-[(3-nitrophenyl)thio]-2,4,6-triphenylphenylaminyl radical are reported in a previous paper.[3] The temperature dependence of the ESR spectra was measured in the temperature range of 1.8 - 300 K for the cw-ESR and that of 5 - 298 K for the pulsed-ESR using a Bruker ESP300 spectrometer and an ESP380E pulsed ESR spectrometer both equipped with Helium-gas-flow temperature controllers. The polycrystalline samples were used for all the solid-state ESR measurements. For the solution ESR measurements 2-methyltetrahydrofuran (2-MTHF) was used as a solvent.

RESULTS AND DISCUSSION

(A) Brief Summary of the Magnetic Properties

The magnetic susceptibility data and a part of our ESR results have been already published in our previous paper.[4] The results of our previous magnetic susceptibility measurements are briefly summarized in this section. As described below, the temperature dependence of χ_{mol} is interpreted in terms of the alternating infinite linear chain model,

$$\mathcal{H} = -2J \sum (S_{2i}S_{2i-1} + \alpha\, S_{2i}S_{2i+1}), \qquad (1)$$

where α is the alternating parameter. Thus, the magnetic interaction of **1** in the crystalline phase is one-dimensional. The best fit values of J/k and α are -26 K (antiferromagnetic) and 0.92, respectively. The α value of

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0.92 means that the radical molecules align almost regularly in the crystal.

(B) **cw-ESR Spectra**

Figure 1(a) shows a solution ESR spectrum of **1** in 2-MTHF, which consists of a 1 : 1 : 1 triplet with a interval of 0.897 mT due to the interaction with the central nitrogen. The π-spin density on the nitrogen atom has been estimated to be 0.425 using McConnell's equation (Q = 2.1 mT).

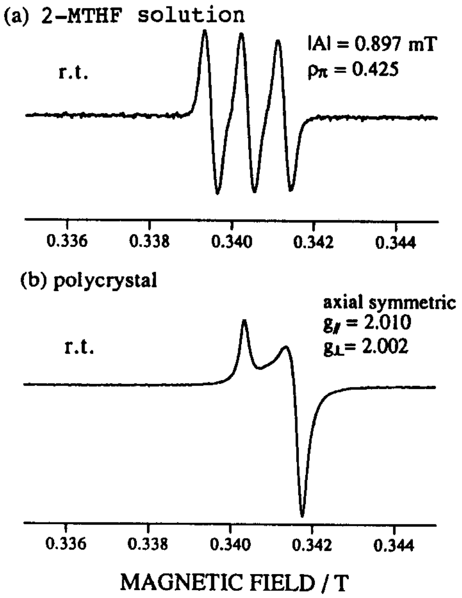

FIGURE 1 Typical ESR spectra of **1**
(a) in a 2-MTHF solution,
(b) polycrystal

This splitting is, however, completely smeared out in the spectrum of the polycrystalline sample by the large intermolecular exchange interaction among the radical species. As seen in Figure 1(b), the polycrystalline sample gives a typical powder-pattern ESR spectrum characteristic of the doublet species with an axially symmetric g anisotropy and without hyperfine splittings. The anisotropic g values were determined to be $g_{//}$ = 2.010 and $g_{\perp}$ = 2.002.

As already described in our previous paper,[4] the ESR line width of the spectrum increased when the temperature was decreased from room temperature to 20 K. However, when the temperature was further decreased below 10 K, the

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exchange narrowing of the the line shape took place, and the most significant exchange narrowing was observed at 1.7 K. This spectral behavior is presented in Figure 2 which shows typical ESR spectra observed at 1.7, 20, and 100 K. This line broadening followed by the exchange narrowing observed with decreasing temperature is more prominent in the $g_{//}$ direction than in the $g_{\perp}$ direction, indicating that there is a large anisotropy of the magnetic interactions in this crystal. This temperature dependence of the ESR line shapes shows that the interacting chain is nearly parallel to the $g_{//}$ direction. The temperature giving the maximum line width (20 K) is consistent with the magnitude of the antiferromagnetic interaction of $J/k = -26$ K. These phenomena are considered to be closely related to the spin fluctuation and spin dynamics arising from a low dimensional (1D) magnetic interaction in the radical crystal. To examine the temperature dependence of the lineshape in more detail, we have carried out a pulsed-ESR study of the magnetic relaxation.

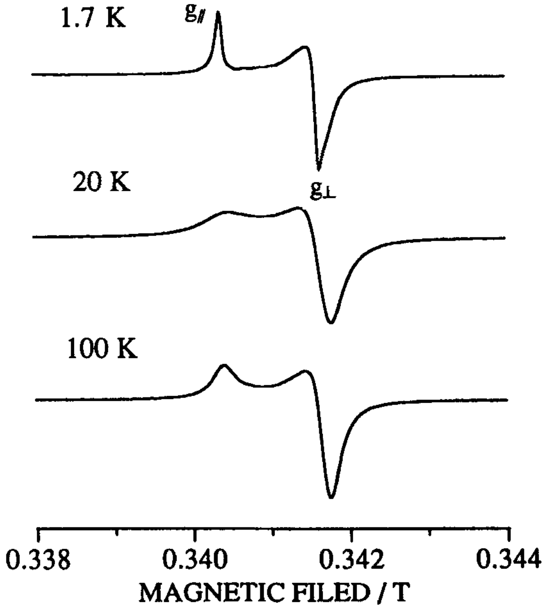

FIGURE 2 Temperature dependence of the powder-pattern ESR spectrum of **1**

(C) pulsed ESR Spectra

A typical free induction decay (FID) and the inversion recovery observed at 5 K are shown in Figures 3(a) and 3(b), respectively, together with the exponential fit. The

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determined transverse (T_2) and longitudinal (T_1) electron spin relaxation times at this temperature are 50.5 and 135.0 ns, respectively. Thus, T_2 is much shorter than T_1. In addition, the spin echo signal could not be detected in the whole temperature range from 5 to 300 K because of the homogeneity of the ESR signal. These results show that the phase memory time in this system is dominantly governed by the intermolecular spin exchange interaction at low temperatures.

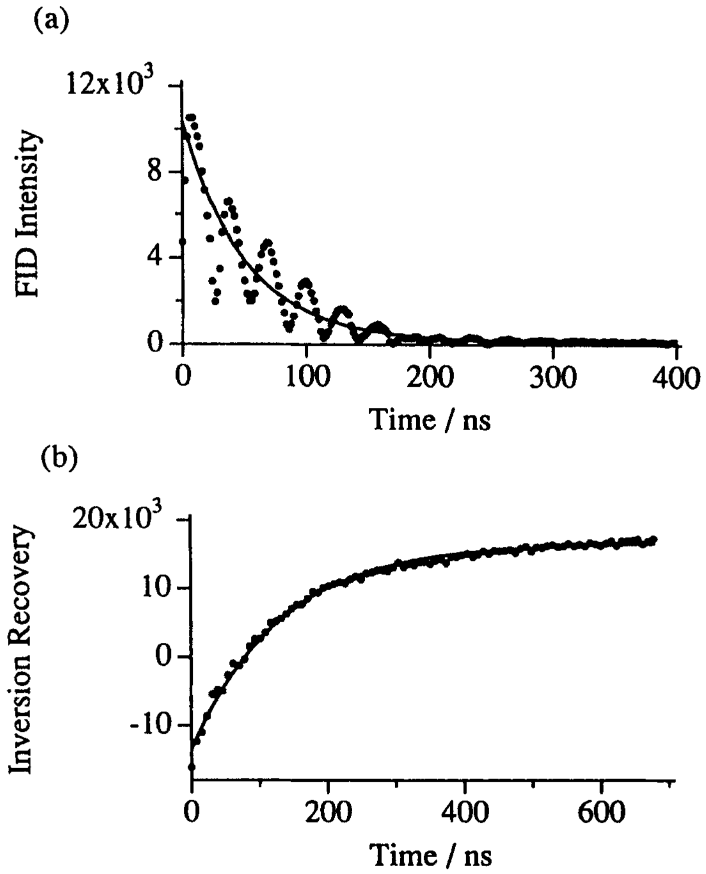

FIGURE 3 Typical FID signals and the inversion recovery

Figure 4 shows the temperature dependence of T_2^{-1} determined by the analyses of FID which was measured at the external magnetic field corresponding to the resonance field

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for of $g_{//}$. From room temperature down to 60 K, T_2^{-1} increased gradually (almost constant). With decreasing temperature from 60 to 20 K, T_2 became shorter significantly, i.e., T_2^{-1} have a peak at ca. 20 K. Below 20 K T_2 increases with decreasing temperature. This behavior of T_2 corresponds to the line-width change in the cw-ESR spectra shown in Figure 2, although the change has been clearly observed for T_2^{-1} in the case of pulsed ESR experiments. These findings reveal that the change in line-width originates from the change in the phase memory time (the transverse electron spin relaxation) caused by the intermolecular exchange interaction, i.e., from the spin dynamics characteristic of the low-dimensional (1D) magnetic material of **1**.

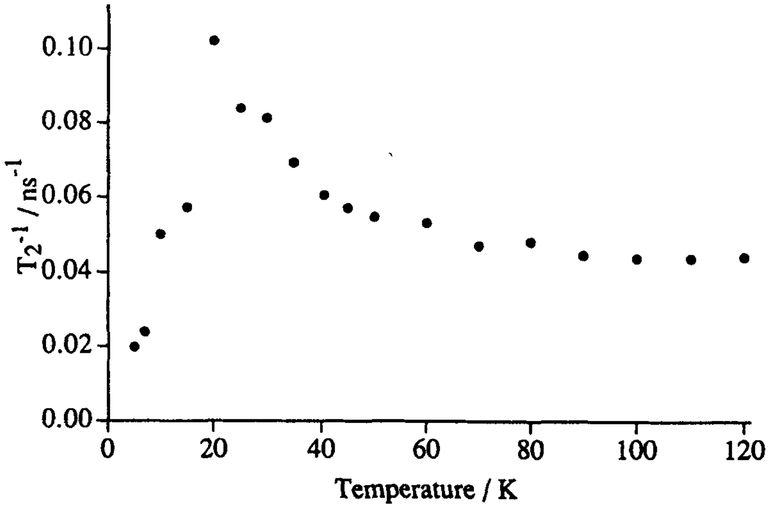

FIGURE 4 Temperature dependence of the inverse of the transverse electron spin relaxation time, T_2^{-1}

(D) Spin Dynamics and Spin Relaxation of 1

A qualitative explanation of the temperature dependence of the ESR line-width and the phase memory time observed is

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given in this paper. It is well-known that a Gaussian decay part and a long-time diffusive decay part exist in the spin correlation function of the low-dimensional magnetic materials.[5,6] According to the theory of ESR line-width for the regular low-dimensional antiferromagnetic system (α = 1.0 in eq. (1)),[6-8] the line-width ΔH and therefore T_2^{-1} are given in the high-temperature region ($T \gg J/k$) where the diffusive part plays an important role by

$$T_2^{-1} \propto \Delta H(T) = \Delta H(\infty)\ \frac{\chi_0 T}{C} \left(\frac{D\infty}{D_T}\right)^{d/2} \qquad (2)$$

where d is the dimension of the system and D the spin diffusion constant. For the one-dimensional antiferromagnetic regular chain system, eq. (2) leads to a gradual decreasing of the ESR line-width with decreasing temperature. In the near critical region ($T \sim J/k$) on the other hand, the Gaussian decay part plays a dominant role in the ESR line broadening. In this region $\Delta H(T)$ increases proportionally to T^{-3} (eq.(3)) is given by

$$T_2^{-1} \propto \Delta H(T) = C' T^{-3}\ . \qquad (3)$$

The present system is not a regular chain system because there exists some weak alternation indicated by α = 0.92. The alternating property cuts off the long-time tail (LTT)[9] of the spin correlation function which is responsible for the line-width decreasing as the temperature is increased from 20 K. This also results in the line-width becoming constant in the high-temperature region. On the other hand, the Gaussian decay part still leads to the line broadening in the near critical region, since the degree of alternation is small. In the low temperature region ($T \ll J/k$) spin pairing occurs since there is an energy gap between the spin singlet ground state and other spin states for a system with $\alpha < 1.0$. The spin pairing leads to a decreasing of the spin exchange. Consequently, the phase memory time is longer. The temperature dependence of the inverse of the transverse relaxation time T_2^{-1} for the alternating chain system is, therefore, expected to give a curve as shown in Figure 5, in agreement with the observed behavior shown in Figure 4.

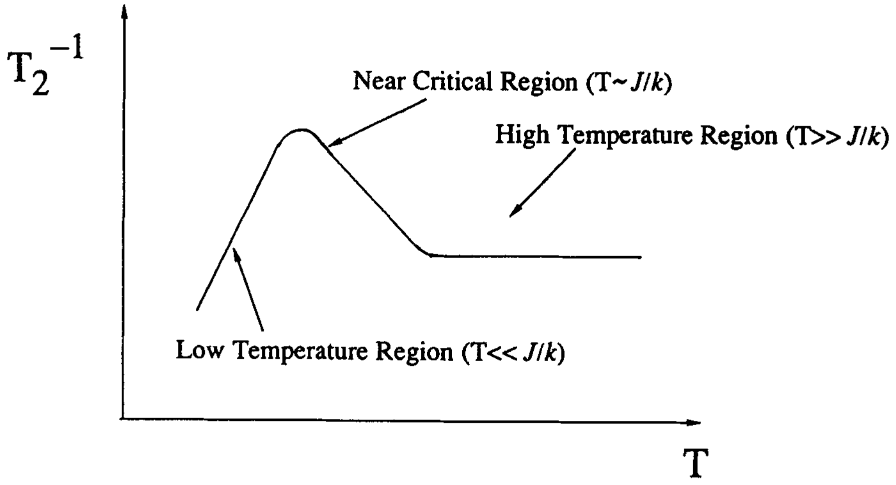

FIGURE 5 Temperature dependence of T_2^{-1} expected of the alternating chain system.

The observed temperature dependence of T_2 can be understood qualitatively on the basis of the above consideration of the spin dynamics for the present system with the alternating property. A more detailed experiment is in progress. A semi-quantitative theoretical discussion will be published together with the detailed experimental results.

CONCLUSIONS

We have investigated the spin relaxation and the spin dynamics of the stable radical crystal of **1** using both cw- and pulsed-ESR. The temperature dependence of T_2 has been measured. The anomalous behavior has been understood on the

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basis of the spin dynamic of a one-dimensional magnetic material.

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