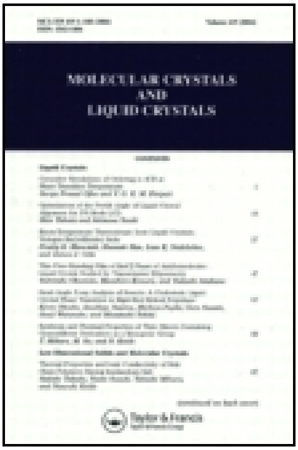


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

One-Dimensional Ferrimagnetic Behavior of a Hetero-Spin Chain in an Organic Radical Crystal as Probed by Susceptibility and Relaxation Time Measurements

Daisuke Shiomi [a] , Masahiro Nisheawa [a] , Kazunobu Sato [b] , Takeji Takui [b] , Koichi Itoh [a] , Hiromi Sakurai [c] , Akira Izuoka [c] & Tadashi Sugawara [c]

[a] Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[c] Department of Pure and Applied Sciences, College of Arts and Science, The University of Tokyo, Meguro-ku, Tokyo, 153, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Daisuke Shiomi , Masahiro Nisheawa , Kazunobu Sato , Takeji Takui , Koichi Itoh , Hiromi Sakurai , Akira Izuoka & Tadashi Sugawara (1996): One-Dimensional Ferrimagnetic Behavior of a Hetero-Spin Chain in an Organic Radical Crystal as Probed by Susceptibility and Relaxation Time Measurements, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 278:1, 279-294

To link to this article: http://dx.doi.org/10.1080/10587259608033686

Mol. Cryst. Liq. Cryst., 1996, Vol. 278, pp. 279–294
Reprints available directly from the publisher
Photocopying permitted by license only

ONE-DIMENSIONAL FERRIMAGNETIC BEHAVIOR OF A HETERO-SPIN CHAIN IN AN ORGANIC RADICAL CRYSTAL AS PROBED BY SUSCEPTIBILITY AND RELAXATION TIME MEASUREMENTS

DAISUKE SHIOMI,[1] MASAHIRO NISHIZAWA,[1] KAZUNOBU SATO,[2]
TAKEJI TAKUI,[2] KOICHI ITOH[1], HIROMI SAKURAI,[3] AKIRA IZUOKA[3], and
TADASHI SUGAWARA[3]
[1]Department of Material Science and [2]Department of Chemistry, Faculty of
Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan
[3]Department of Pure and Applied Sciences, College of Arts and Science, The
University of Tokyo, Meguro-ku, Tokyo 153, Japan

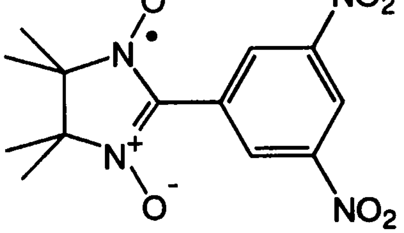
Abstract Spin state energies were calculated for a linear chain composed of a doublet radical and a biradical with a triplet ground state by numerical diagonalization of finite-size Heisenberg spin Hamiltonian. When all the intermolecular antiferromagnetic interactions couple the S=1/2 sites uniformly, a ferrimagnetic-like ground state appears. This finding is consistent with the simple picture of antiparallel alignment of different S's. On the other hand, quasi-degenerate low-lying excited states appear as the spatial symmetry of intermolecular antiferromagnetic interactions is lowered. The quasi-degeneracy breaks the stability of the ferrimagnetic-like ground state. This result gives a qualitative explanation of the susceptibility and the spin-spin relaxation time measured for a nitronylnitroxide-based molecular crystal composed of an $S=1/2$ and $S=1$ molecules. The instability of the ferrimagnetic-like ground state is inherent in multi-centered antiferromagnetic interactions between the open-shell organic molecular systems, suggesting a prerequisite for purely organic ferrimagnetic ordering.

INTRODUCTION

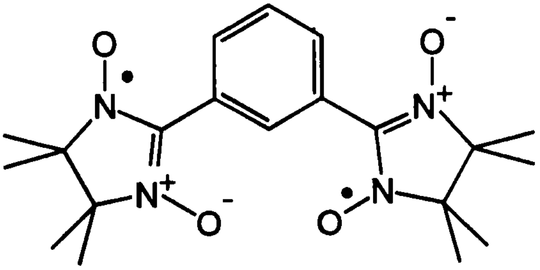
After the discovery of the first purely organic ferromagnet p-NPNN,[1] efforts to study organic molecule-based magnetic materials have been concentrated on the full understanding of the underlying mechanism for intermolecular ferromagnetic interactions and on materials challenges for higher T_C ferromagnets.[2] On the other hand, ferrimagnets, another type of magnetically ordered material with spontaneous magnetization, have not been documented so far in organic molecular crystalline solids.

One of the most salient features of organic open-shell systems as building blocks of magnetic materials is isotropic nature of exchange interactions among them.[3] This feature results from low symmetry of organic molecules and their weak spin-orbit interactions compared with those of transition metal ions. Particularly for antiferromagnetic spin systems, including ferrimagnets, both the isotropic nature of electron spins and the low lattice-dimensionality commonly appearing in organic solids provide large quantum fluctuation of the spins. The quantum fluctuation favors a diamagnetic singlet pair more than an antiparallel alignment of the adjacent spins. The disappearance of magnetic moment due to the singlet pair formation prevents long range magnetic order or reduces the transition temperature to antiferromagnetic or ferrimagnetic ordered state. In realizing the ferrimagnetic ordered state in the organic molecular system, the quantum nature inherent in the exchange interactions in the organic crystals is of crucial importance.

Izuoka et al have reported the crystal structure and static paramagnetic susceptibility of a molecular complex composed of an $S=1/2$ radical (**1**) and a biradical (**2**) with a triplet ($S=1$) ground state, both of which are chemically stable nitronylnitroxide radical derivatives.[4] The crystal of the complex **1**+**2** consists of alternating chains of the $S=1/2$ and $S=1$ molecules. The product of susceptibility and temperature, χT, has been found to decrease with lowering the temperature, indicating the occurrence of intermolecular antiferromagnetic exchange interactions (J_{AF}) between **1** and **2** along the chain.[4] The intramolecular ferromagnetic interaction within the molecule **2** is comparable in magnitude with the intermolecular antiferromagnetic



1



2

interactions, which mask the intramolecular ferromagnetic interaction. As far as we know, this molecular complex can be the first model system of organic ferrimagnets with well-characterized molecular and crystal structure although ferrimagnetic phase transition has not been observed in the compound yet.

In the following sections, the temperature dependence of χT of the complex **1**+**2** is re-examined with particular focus on its low temperature behavior reflecting the ground state. Transverse relaxation time (spin-spin relaxation time), T_2, measured using a pulsed EPR technique is discussed in order to elucidate microscopic magnetic environments in the chain. A physical picture of the ground state of the spin-chain is deduced from numerical calculations of spin state energies and susceptibility in terms of a Heisenberg spin Hamiltonian. A prerequisite for the ferrimagnetic order in organic molecular spin systems is discussed on the basis of the experimental and theoretical results.

EXPERIMENTAL

The static magnetic susceptibility was measured for the polycrystalline sample using a Quantum Design SQUID magnetometer MPMS with an applied field of 1000 Oe in the temperature range of 2 to 300 K. The magnetization curve was measured below 6 K with an applied field up to 6 T. The pulsed EPR measurements were carried out on a Bruker FT-EPR spectrometer ESP380E equipped with a dielectric cavity of tunable Q=100~5000. Spin state energy and susceptibility were calculated numerically by exact diagonalization of a Heisenberg Hamiltonian for finite-size model systems on a Sony workstation NWS-5000TG.

RESULTS AND DISCUSSION

Susceptibility and Magnetization

The temperature dependence of χT below 30 K is depicted in Figure 1. At higher temperature the χT value increased and reached the room temperature value of 1.13 emu K mol^{-1} corresponding to three S=1/2 spins in a unit cell. The temperature dependence above 30 K is essentially identical to that previously reported.[4] Below 30 K, as shown in Figure 1, the χT value took both a minimum at T_{max}= 6 K and a maximum at T_{min}=3 K and decreased at lower temperature. This "re-entrant" behavior of χT has been observed more clearly in the present measurement than in the previous one.[4] The difference in the absolute value of χT in the "re-entrant" region might result from the static field value applied in the experiments or the chemical freshness of the sample. The reproducibility of the present susceptibility measurements has been corroborated by the independent experiments on two different SQUID magnetometers. The discussion on the susceptibility in the present study is based on the new result shown in Figure 1.

The minimum in χT as a function of temperature is generally indicative of ferrimagnetic-like behavior in low-dimensional lattice.[5] In a chain composed of two kinds of spins S_1 and S_2 ($S_1 > S_2$) which are antiferromagnetically coupled, the ground state of the chain has a spin $S=N(S_1 - S_2)$ (N: the number of the repeating units). The highest energy corresponds to $S=N(S_1+S_2)$. Between these two levels, spin states with S

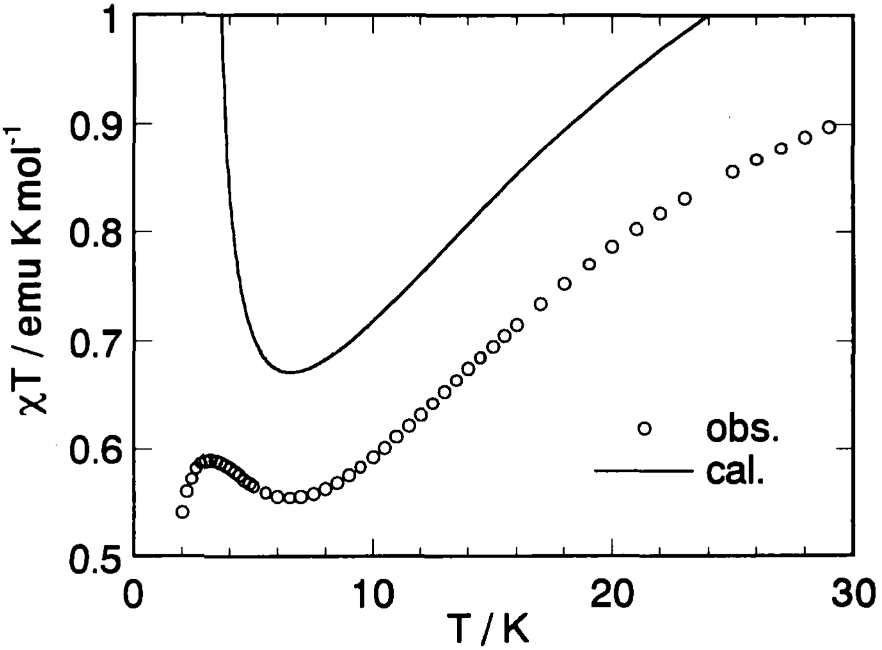


FIGURE 1 Temperature dependence of χT measured for the polycrystalline sample. The solid line represents the calculation based on the infinite antiferromagnetic chain of $S=1/2$ and $S=1$ with the exchange interaction of $2J/k_B$ = -10 K.

values both larger and smaller than $N(S_1\text{-}S_2)$ are distributed. In the high temperature limit, all the states are populated to give a susceptibility value for 3*N* mol of free S=1/2 spins. On lowering the temperature, the highest state with S=$N(S_1$+$S_2)$ is depopulated first, resulting in decrease in χT. The decrease in χT is interpreted as the depopulation of the states with S=$N(S_1$+$S_2)$, $N(S_1$+$S_2)$-1, $N(S_1$+$S_2)$-2, • • •. At low temperature, low-lying excited states with $N(S_1\text{-}S_2)$-1, $N(S_1\text{-}S_2)$-2, • • • are, in turn, depopulated and the χT value is increased. It is concluded from the observed χT minimum that ferrimagnetic-like spin correlation (or short range magnetic order) develops along the chain of the complex around T_{min}=6 K.

From the magnetization curvature observed around T_{min}, the thermally-averaged spin number has been found to be S=1~3/2;[4] the ferrimagnetic-like spin correlation appeared to develop over two or three repeating units. This finding supports the ferrimagnetic-like short range order deduced above from the χT results. However, the observed saturation magnetization of 5500 erg Oe^{-1} mol^{-1} in the "re-entrant" region of χT corresponds exactly to only 1/3 of the total spins.[4] Within the static field range of B < 6 T, no spin flop-like anomaly in the magnetization curve was observed. It can only be stated from the χT and magnetization results that the ground state or low-lying excited states have an effective spin of S=1~3/2 in the chain.

An infinite antiferromagnetic chain model of alternately stacking S=1/2 and S=1 spins[5] does not quantitatively reproduce the observed χT behavior; the observed minimum value of χT is smaller than the calculated one as shown in Figure 1. Although the intramolecular ferromagnetic interaction within the biradical **2** ($2J_F$ / k_B ~ +20 K)[6] is larger than the thermal energy of $k_B T_{\text{min}}$, an S=1 on **2** cannot be regarded as a "good" spin quantum number. A novel mechanism should be invoked in order to explain the reduced minimum value of χT.

Decrease in χT at low temperature for one-dimensional magnetic materials is usually attributed to additional interchain antiferromagnetic interactions. For the complex **1**+**2**, however, such a conventional interpretation is not valid for χT below T_{max}: Firstly, the methyl groups facing to each other between the chains have low spin density in the molecules and thus are expected to have little contribution to the interchain interactions of the order of $k_B T_{\text{min}}$. Secondly, relatively short interchain distance is found between **1** and **2** instead of **1** and **1** or **2** and **2**.[4] This molecular arrangement in the crystal is favorable to three-dimensional ferrimagnetic spin correlation giving rise to the divergence of χT. Therefore, on the basis of only the static magnetic measurements (χT and magnetization), the decrease in χT below T_{max} as well as the reduced χT minimum is an open problem.

Spin-Spin Relaxation Time

The transverse relaxation time T_2 was measured by Hahn's echo method (π/2-π pulse sequence) on the single crystals of the complex **1**+**2** with static magnetic field parallel as well as perpendicular to the chain. The chains are parallel to the *c*-axis in the crystal. Anisotropy in the plane perpendicular to the chain (a*b* plane) is almost averaged since about twenty pieces of the single crystal have been aligned in the experiment so that only the *c*-axes are parallel to each other. By monitoring the echo peak intensity with incrementing the interval τ between the π/2- and π-pulse, echo decay curves were obtained. The T_2 value was estimated as the time constant of the exponential decay of the echo intensity as a function of τ. The results are shown in Figure 2.. For both parallel and perpendicular directions of the static field, the T_2 values were found to increase gradually as the temperature was lowered. The T_2 value showed a plateau of 7.5×10^{-7} second below 10 K.

For low-dimensional antiferromagnetic systems, transverse relaxation time T_2 is known to vary as a function of temperature only at low temperature region of $T \sim |J_{AF}|/k_B$ (J_{AF}: antiferromagnetic exchange interaction). This kind of variation in T_2 has been explained in terms of development of antiferromagnetic spin correlation within the low-dimensional lattice. For the complex **1**+**2**, the T_2 value was dependent on temperature in the wide range of $T > |J_{AF}| / k_B$. Thus, the spin-spin relaxation in the complex **1**+**2** contrasts with those of usual low-dimensional antiferromagnetic systems. Considering that the echo decay-detected T_2 is the life time of a homogeneous spin packet subject to magnetic interactions with surrounding magnetic moments, the observed temperature dependence of T_2 suggests that the magnetic environments of the spin monitored in the pulsed experiments vary with temperature. The increase in T_2, i.e., a reduction in spin-spin relaxation rate, implies that the spatial distribution of the spin magnetic moment becomes more and more sparse as the temperature is lowered.

Numerical Calculation of Susceptibility and Spin Eigenstate Energies

(a) Symmetric Hamiltonian

For expounding the peculiar behavior of the exchange-coupled spin system of the complex **1**+**2**, the spin state energies and the temperature dependence of χT were calculated by numerical diagonalization of a Heisenberg Hamiltonian for finite-size systems. The Hamiltonian examined is given as follows:

$$H=-2J_{\mathrm{F}}\Sigma\,(S_{3i-2}\bullet S_{3i-1})$$
$$-2J_{\mathrm{AF}}\,\Sigma\,(S_{3i-2}\bullet S_{3i}+S_{3i-1}\bullet S_{3i}+S_{3i}\bullet S_{3i+1}+S_{3i}\bullet S_{3i+2}), \qquad (1)$$

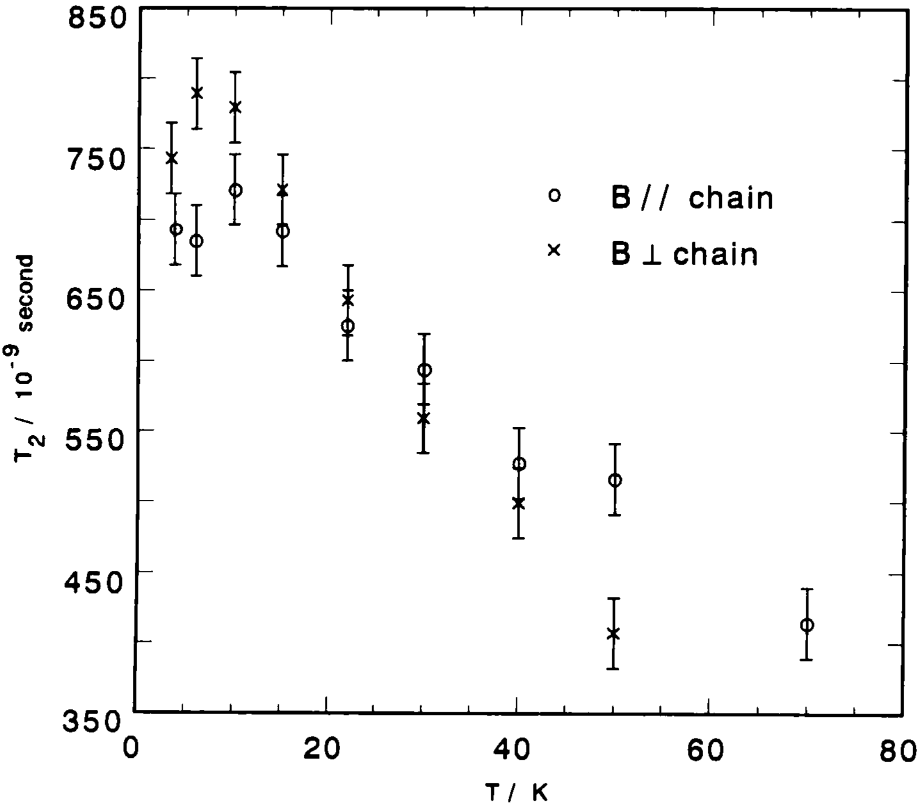


FIGURE 2 Temperature dependence of the spin-spin relaxation time, T_2, measured on the aligned single crystals. The static field is applied parallel or perpendicular to the chain (// c-axis).

(i=1,2,•••,N; N is the number of the repeating units), where S_j (j=3i-2, 3i-1, 3i, 3i+1, 3i+2) is the spin-1/2 operator on the j-th site. J_F and J_{AF} denote the intramolecular ferromagnetic and intermolecular antiferromagnetic exchange interaction, respectively. The model is schematically illustrated in Figure 3. The total number of the spin-1/2 sites is $3N$. A periodic boundary condition, $S_{3N+1}=S_1$, is adopted in the calculation for avoiding an "edge effect" as expected in linear chain models with free edges. The expectation value of S^2, $<S^2>=<S^+S^-+S_z^2-S_z>=S(S+1)$, for each eigenstate was also calculated using the eigenvectors obtained in the diagonalization procedure of the Hamiltonian (1). All the calculations have been made for the spin subspace with the z-component of the total spin,

$$S_z^{\text{total}} = \Sigma S_i^z = 0 \ (3N \text{ even}) \text{ or } 1/2 \ (3N \text{ odd}), \qquad (i=1,2,\cdots,N). \tag{2}$$

The state energies were calculated for the rings of up to twenty-one S=1/2 spins by Lanczos method.[7] The temperature dependence of susceptibility was simulated for the rings of up to twelve S=1/2 spins by using the state energies obtained from Householder method.

The spin state energies and S values of the ground state as well as three low-lying excited states are shown in Figure 4 for some selected ratios of J_F : J_{AF}. For any ring-

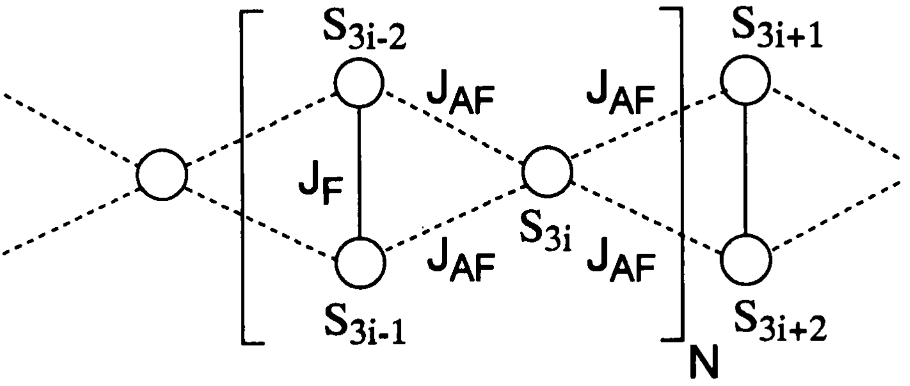


FIGURE 3 Schematic drawing of the Heisenberg Hamiltonian with the uniform intermolecular antiferromagnetic interactions, J_{AF}, in N of the repeating units. J_F denotes the intramolecular ferromagnetic interaction. S is the spin-1/2 operator.

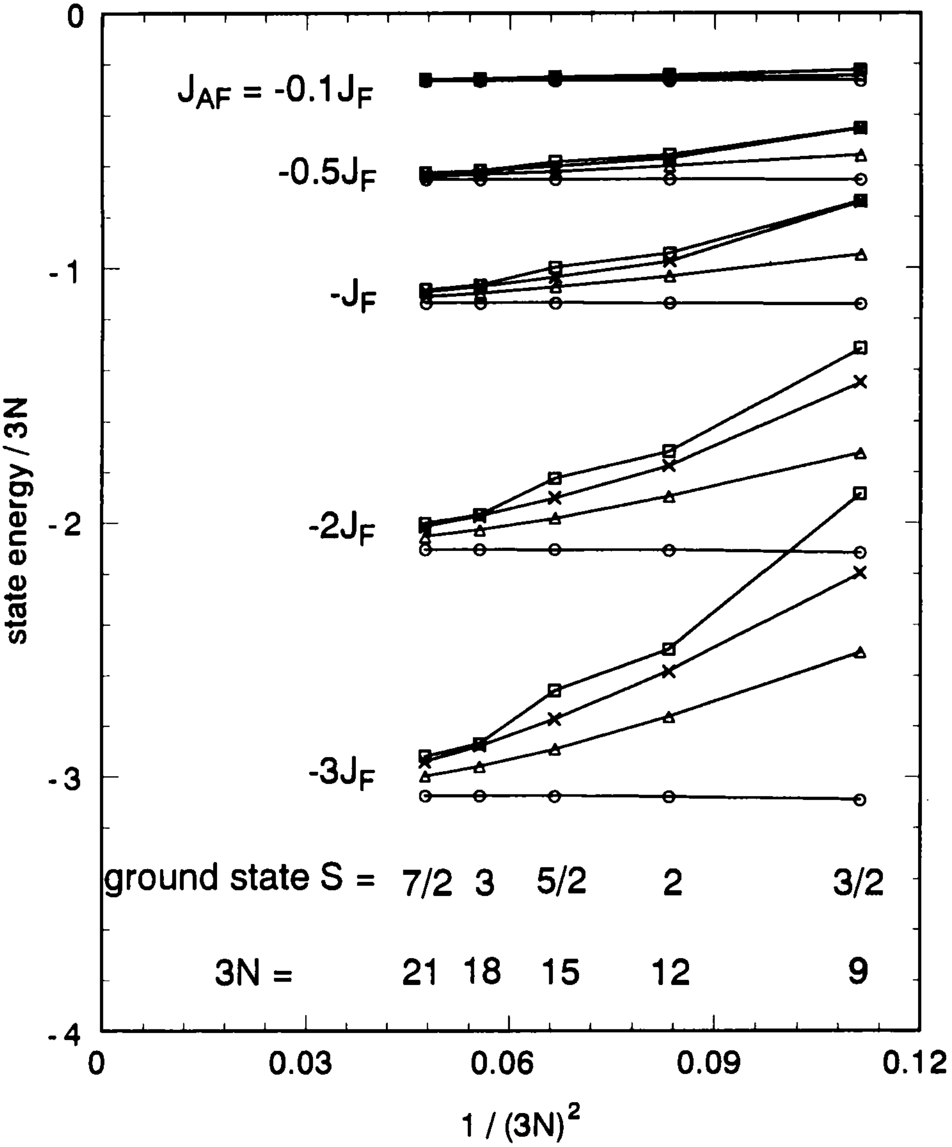


FIGURE 4 Eigenstate energies and spin quantum numbers of the ground and low-lying excited states of the model Hamiltonian shown in Figure 3. $3N$ denotes the total number of the S=1/2 sites.

size ($3N$) and interaction-ratio (J_F:J_{AF}) examined, a ferrimagnetic-like ground state with $S=N(1-1/2)=N/2$ appears. This finding is consistent with the simple picture of antiparallel coupling of different S's. It has been demonstrated that the ferrimagnetic-like ground state appears even when an $S>1/2$ site is a composite system of two isotropic (i.e., ideally quantum) $S=1/2$ spins coupled by finite ferromagnetic interactions (J_F).

In the limit of $T=0$, χT should approach a finite value corresponding to the ground state spin value of $S=N/2$;

$$\chi T(T=0) = N_A g^2 \mu_B^2 (N+2)/36 k_B, \tag{3}$$

(N_A: Avogadro's constant, g: g-factor, μ_B: Bohr magneton, k_B: Boltzmann constant) for one repeating unit with three $S=1/2$ sites. Thus, the low temperature limit of χT diverges as the number of spins in the chain is increased. The temperature dependence of χT calculated for $3N=6$, 9 or 12 is shown in Figure 5. Since all the state energies with $S=N/2$~0 (or $N/2$ ~1/2) are needed in calculating the temperature dependence of χ (or χT), the largest system size ($3N=12$) is severely restricted compared with that in the Lanczos calculation for only a few low-excitations as described above. However, the calculated χT value exhibits a minimum similar to the observed one. From the calculation, it is concluded that the ferrimagnetic-like behavior of χT can be observed in the low-dimensional molecular systems with finite J_F comparable with intermolecular antiferromagnetic J_{AF}.

(b) Asymmetric Hamiltonian

As described above, when all the intermolecular antiferromagnetic interactions couple the $S=1/2$ sites uniformly, the ferrimagnetic-like ground state, together with the divergence of χT, appears even for isotropic (i.e., Heisenberg-type) spins which favor the singlet pair formation more than the "Neel state" of antiparallel alignment of the adjacent spins. However, the experimental χT suggests the tailing-off of the magnetic moment after the apparent onset of ferrimagnetic-like short range order. Furthermore, the increase in T_2, i.e., the reduction in spin-spin relaxation rate, shows that the spatial

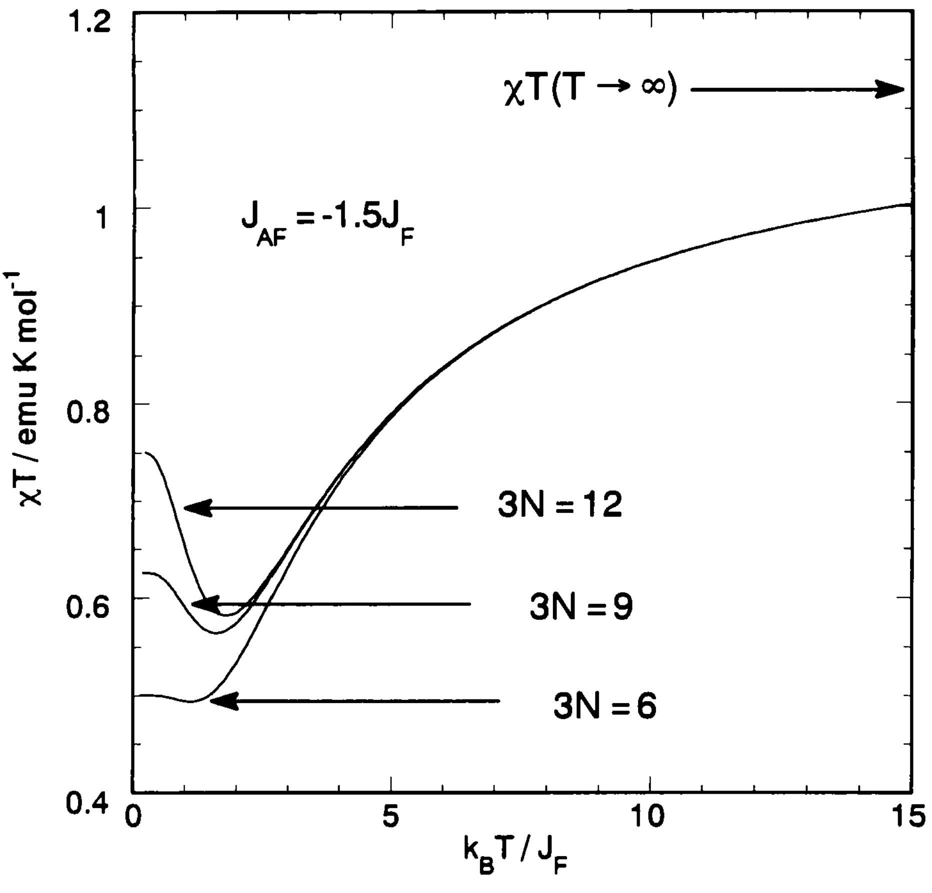


FIGURE 5 Calculated temperature dependence of χT for the model Hamiltonian in Figure 3. The high temperature limit of χT is also indicated.

distribution of the spin magnetic moment becomes more and more sparse as the temperature is lowered. For removing the contradiction between the experimental results and the calculation, we have to introduce some symmetry-breaking giving rise to the singlet pair formation. This symmetry-breaking responsible for the tailing-off of magnetic moment is analogized with the lattice alternation in $S=1/2$ antiferromagnetic linear chains. The lattice alternation, i.e., the loss of translational symmetry, changes the ground state with non-zero χ for the uniform separation of the spin sites into a diamagnetic one for the alternating separation.[8]

The crystal structure analysis of the complex **1**+**2**[4] has revealed that the intermolecular distances between **1** and the two adjacent molecules **2** along the *c*-axis (// chain) are not distinctly different. However, considering the lattice symmetry of the space group P1,[4] the intermolecular antiferromagnetic interactions lack not only uniformity along the chain but also C_2-symmetry around the chain axis. In order to examine the influence of the symmetry-lowering on the ground eigenstate and low-lying excited states, the following Heisenberg Hamiltonian with lowered symmetry has been exploited;

$$\begin{aligned} H= & -2J_F\Sigma\,(S_{3i-2}\bullet S_{3i-1}) \\ & -2\Sigma(J_{AF1}\,S_{3i-2}\bullet S_{3i}+J_{AF2}\,S_{3i-1}\bullet S_{3i}+J_{AF3}\,S_{3i}\bullet S_{3i+1}+J_{AF4}\,S_{3i}\bullet S_{3i+2}), \\ & (i=1,2,\bullet\bullet\bullet,N;\ S_{3N+1}=S_1). \end{aligned} \tag{4}$$

In Figure 6, the low-lying eigenstates of the asymmetric Hamiltonian (4) are compared with those of the symmetric Hamiltonian (1) for $3N=9$. For both the models, the ground state has $S=3/2$ ($=N/2$). However, in the asymmetric model, the first excited state with $S=1/2$ is quasi-degenerate with the ground state of $S=3/2$. Quasi-degeneracy of one $S=3/2$ state and two $S=1/2$ states corresponds to three $S=1/2$ spins which are magnetically independent each other. Thus, at very low temperature where the difference in the magnitude of J_{AF}'s is not negligible compared with the thermal energy, the $3N=9$ chain (ring) with the asymmetric antiferromagnetic interactions behaves as three decoupled $S=1/2$ spins; one of the apparently free $S=1/2$ spins in a repeating unit is labeled by an asterisk in Figure 6(b) for $|J_{AF1}| \sim |J_{AF2}| >> |J_{AF3}| \sim |J_{AF4}|$. In the limit of $T=0$, χT should approach a finite value,

$$\chi T(T=0) = N_A g^2 \mu_B{}^2/4k_B, = 0.38 \text{ emu K mol}^{-1} \quad (g=2.0), \tag{5}$$

for one repeating unit with one $S=1/2$ spin, which is smaller the χT minimum at T_{min}. Thus, the quasi-degeneracy is proposed to be responsible for the decrease in χT below T_{max}. The reduced χT minimum mentioned above is attributed to the partial disappearance of magnetic moment due to the intermolecular singlet pair formation around T_{min}.

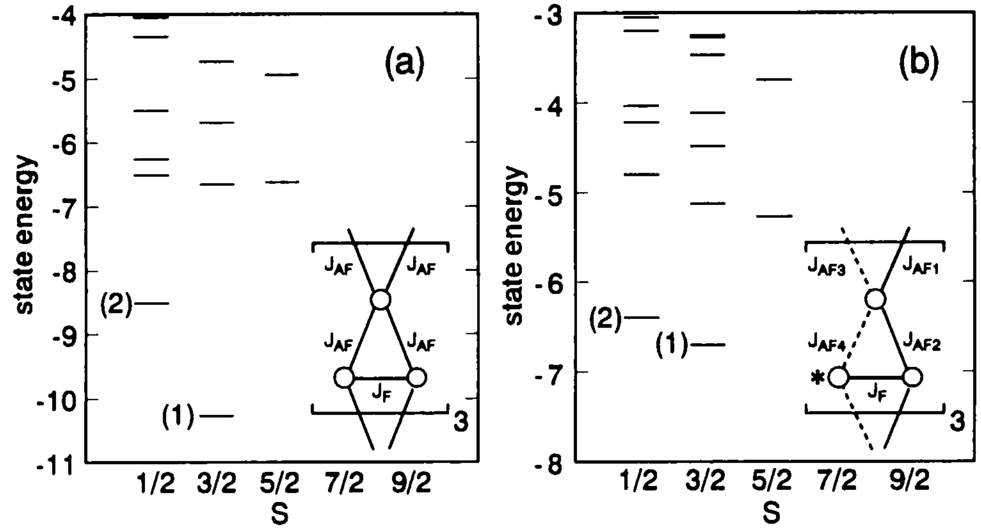


FIGURE 6 State energies of the $3N$=9 system calculated for the symmetric (a) and asymmetric (b) Hamiltonians shown in the insets. The exchange interaction parameters are; J_F =1, J_{AF} =-1 in (a) and J_{AF1} =-1, J_{AF2} =-1.1, J_{AF3} =0, J_{AF4} =0 in (b).

Unfortunately, the quasi-degeneracy equivalent to "one S=1/2 spin per repeating unit" has not been verified for general $3N$ owing to the memory-size limitation for computation. In the $3N$=12 system, for example, four S=1/2 spins correspond to a set of six-fold degenerate eigenstates; two S=0, three S=1 and one S=2 states. The degeneracy is beyond the calculation capacity at the moment.

The quasi-degeneracy breaks the stability of the ferrimagnetic-like ground state. This instability is regarded as inherent in multi-centered antiferromagnetic interactions connecting ground-multiplet molecules with S=1/2 molecules. It is concluded that the spatial symmetry of intermolecular antiferromagnetic interactions is vitally important for the spin state distribution in the vicinity of the ground state when internal magnetic degree of freedom in an S>1/2 spin is not negligible (i.e., finite J_F associated with the multi-centered J_{AF}'s).

CONCLUSION

The magnetic properties of the molecular complex composed of nitronylnitroxide-based radical molecules with different spin multiplicities were investigated from the viewpoint of a model system of low-dimensional ferrimagnetic materials. The complex crystal is regarded as an assembly of one-dimensional alternating chain of $S=1/2$ and $S=1$. The $S=1$ site is a composite system of two isotropic $S=1/2$ spins coupled by finite ferromagnetic interaction. The salient feature of the molecular complex at hand is that ferromagnetic interaction is comparable with both the intermolecular antiferromagnetic interaction and the thermal energy.

The ferrimagnetic-like ground state was given from the numerical calculation of a finite-size Heisenberg Hamiltonian with antiferromagnetic interactions connecting the $S=1/2$ sites uniformly. On the other hand, from the susceptibility, magnetization curve and spin-spin relaxation time measurements, it was found that the magnetic moment in the chain tailed off below 3 K although the ferrimagnetic-like short range order appeared to develop along the chain around 6 K. By lowering the symmetry of the Hamiltonian according to the spatial symmetry of the crystal structure, we have found the appearance of the quasi-degeneracy of the ground state and low-lying excited states. The quasi-degeneracy breaks the stability of the ferrimagnetic-like ground state. The contradiction between the experimental results and the theoretical calculation based on the symmetric Hamiltonian has been qualitatively removed by invoking the symmetry lowering of the Hamiltonian.

After Buchachanko's proposal,[9] many efforts have been devoted to construct ferrimagnetic materials from purely organic molecules. However, all the long range-ordered molecule-based ferrimagnets reported so far contained transition metal ions.[10] The difficulty in achieving ferrimagnetic order in the organic molecule-based materials should stem from the isotropic exchange interaction, as mentioned in the introduction, which favors "quantum mechanically disordered ground states", i.e., singlet pairs formed between the adjacent $S=1/2$ spins.

In considering that achieving a stable ferrimagnetic-like ground state is not equivalent to realizing a long range order, a prerequisite for the ferrimagnetic order can be proposed from the present study: The spatial symmetry of intermolecular antiferromagnetic interaction is crucial to the stability of ferrimagnetic-like ground state. The spatial symmetry becomes important only when the intermolecular antiferromagnetic interactions have multi-centered feature. In this sense, careful molecular-orbital consideration is needed, as the next step, for designing ground-multiplet molecules with the spin density distributed over the molecule due to robust spin polarization from the viewpoint of intermolecular exchange interactions.

ACKNOWLEDGMENTS

The authors are grateful to Professor Kizashi Yamaguchi and Professor Wasuke Mori at Osaka University for their kind help in susceptibility measurements. This work has been supported by Grants-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/04 242 103, 04 242 104 and 04 242 105) and for Encouragement of Young Scientists (No. 07740553) from the Ministry of Education, Science and Culture, Japan and also partly by the Ministry of International Trade and Industries, Japan (NEDO project on "Organic Magnets").

REFERENCES

1. M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashim and M. Kinoshita, Chem. Phys. Lett., 186, 401(1991); Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashim, M. Kinoshita and M. Ishikawa, Phys. Rev. B, 46, 8906(1992).
2. For recent developments in the molecule-based magnetism, see Proceedings of the fourth International Conference on Molecule-Based Magnets, Salt Lake City, 1994; Mol. Cryst. and Liq. Cryst., in press.
3. D. Shiomi, M. Tamura, H. A. Katori, T. Goto, A. Hayashi, Y. Ueda, H. Sawa, R. Kato and M. Kinoshita, J. Mater. Chem., 4, 915(1994).
4. A. Izuoka, M. Fukuda, R. Kumai, M. Itakura, S. Hikami and T. Sugawara, J. Am. Chem. Soc., 116, 2609(1994).
5. Y. Pei, M. Verdaguer, O. Kahn, J. Sletten and J. P. Renard, Inorg. Chem., 26, 138(1987); M. Verdaguer, M. Julve, A. Michalowicz and O. Kahn, Inorg. Chem., 22, 2624(1983).
6. A. Izuoka, M. Fukuda and T. Sugawara, Mol. Cryst. Liq. Cryst., 232, 103(1993).
7. We have modified the program package "TITPACK" version 2 supplied by H. Nishimori at Tokyo Institute of Technology.
8. J. C. Bonner and H. W. J. Brote, Phys. Rev. B, 25, 6959(1982).
9. A. L. Buchachenko, Dokl. Akad. Nauk. Eng. Ed., 244, 107(1979).

10. For example, see O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard and J. Sletten, J. Am. Chem. Soc., 110, 782(1988); A.Caneschi, D. Gateschi, J. P. Renard, P. Rey and R. Sessoli, Inorg. Chem., 28, 1976(1989); H. O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat and O. Kahn, J. Am. Chem. Soc., 116, 3866(1994).