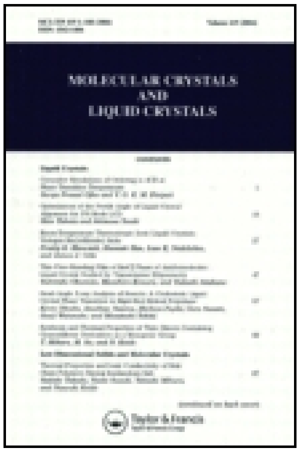

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Low Temperature Spin State of a Model System for Organic Ferrimagnets as Studied by Single Crystal Cw-Esr Spectroscopy

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LOW TEMPERATURE SPIN STATE OF A MODEL SYSTEM FOR ORGANIC FERRIMAGNETS AS STUDIED BY SINGLE CRYSTAL CW-ESR SPECTROSCOPY

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Abstract We have studied a model compound for purely organic ferrimagnets by single crystal cw-ESR spectroscopy. The system under study is composed of two kinds of nitronylnitroxide molecules with the ground states of $S=1/2$ and $S=1$. These molecules are stacked in an alternating chain in the crystal. The cw-ESR signal of the compound split below 10 K into two lines, which were reproduced by the superposition of two Lorentzian lines. The X-ray measurements at 9.6 K disclosed that the crystal structure remained unchanged at low temperatures, indicating that the origin of the ESR line splitting is not attributable to structural phase transitions but to some change inherent in the spin state: Two distinguishable spin species appear in the crystal to give the line splitting. The magnetic interaction fields from the two species are elucidated on the basis of the angular dependence of the ESR linewidths: One is a three-dimensional interaction field, while the other is a one-dimensional interaction field which is axially symmetric along the alternating chain. The appearance of the two kinds of spin species demonstrates that the classical picture of ferrimagnetic states (antiparallel alignment of adjacent spins with different spin quantum numbers) can not apply to purely organic ferrimagnets and it leads to miss an essential part of their nature. This results from the internal magnetic degree of freedom within the $S=1$ molecule, i.e., finite intramolecular ferromagnetic interaction.

INTRODUCTION

After the discovery of the first purely organic ferromagnet *p*-NPNN (T_C = 0.64 K),[1] extensive studies have been done to construct the organic molecule-based ferromagnets with higher T_C.[2] After Buchachenko's proposal for organic ferrimagnetism in 1979,[3] ferrimagnets have been attracting attention as one of the facile approach to organic ferromagnets. However, long-range ferrimagnetic order has not been documented so far

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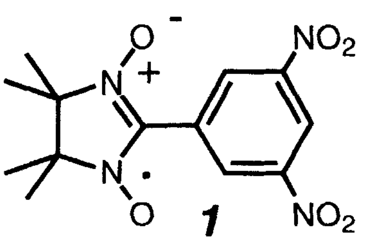
in organic molecular crystalline solids. Only a "model compound" of organic ferrimagnet was synthesized as late as in 1994. The crystal of the model compound consists of alternating chains of two kinds of nitronylnitroxide molecules with the ground states of $S=1/2$ (*1*) and $S=1$ (*2*).[4] The crystal structure seemingly favors a antiferromagnetic spin alignment between neighboring spins with differing magnetic moments (we define this spin arrangement as ferrimagnetic). However, the χT value has been found to decrease below 3 K, demonstrating that ferrimagnetic spin alignment has not been achieved.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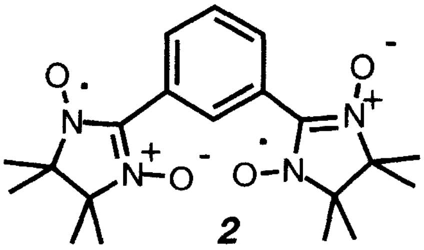
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We have calculated the spin state energy of an $S=1/2$ and $S=1$ alternating chain in which the intramolecular magnetic degree of freedom remains within the $S=1$ site,[5] assuming that the $S=1$ spin is composed of two $S=1/2$ spins coupled by finite ferromagnetic interaction. The calculation has shown that one $S=1/2$ spin in the repeating unit of the chain remains free of magnetic coupling in the ground state. This peculiar result suggests that two of the three $S=1/2$ spins in the repeating unit disappear owing to the formation of a singlet pair leading to the quenched magnetic moments so that they no longer contribute to the bulk magnetic moment at low temperatures. Thus we attributed the decrease in χT value below 3 K observed for the complex (*1*+*2*) to the partial disappearance of spin magnetic moments suggested in the calculation. Such disappearance of magnetic moments has been supported by an increase in the spin-spin relaxation time T_2 at low temperatures in the single-crystal pulsed ESR measurements,[5] but no direct evidence for the interaction-free $S=1/2$ spin mentioned above has been obtained yet.

The ground state calculated corresponds to the low-temperature limit of the spin state of the chain. At finite temperatures, the two of the three spins described above should recover their contribution to the bulk magnetic moment. Such thermally activated spins are to be regarded as a one-dimensional array of $S=1/2$ spins since the thermal energy partially destroys the intermolecular antiferromagnetic couplings along the chain. Thus, two kinds of paramagnetic species are expected to appear at finite temperatures: one is free of magnetic coupling and the other undergoes one-dimensional magnetic interaction.

In this paper, single crystal cw (continuous-wave)-ESR and the low temperature crystal structure of the compound are examined in order to clarify the spin state of the molecular chain of (***1***+***2***). The spin state of (***1***+***2***) deduced from the experiments is compared with the calculated result. The discrepancy between the spin state obtained and the ferrimagnetic spin alignment based on the classical picture is emphasized.

EXPERIMENTAL

The single crystal cw-ESR spectra were recorded in the X band on a Bruker ESR spectrometer ESP 300. The crystal structure determination at low temperatures was performed using a MAC Science Weissenberg-type imaging plate system equipped with a DAIKIN closed-cycle helium refrigerator.

RESULTS AND DISCUSSION

ESR Line Splitting at Low Temperature

The cw-ESR spectrum exhibited a single Lorentzian line at room temperature. Below 10 K the spectrum split into two lines. The splitting was reversible on cooling and warming. The resulting spectrum was well reproduced by the superposition of two Lorentzian lines A (strong) and B (weak) as shown in Figure 1.

Low-Temperature Crystal Structure

Two mechanisms can be proposed for the splitting of the ESR spectrum on lowering the temperature: (i) The "site-splitting" owing to symmetry reduction associated with structural change and (ii) spin-state change due to magnetic interaction. The X-ray crystal structure analyses of the single crystal of (***1***+***2***) at 9.6 K, 30K and 298K showed that the crystal structure, including the molecular conformations of (***1***+***2***), remained unchanged on lowering the temperature. The lattice parameters of (***1***+***2***) determined by the X-ray measurements are shown in Table I. Only a shrinkage of the unit cell was observed at low temperatures. Thus, the splitting of the cw-ESR spectrum below 10 K is attributable to some change inherent in the spin state of the system under study.

TABLE I Lattice parameters of (***1***+***2***).†

T/K	a / Å	b / Å	c / Å	α /deg.	β/deg.	γ/deg.	Vol./Å^3
298	11.527(3)	13.198(3)	7.294(3)	105.45(2)	106.30(2)	80.691(2)	1022.1(5)
30	11.15(1)	12.82(1)	7.134(7)	105.9(1)	101.9(1)	70.09(7)	976.1(9)
9.6	11.15(1)	12.82(1)	7.133(7)	105.9(1)	101.8(1)	70.08(7)	976.0(9)

† The space group is P1 at all temperature examined.

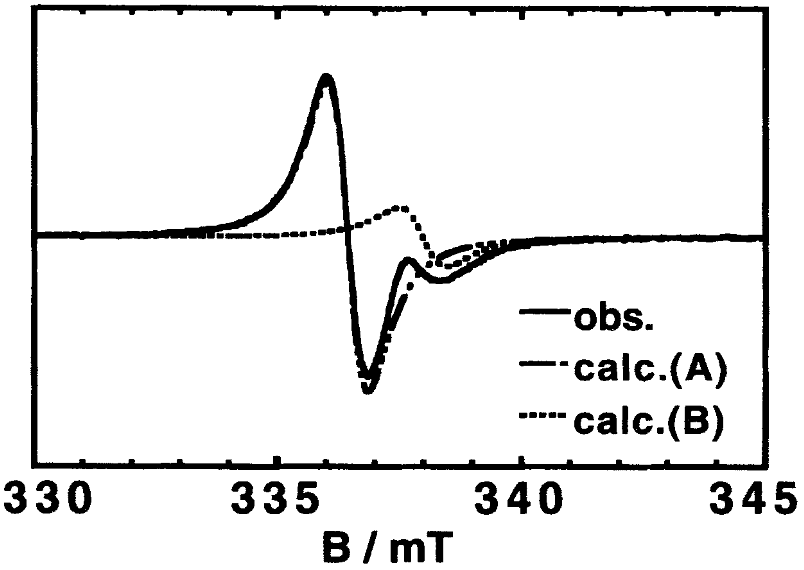

FIGURE 1 Observed and calculated (decomposed) ESR spectra of the single crystal of the molecular complex (*1*+*2*). The solid line represents the observed spectrum at 3 K with the static field in the a*b* plane (130° from the a*-axis). The dashed lines, A and B, show the decomposed spectra calculated by assuming the Lorentzian line shapes.

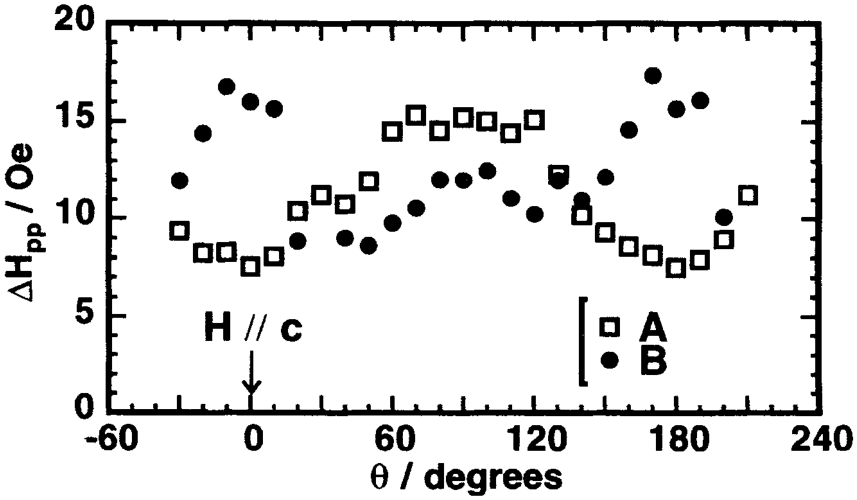

FIGURE 2 Angular dependence of the ESR linewidths in the a*c plane at 3 K. The squares (A) and closed circles (B) denote the Lorentzian lines obtained from the deconvolution of the observed spectrum.

ESR Linewidth and Magnetic Structure

We analyzed the angular dependence of the peak-to-peak linewidths ΔH_{pp} of the ESR signals A and B. The angular dependence of the linewidths in the a*c plane at 3 K is shown in Figure 2.

The component B shows a maximum of ΔH_{pp} in the magnetic field direction parallel to the molecular stacking chain (// c-axis) and minima at the two magic angles (54.7° and 125.3°). This finding is characteristic of axially symmetric (one-dimensional) magnetic structure along the chain.[6] The intensity of the B signal decreased on lowering the temperature. These results indicate that the component B corresponds to the thermally activated paramagnetic spins coupled by the antiferromagnetic interactions along the chain as expected above on the basis of the calculation. On the other hand, the ΔH_{pp} value of A is proportional to $\sin^2\theta$ (θ is the angle between the c-axis and the magnetic field), suggesting that there is no preferential direction of magnetic interaction such as the one-dimensional chain axis found in B. The signal intensity of A was enhanced with decreasing temperature. From these results, the component A can be assigned to the apparently free $S=1/2$ spin appearing in the ground state as calculated.[5]

A schematic picture of the ground state of the alternating chain composed of the $S=1/2$ and $S=1$ molecules is represented in Figure 3(a), which is based on the theoretical calculation[2] in accordance with the experimental results of the present ESR study.

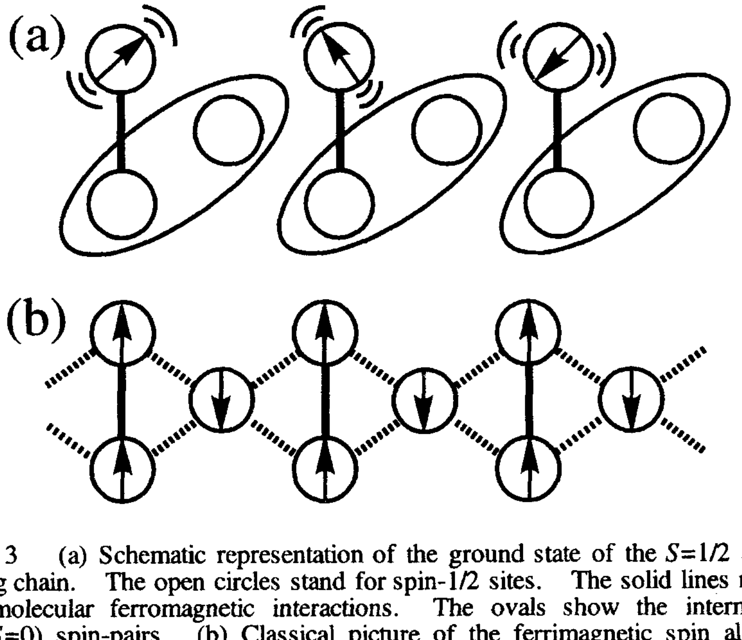

FIGURE 3 (a) Schematic representation of the ground state of the $S=1/2$ and $S=1$ alternating chain. The open circles stand for spin-1/2 sites. The solid lines represent the intramolecular ferromagnetic interactions. The ovals show the intermolecular singlet ($S=0$) spin-pairs. (b) Classical picture of the ferrimagnetic spin alignment. The dashed lines show the intermolecular antiferromagnetic interactions.

The intramolecular ferromagnetic interaction in the molecule ***2*** (the solid line in Figure 3(a)) should still hold at low temperatures since the molecular framework remains unchanged. However, antiferromagnetic coupling between the quantum (magnetically isotropic) spins of organic molecules inherently favors the non-magnetic singlet rather than antiparallel alignment of adjacent spins as described in the classical picture of antiferromagnetic (ferrimagnetic) system (Figure 3(b)). Such nature of the quantum spins brings about the peculiar spin structure as shown in Figure 3(a); one of the two $S=1/2$ spins in the $S=1$ site participates in the formation of the intermolecular singlet pairs along the molecular chain, leaving the other $S=1/2$ spin at the $S=1$ site nearly free of magnetic interactions. This peculiarity is only apparent and is intrinsic to multi-centered high spins with weak intramolecular ferromagnetic interactions.

CONCLUSION

The splitting of the ESR signal was observed for the nitronylnitroxide-based molecular crystal, (***1***+***2***). The X-ray measurements showed that the crystal structure remained unchanged at low temperatures. The origin of the ESR line splitting is attributable to the change in the spin state: Two kinds of spin species appear in the crystal on lowering the temperature. The angular dependence of the ESR linewidths disclosed the existence of the two kinds of magnetic interaction fields: One is the three-dimensional interaction field, while the other is the axially symmetric (one-dimensional) interaction field along the molecular stacking chain. The appearance of the two kinds of spin species in the (***1***+***2***) stacking chain demonstrates that the classical simple picture of organic ferrimagnetic spin alignment shown in Figure 3(b) is invalid for purely organic spin systems as illustrated in Figure 3(a). This results from the internal magnetic degree of freedom within the $S=1$ molecules, i.e., from the combined effect of the quantum nature of the magnetically isotropic spins and the finite magnitude of intramolecular ferromagnetic interaction comparable to thermal activation energy.

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REFERENCES

1. M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takashima and M. Kinoshita, Chem. Phys. Lett., 186, 401(1991); Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takashima, M. Kinoshita and M. Ishikawa, Phys. Rev. B, 46, 8906(1992).
2. For recent developments in the molecule-based magnetism, see Proceedings of the fifth International Conference on Molecule-Based Magnets, Osaka, 1996; Mol. Cryst. Liq. Cryst.
3. A. L. Buchachenko, Dokl. Akad. Nauk. Eng. Ed., 244, 107(1979).
4. A. Izuoka, M. Fukuda, R. Kumai, M. Itakura, S. Hikami and T. Sugawara, J. Am. Chem. Soc., 116, 2609(1994).
5. D. Shiomi, M. Nishizawa, K. Sato, T. Takui, K. Itoh, H. Sakurai, A. Izuoka and T. Sugawara, Mol. Cryst. Liq. Cryst., 278, 989(1996).
6. For example, see R. E. Dietz, F. R. Merritt, R. Dingle, D. Hone, B. G. Silbernagel and P. M. Richards, Phys. Rev. Lett., 26, 1186(1971).