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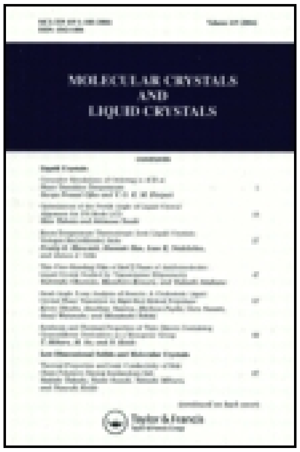

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# Low-Temperature Magnetic Properties of Nitronyl Nitroxides

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# LOW-TEMPERATURE MAGNETIC PROPERTIES OF NITRONYL NITROXIDES

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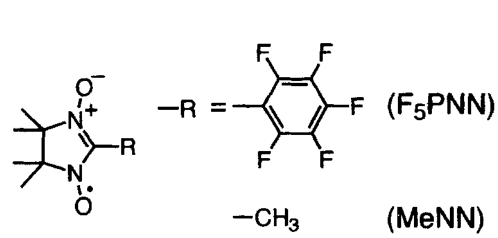
Abstract Magnetic properties of two nitronyl nitroxide (4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide) radicals which show nearly isotropic $S=1/2$ alternating linear chains are investigated down to 0.5 K and up to 9 T. Pentafluorophenyl nitronyl nitroxide at low temperatures shows an antiferromagnetic chain with alternation, while the material at room temperature shows a uniform chain structure. 2-Methyl nitronyl nitroxide, which contains an alternating chain with ferromagnetic and antiferromagnetic interactions, exhibits a three-dimensional phase transition at 1.3 K.

## INTRODUCTION

After a genuine organic ferromagnet was discovered,[1] molecular magnetic materials have attracted more and more interest. Organic radicals have highly isotropic spin which results from an unpaired electron in a molecule containing only light elements. Thus these radicals are suitable for investigating magnetism of isotropic quantum spin systems.

In recent years, magnetism of the nitronyl nitroxide (NN) family has extensively been studied by many researchers. These materials afford excellent stability and good crystallinity. Magneto-structural correlations in this family have been studied. Previous papers [2-5] have reported that antiferromagnetic or ferromagnetic interactions are attributed to contacts between NO groups or between NO and 2-substituent groups, respectively.

Among the family of NN radicals, we focus on pentafluorophenyl nitronyl nitroxide ($F_5PNN$) and methyl nitronyl nitroxide (MeNN).



Properties of these materials have already been partly investigated. It has been reported that $F_5PNN$ at low temperatures can be described by an alternating model with two antiferromagnetic interactions in one dimension.[2] MeNN is known to contain an alternating chain with ferromagnetic and antiferromagnetic interactions.[6]

These systems in one dimension are described by the following Heisenberg Hamiltonian:

$$H = -2J \sum_{i=1}^{N/2} (S_{2i-1} \cdot S_{2i} + \alpha S_{2i} \cdot S_{2i+1}) , \qquad (1)$$

where $S$ denotes the $S$=1/2 spin operator and $N$ is the number of sites which should be even. We define $J < 0$. The periodic boundary condition is imposed. There are three cases, $\alpha = 1$, 0 and $-\infty$, which have well been studied. For $\alpha = 1$, the system describes an $S$=1/2 uniform chain, which has no energy gap above the ground state. When $\alpha = 0$, the system is reduced to the dimer model. In the limit of $\alpha \to -\infty$, the system becomes an $S$=1 uniform chain. It is known that the system has a gapped excitation spectrum above the unique ground state.[7] This gap is called the Haldane gap. The magnetization curve for this system at 0 K is also known.[8]

There remain two intermediate regions, $0< \alpha <1$ and $\alpha < 0$. The model for $0< \alpha <1$ describes an alternating chain with strong and weak antiferromagnetic interactions. It is known that this system has an energy gap. Calculations for finite systems up to 12 spins have been reported.[9-12] When $\alpha < 0$, the alternating chain has both antiferromagnetic and ferromagnetic interactions. The magnetic susceptibilities using these models up to 14 spins have been calculated.[13] As $\alpha$ decreases, this system is expected to go continuously into the Haldane-gap phase.[14]

In this paper, we discuss low-temperature magnetism of $F_5PNN$ and MeNN in static fields. We analyze our experimental results within the framework of the models for the intermediate regions.

## EXPERIMENTAL AND CALCULATION

The two radicals were synthesized by a procedure reported previously.[3, 15] Single crystals of $F_5PNN$ were packed in the cylindrical sample space so as to avoid stress, because the magnetic properties of this compound are very sensitive to pressure.[16] For MeNN, a powdered sample was used for magnetic measurements.

The magnetization was measured by the sample-extraction method in static fields. The temperature was determined by a ruthenium oxide thermometer ( RO600B2, SCIENTIFIC INSTRUMENTS, INC. ) with an AC resistance bridge ( AVS-47, RV-

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Elektroniikka Oy PICOWATT ). Magnetic measurements were carried out in static magnetic fields up to 9 T. Susceptibilities at low temperatures are defined as the ratios of magnetization to a static field of 0.05 T, in which the linear field dependence of magnetization is retained. Temperatures from 0.5 to 4.2 K were obtained in a $^3$He cryostat. The temperature accuracy was within 0.1K above 1 K and within 0.05K below 1K.

In order to accurately analyze the observed data for $F_5$PNN using an antiferromagnetic chain with alternation, we performed exact diagonalizations of a chain with increasing even length up to $N = 14$ and calculated magnetization curves and susceptibilities at finite temperatures. Differences between the results for $N = 14$ and those for $N = 12$ are so small in the range of magnetic field and temperature considered here, that the curves for $N = 14$ and for $N = 12$ are indistinguishable. Such rapid convergences as $N$ increases confirm that the results for $N$=14 approximate well the behavior for $N = \infty$. Thus we use the curves for $N = 14$ in our analysis.

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## RESULTS AND DISCUSSION

### $F_5$PNN

Reference 2 have reported the crystal structure at room temperature and the magnetic properties of $F_5$PNN above 1.5 K. The compound has a uniform chain structure at room temperature as is shown in Fig. 1. However, the magnetism is better described by the alternating chain with $2J/k_B = -5.6$ K and $\alpha = 0.4$ than by the uniform chain. The difference is considered to come from symmetry breaking of the crystal structure at low temperatures. Evidence supporting this is provided by single-crystal EPR measurements.[2]

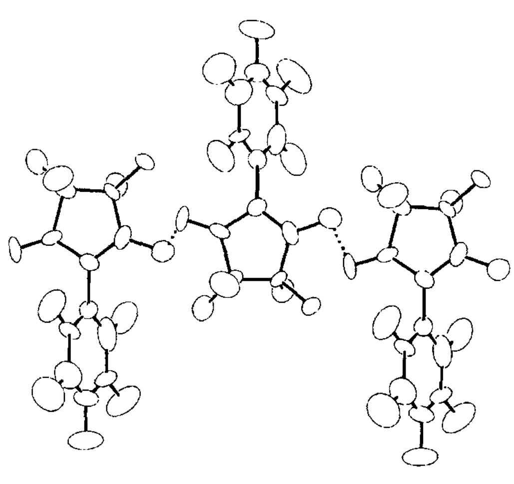

FIGURE 1 Uniform chain structure of $F_5$PNN at room temperature.[2] Dotted lines represent the NO...NO contacts.

The purpose of this study is to establish the low-temperature magnetic properties of this system from magnetic measurements down to 0.5 K. Figure 2 shows the temperature dependence of paramagnetic susceptibility, $\chi_p$, below

3.8 K. This result is consistent with the one above 1.8K reported previously.[2] The susceptibility has a maximum at 3.4 K, decreases continuously and rapidly below 3.4 K and seems to vanish as $T \to 0$. This suggests the existence of an energy gap above the unique singlet ground state. The qualitative analysis confirms that the temperature dependence of $\chi_p$ down to 1.2 K is well described by an alternating antiferromagnetic chain with reported exchange parameters, $2J/k_B$ = -5.6 K and $\alpha$=0.4.[2]

The magnetization processes at low temperatures were also examined. In Fig. 3 (a), we find that the gradient at $H = 0$ tends to vanish below 2 K.This

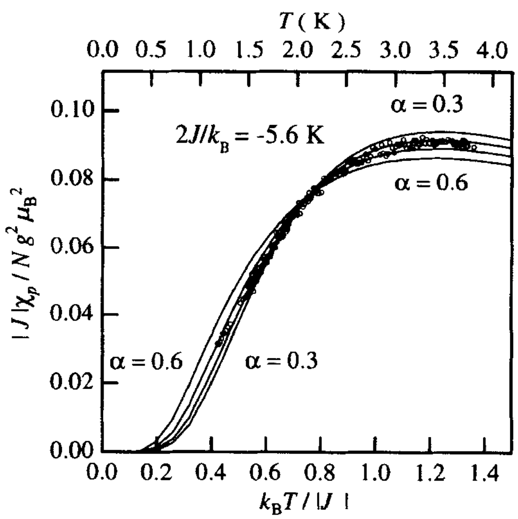


FIGURE 2 Analysis of the susceptibility of $F_5$PNN at low temperatures with the alternating Hamiltonian (1). Solid curves are obtained for $\alpha$ = 0.3, 0.4, 0.5 and 0.6. Here we use $g$ = 2.0.

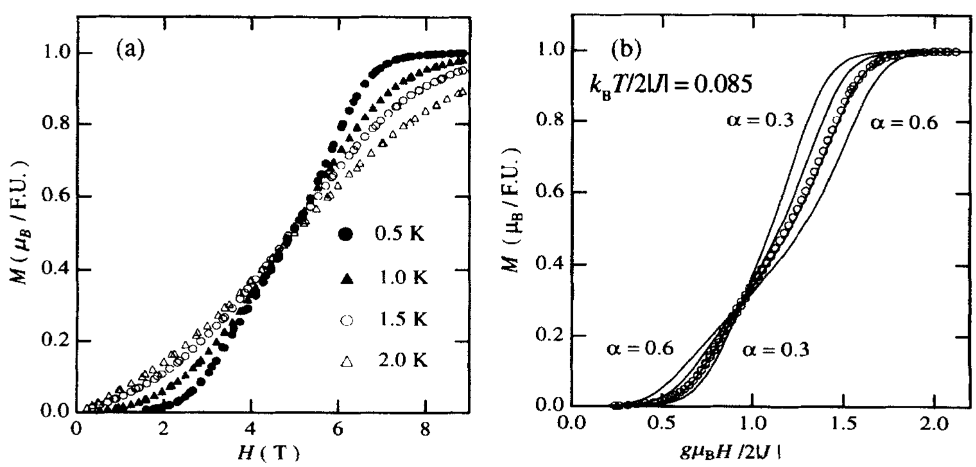


FIGURE 3 Magnetizations of $F_5$PNN. (a) Observed data at low temperatures. (b) Analysis of the magnetizations. Circles denote the observed data at 0.5 K. We use $2J/k_B$ = -5.6 K and $g$ = 2.0 to scale the field. Solid curves represent the theoretical results for $\alpha$ = 0.3, 0.4, 0.5 and 0.6.

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also confirms the existence of an energy gap, which is suggested by the measurement of susceptibility. It is necessary to check whether these magnetization data are reproduced by the alternating antiferromagnetic chain with $2J/k_B$ = -5.6 K and $\alpha$ = 0.4. For this purpose, we use the theoretical curves at finite temperatures. In Fig. 3 (b), the observed data at 0.5 K are compared with the theoretical curves for various $\alpha$ and $2J/k_B$ = -5.6 K. In low fields, the observed data agree well with the curve for $\alpha$ = 0.4. In higher fields, however, they agree better with the curve for $\alpha$ = 0.5 than with the one for $\alpha$ = 0.4. The change arises near the crossing point of the curves for $\alpha$ = 0.4 and 0.5. This behavior indicates that the changes of the interactions in this material are also induced by magnetic fields.

MeNN

The structure of MeNN at room temperature is shown in Fig. 4. Details of the structure will be reported in a separate paper.[6] The crystal consists of an alternating chain with NO...NO contacts and NO...Me ones. According to the magneto-structural correlations in NN family in Ref. 2-5, we expect that the NO...NO contact corresponds to an antiferromagnetic interaction and that the NO...Me contact corresponds to a ferromagnetic

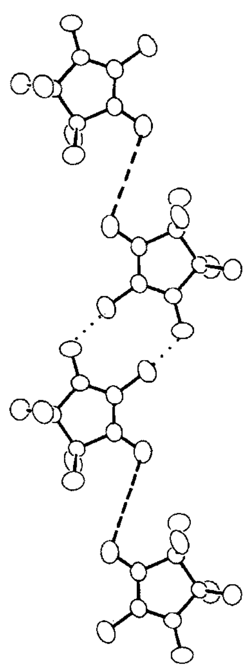

FIGURE 4 Alternating chain structure of MeNN. Dotted and dashed lines denote the NO...Me and NO...NO contacts, respectively.

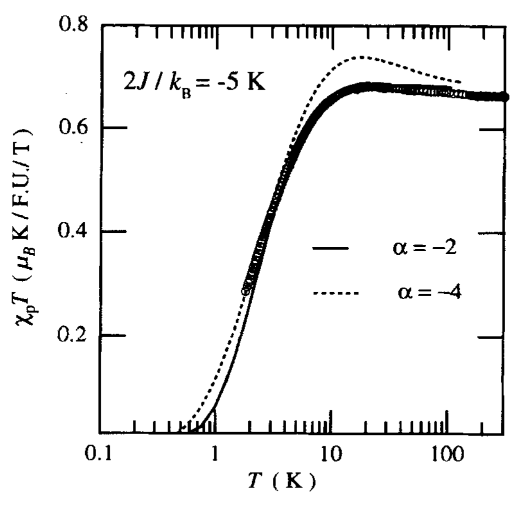


FIGURE 5 Temperature dependence of $\chi_p T$ of MeNN. Circles denote our observed data. The solid and dashed curves are obtained theoretically for $2J / k_B$ = -5 K and $g$ = 2.0.[13] The dashed one for $\alpha$ = -4 is for comparison.

interaction. It is reasonable to consider that this material is described by the Hamiltonian(1) with alternation of ferromagnetic and antiferromagnetic interactions.

Figure 5 shows the plot of $\chi_p T$ *versus* $T$. The maximum near $T = 20$ K indicates the existence of ferromagnetic interactions. Below about 10 K, $\chi_p T$ decreases as $T$ is decreased. This suggests that there are also antiferromagnetic interactions. The existence of these two kinds of interactions, indicated by the $\chi_p T$ *versus* $T$ plot, is consistent with the application of the Hamiltonian (1) with negative $\alpha$. Our susceptibility data above about 3 K fitted by the calculations reported in Ref. 14 give $2J / k_B = -5$ K and $2\alpha J / k_B = +10$ K. It should be noted that the ferromagnetic interaction is larger than the antiferromagnetic interaction. Below 3K, the ferromagnetic interaction seems to become larger than +10 K.

The magnetization processes below 1 K were also examined. In Fig. 6, they are compared with the theoretical curve [8] for the $S$=1 antiferromagnetic uniform chain at 0 K. We find that, except for the low-field region, our data have similar curvatures to the one for the $S$=1 system. This suggests that, in high fields, two $S$=1/2 spins which are ferromagnetically coupled behave approximately as an $S$=1 spin. The saturation field (4.7T)

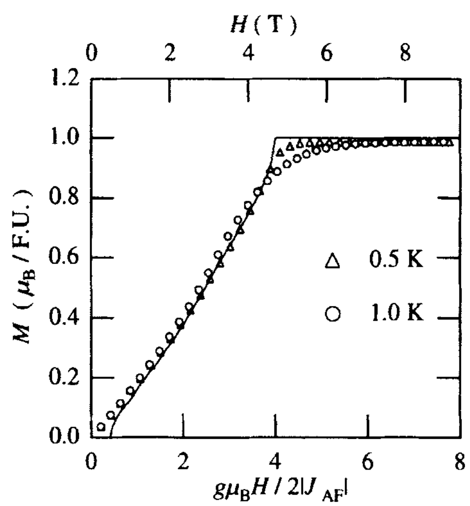


FIGURE 6 Magnetization curves of MeNN at low temperatures as a function of reduced field. The solid curve is normalized and represents an $S$=1 uniform chain,[8] where $2J_{AF}$ represents the antiferromagnetic interaction in the $S$=1 chain. Note that $J = 4\ J_{AF}$. We use $g = 2.0$.

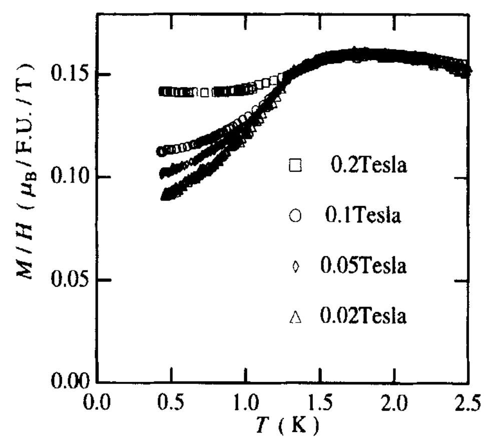


FIGURE 7 Temperature dependences of the ratios of magnetization of MeNN to magnetic field at low temperatures. They are measured in various static fields.

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can give a rough estimate of $2J / k_B = -6.3$ K for the antiferromagnetic exchange interaction. This estimate of the antiferromagnetic interaction from the *M versus H* curves agrees well with that from the fit of the susceptibility data. Almost linear dependence of the magnetization process in low field, however, disagrees with the theoretical curve for the $S$=1 system with a gap.

To investigate this disagreement further, the temperature dependences of the magnetizations were examined in various fields. In Fig. 7, we can clearly see that the behaviors of $M / H$ change at 1.3 K. The linear field dependence of the magnetization is lost below this temperature. It is considered that this change in the field dependence corresponds to a three-dimensional Néel order at $T_N$ = 1.3 K. It is thus found that interchain interactions in this material are not negligible even in our range of temperature.

In conclusion, MeNN is a compound described by the $S$=1/2 ferromagnetic and antiferromagnetic alternating chain with weak interchain interactions.

## SUMMARY

The magnetization processes and the susceptibilities of two nitronyl nitroxide radicals have been studied down to 0.5 K and up to 9 T.

We have observed that, for $F_5$PNN, there exists an energy gap above the singlet ground state. It has been confirmed that this material at low temperatures is described by a one-dimensional Heisenberg model with alternating antiferromagnetic interactions, despite a uniform-chain structure at room temperature. Moreover, we have found that the interactions in a chain depend on the applied magnetic fields.

We have found that, from the measurement of the susceptibility and magnetization, MeNN is a quasi-one-dimensional system of a ferromagnetic and antiferromagnetic alternating chain with weak interchain interactions.

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