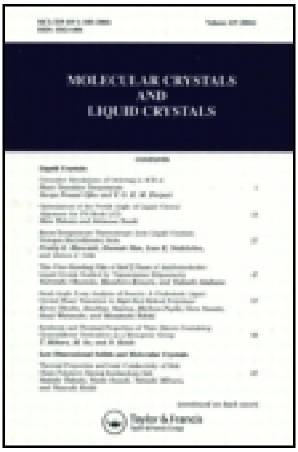

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Ferromagnetism in Organic Radical Crystal

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FERROMAGNETISM IN ORGANIC RADICAL CRYSTAL

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Abstract The search for bulk ferromagnetism in a genuine organic substance has long been one of the major subjects in the field of molecular magnetism. Recently, we have reported the successful results for orthorhombic β-phase crystal of p-nitrophenyl nitronyl nitroxide (abbreviated as p-NPNN). This provides an example of the first genuine organic bulk ferromagnet composed only of light elements. In this article, our recent studies on the ferromagnetic properties of β-phase of p-NPNN are reviewed.

INTRODUCTION

The intermolecular magnetic interaction in organic crystal has been studied for various ion radical salts[1-10] and neutral radical crystals[11-25] for a long time. In most cases, the unpaired electron on a radical is coupled antiferromagnetically with that on the neighboring radicals in a solid state. Such an antiferromagnetic (AFM) exchange originates in the charge transfer interaction between the neighboring radicals[1-4], which is, in turn, mainly governed by the SOMO-SOMO overlap of the neighboring radicals, where SOMO means the singly occupied molecular orbital. When the overlap is finite, the exchange becomes antiferromagnetic, just as two hydrogen atoms form a chemical bond between them with antiparallel electron spin alignment.

On the other hand, however, there are known some organic stable radicals, which show the intermolecular ferromagnetic (FM) exchange in the sense that the temperature dependence of magnetic susceptibility gives rise to a positive Weiss constant (θ) in the Curie-Weiss equation;

$$\chi = \frac{C}{T - \theta}$$

Our approach for searching bulk ferromagnetism in organic crystal consisted of two steps; the first step was to learn or extract the conditions governing FM coupling from detailed studies on the radical crystals having FM exchange[19,20], and the second step was to design radicals meeting with those conditions. For the first step, we chose the galvinoxyl radical as a typical example[26]. What we learned from the studies on galvinoxyl has been reviewed elsewhere [18-20]; only the essence of the conditions for FM coupling[17] is summarized here as follows;

(1) Large spin polarization within a radical.

(2) Small SOMO-SOMO overlap, but large SOMO-NHOMO and/or SOMO-NLUMO overlap between the neighboring radicals, where NHOMO and NLUMO means the next highest occupied and the next lowest unoccupied molecular orbital, respectively.

The first condition (1) means that the radical should have a large intramolecular exchange interaction. The second condition (2), if it is combined with (1), implies that the charge transfer interaction between neighboring radicals is ineffective for the nonmagnetic configuration, but effective for the magnetic configuration. In other words, when an unpaired electron on a radical is transferred to the neighboring radical, open-shell configurations with spin parallel alignment would be lower in energy because of the large intramolecular exchange interaction. Therefore, the intermolecular FM coupling has its origin in the cooperative effect of intramolecular spin polarization and intermolecular charge transfer interaction[17].

After learning these conditions, it is rather easy matter to design radicals satisfying these conditions. As a matter of fact, nitronyl nitroxides are well known to have large spin polarization in the field of radical chemistry and their magnetic properties have first been studied[27-30]. Among the radicals studied, p-nitrophenyl nitronyl nitroxide (abbreviated as p-NPNN; in IUPAC nomenclature, 2-(4'-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1- oxyl-3-N-oxide, $C_{13}H_{16}N_3O_4$, see fig. 1) seems to be quite interesting, because it is shown that p-NPNN exhibits polymorphism and shows FM interaction even in different phases[31].

CRYSTAL STRUCTURES

p-NPNN is now known to crystallize in four different phases; the monoclinic α-phase[31], orthorhombic β-phase[29], ticlinic γ-phase[21] and monoclinic δ-phase(or β_h-phase[31]). The crystal structure data of all these phases are summarized in Table I.

Among these phases, the β-phase is most stable at room temperature; the other phases gradually transform to the β-phase at or below room temperature[25]. All our measurements on the β-phase were done using the single crystals.

FERROMAGNETIC INTERACTION

The field dependence of the magnetization measured at several temperatures between 1.8 and 6 K is shown in Fig. 1. The magnetization grows slowly in accordance with the Brillouin function for the S=1/2 free spins at high temperature, but its growth becomes steeper on cooling. In this way, it is confirmed that the FM coupling is opera-

TABLE I Crystallographic constants for the four phases of p-NPNN

Phase	α-phase	β-phase	γ-phase	δ-phase (β_h-phase)
System	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/c$	F2dd	$P\bar{1}$	$P2_1/c$
a/Å	7.307	12.347	9.193	8.963
b/Å	7.596	19.350	12.105	23.804
c/Å	24.794	10.960	6.471	6.728
α/deg			97.35	
β/deg	93.543		104.44	104.25
γ/deg			82.22	
Z	4	8	2	4
V/Å^3	1373.5	2618.5	687.6	1391.3
Reference	31	29	21	25, 31

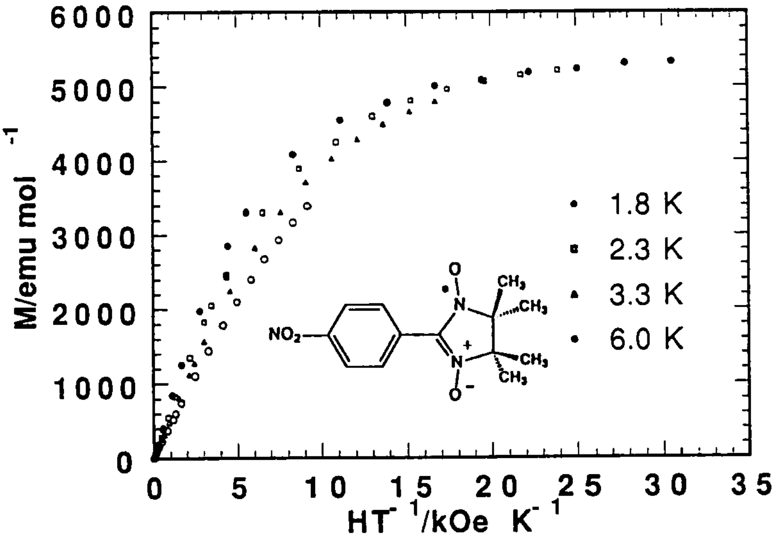


Fig. 1. The molecular structure of p-NPNN and the magnetization isotherms for the β-phase of p-NPNN at 1.8, 2.3, 3.3 and 6.0 K.

tive between the radicals in the β-phase crystal. The saturation value was estimated to be 5500 erg $Oe^{-1}mol^{-1}$ in accordance to the S=1/2 spin (98 %). There was no sizable anisotropy effect when the magnetic field was along any crystallographic axis. Furthermore, the smooth curvature at 1.8 K indicates the absence of ferromagnetic impurity of T_c > 2 K.

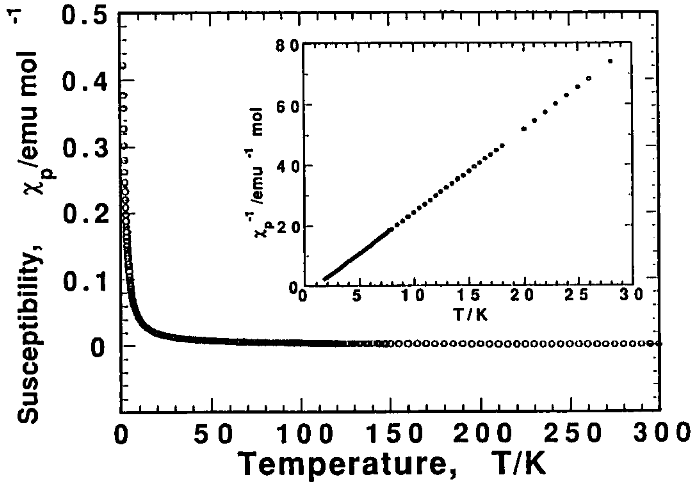


Fig. 2. The temperature dependence of the paramagnetic susceptibility of the β-phase crystal between 1.8 and 300 K.

The temperature dependence of the paramagnetic susceptibility of the single crystal of β-phase of p-NPNN and its reciprocal are shown in Fig. 2. The susceptibility at 300 K, corrected for the diamagnetic contribution, is 1.54×10^{-8} m^3 mol^{-1} in the SI units(=1.23×10^{-3} emu mol^{-1}) in agreement with the Curie law for the S=1/2 spin system (97 %). There was also no sizable anisotropy effect, when the magnetic field was along the a-, b-, and c-axis. The reciprocal susceptibility intersects the abscissa in the positive temperature region. The Weiss constant is 1.2 K. The ferromagnetic coupling is again confirmed to be operative between the adjacent radicals in the crystal.

FERROMAGNETIC TRANSITION

As shown in Fig. 3, the crystal exhibits a transition at T_c = 0.6 K as revealed by the measurements of temperature dependence of heat capacity. The entropy change associated with the transition amounts nearly to Rln2, thereby confirming that the transition is of bulk nature for the S=1/2 system and that the long range magnetic order has been achieved in the crystal below T_c. The existence of the bulk transition indicates that the magnetic interactions are three-dimensional at low temperature.

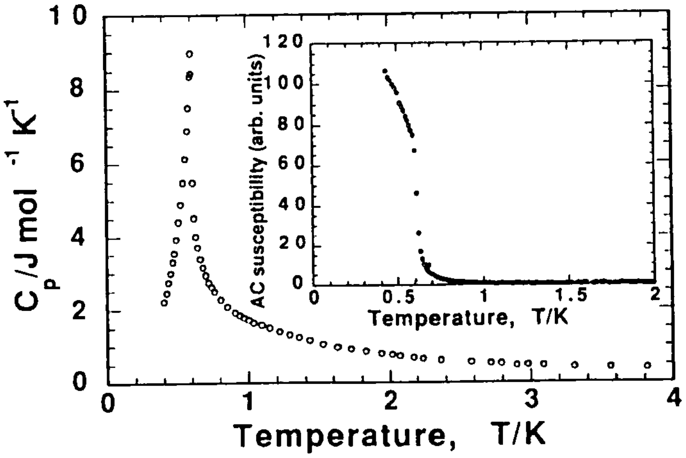


Fig. 3. The temperature dependence of heat capacity and ac susceptibility(inset) of the β-phase crystal of p-NPNN.

The ac susceptibilities were measured on the single crystal at low temperatures using the ac (123 Hz) field of 10 μT. The inset of Fig. 3 shows the results. The ac susceptibility exhibits the diverging behavior at 0.6 K, confirming that the magnetic ground state of the crystal is ferromagnetic.

EVIDENCE FOR BULK FERROMAGNETISM

1. Hysteresis

The magnetization curves observed above and below T_c are shown in Fig. 4 for the β-phase. The magnetization grows slowly at temperatures above T_c. In contrast, the magnetization below T_c saturates very quickly and clearly shows the hysteresis with a small coercive field. The saturation magnetization calibrated against a spherical Ni particle is corresponding to about 0.5 μ_B/molecule at 0.44 K.

2. Heat Capacity in Applied Field

In Fig. 5 is shown the temperature dependence of the heat capacity of the β-phase crystal as a function of applied field. The λ-like peak

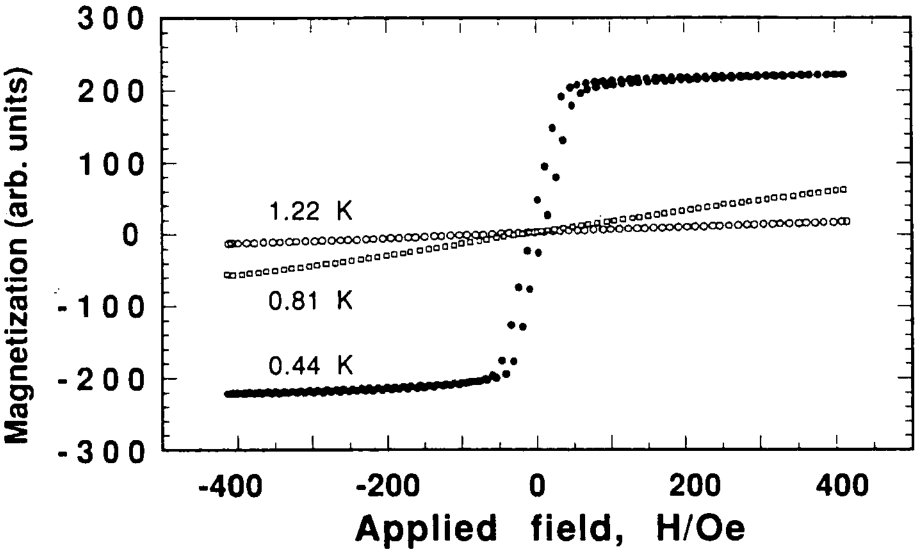


Fig. 4. The magnetic field dependence of magnetization of the β-phase crystal of p-NPNN above and below T_c = 0.6 K.

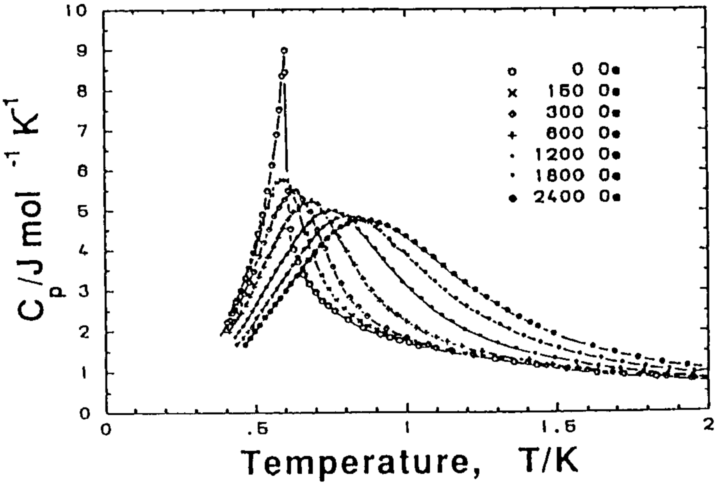


Fig. 5. The temperature dependence of heat capacity of the β-phase crystal of p-NPNN as a function of applied field.

in the zero field disappears at the field around 10 mT and rounded peak gradually shifts to the higher temperature side as the applied field is increased. This is a typical behavior for ferromagnetic substances[32]. In a finite field, the spin system cannot differentiate whether the ordering is achieved spontaneously or by the influence of the applied field. Thus a critical temperature cannot be defined for a ferromagnetic substance in a finite field and the curves gradually change towards those for usual paramagnetic substances. This is the behavior just observed in the β-phase, and supports the assignment to the bulk ferromagnet.

3. ZF-μSR

In order to get more insight into the ferromagnetism of the β-phase crystal, we examined zero-field (ZF) muon spin rotation (μSR) at very low temperature[33]. Figure 6 shows several typical μSR time spectra in β-phase crystal of p-NPNN with the initial muon spin polarization perpendicular to the b-axis. In the paramagnetic phase at 0.70 K, the slowly relaxing signal appears. This is explained by a random internal field of ca. 4 G, which is attributable to static nuclear dipolar fields.

The onset of the spontaneous magnetization in the crystal is directly evidenced by the appearance of oscillation at 0.64 K. In the presence of an internal field, the muon spin undergoes Larmor precession with frequency $\nu_\mu = (\gamma_\mu/2\pi)B_{int}$ and the muon gyromagnetic ratio $\gamma_\mu/2\pi$ =13.553 kHz/G. In ferromagnets at the zero applied field, the internal magnetic field B_{int} consists of dipolar, hyperfine, Lorentz and demagnetization fields and the magnitudes of these fields are directly proportional to the spontaneous magnetization. The oscillation frequency observed in Fig. 6, therefore, represents the muon spin precession around the internal field and is the measure of the magnitude of the spontaneous magnetization.

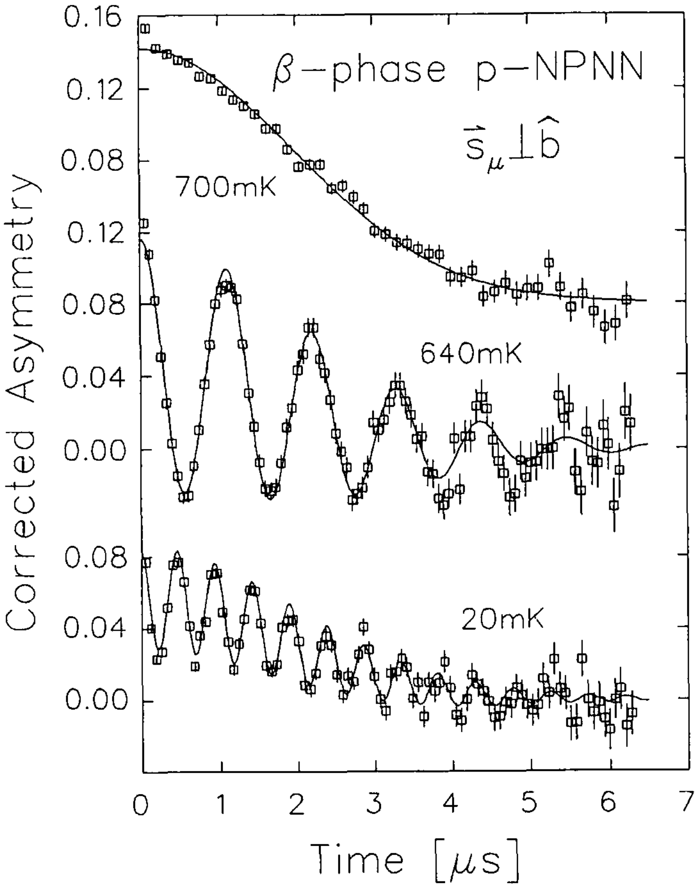


Fig. 6. Zero field muon spin rotation time spectra observed in β-phase single crystals of p-NPNN with initial muon spin perpendicular to the b-axis.

With decreasing temperature, the oscillation frequency increases, reaching a maximum of 2.1 MHz at 0.02 K. The temperature dependence of the frequency $\nu_\mu(T)$ obtained in p-NPNN in zero applied field is shown in Figure 7. Combining the present result of M(0.44 K)/M(0)=0.82 with M(0.44 K)=0.5 μ_B/molecule of Figure 5, we obtain M(0)=0.6 μ_B/molecule. The deviation from the expected value of 1 μ_B/molecule may be due to the systematic uncertainty in the measurements.

The temperature dependence of $\nu_\mu(T)$, namely that of M(T), is very similar to that observed in conventional inorganic ferromagnets. The observed results fit with $M(T)\propto[1-(T/T_c)^\alpha]^\beta$ with α = 1.86 and β=0.32 (the solid curve). The critical magnetization exponent β=0.32 is in agreement with a value of ca. 1/3 expected for a three dimensional Heisenberg system.

The long-lasting oscillation observed below T_c in Figure 6 corresponds to a rather homogeneous local field and indicates that the ferromagnetic spin network is commensurate with the crystallographic structure.

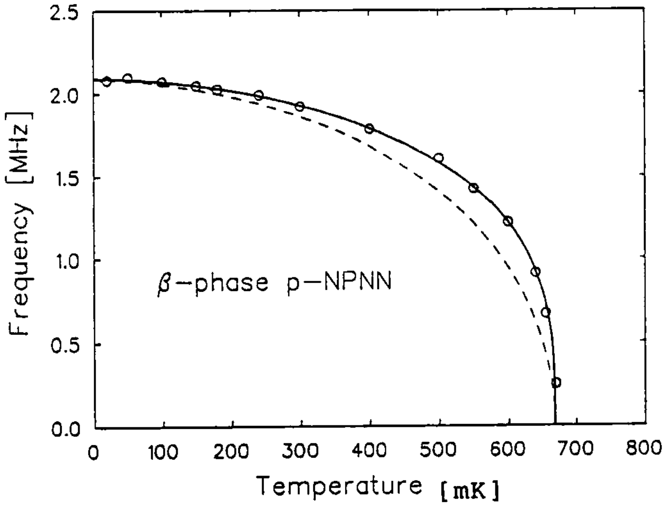


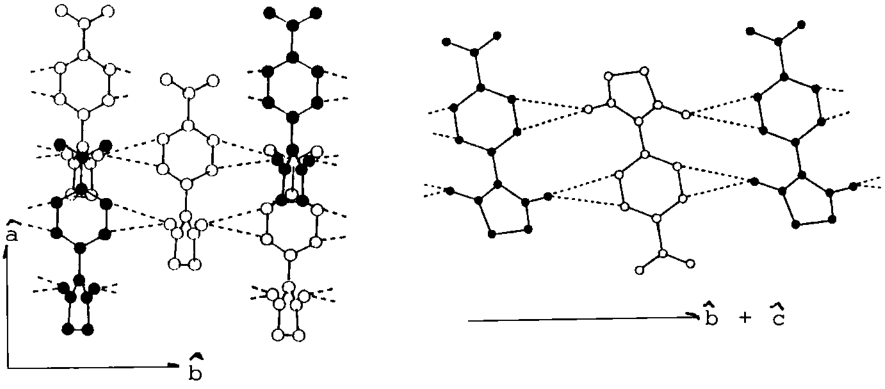
Fig. 7. Temperature dependence of muon precession frequency below T_c in zero external field. The frequency is proportional to the spontaneous magnetization.

When the initial muon spin polarization is parallel to the b-axis, the amplitude of the oscillation is much smaller (about 20 % of that in the perpendicular configuration), indicating that the internal field is nearly along the b-axis. This suggests that the spin alignment in different magnetic domains is not aligned randomly and is most likely along the b-axis.

CONCLUDING REMARKS

From these experiments, we have concluded that the β-phase crystal of p-NPNN undergoes an ordering transition at about 0.6 K towards a bulk ferromagnetic state. The ferromagnetic behavior is well described by an isotropic three dimensional Heisenberg spin system. The present finding provides the first example of a bulk ferromagnet of simple organic compound composed only of light elements.

As for the exchange coupling route, it is adequate to point out that the crystal structure of the β-phase (F2dd) is quite similar to that of a diamond (Fd3m). If all the p-NPNN molecules are replaced by spherical carbon atoms, the orthorhombic lattice of β-phase would become a cubic lattice, which is just the diamond structure. The molecules coordinated tetrahedrally are connected between the NO group and the phenyl ring as shown in Fig. 8a. This kind of molecu-



(a) β-phase p-NPNN (b) γ-phase p-NPNN

Fig. 8. Molecular arrangements leading to ferromagnetic coupling.

lar arrangement is observed quite commonly in the derivatives having FM intermolecular coupling such as p-bromophenyl[34], p-pyridyl[35] nitronyl nitroxide and the γ-phase of p-NPNN[21]. Therefore, we are certain that the molecular arrangement of Fig. 8 plays an essential role for the FM coupling in the series of nitronyl nitroxide derivatives. It is very important to elucidate the nature of this arrangement of FM coupling.

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