Antiferromagnetic Ground State in Organic Quasi-1D Ferromagnet
\(\gamma\)-Phase para-Nitrophenyl Nitronyl Nitroxide

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We have studied the ground state of an organic quasi-one-dimensional (Q1D) ferromagnet, the \(\gamma\)-phase \(\text{para-nitrophenyl nitronyl nitroxide} (\gamma-p\text{-NPNN})\), by low-frequency ESR and magnetic torque measurements, and have found that it is an antiferromagnetically ordered state with an orthorhombic anisotropy. Antiferromagnetic resonance (AFMR) modes are observed below 0.6 K. From the angle dependence of AFMR, the spin easy axis is found to point the [011] direction. The spin-flop (SF) field is estimated to be 520 Oe. From the analysis of the AFMR modes in terms of a mean-field approximation, we have estimated the interchain interactions and the anisotropy field parameters in the ground state. The magnetic phase diagram along the spin easy axis has been determined using a high sensitive microcantilever technique. On the field dependence along the easy axis, the torque response shows anomalies at 520 Oe and around 2100 Oe, corresponding to the spin-flop and the full-polarization of spins, respectively. The easy axis and anisotropy in the antiferromagnetic state are found to be well explained by our calculations of the dipolar energy with respect to the spin structure obtained in this work.

KEYWORDS: \(\gamma\text{-para-nitrophenyl nitronyl nitroxide}, \text{quasi-one-dimensional ferromagnet, electron spin resonance, magnetic torque}

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1. Introduction

Four-type polymorphic structures exist in the \textit{para}-nitrophenyl nitronyl nitroxide (\(p\)-NPNN) family, which is called \(\alpha, \beta, \gamma, \text{and} \delta\). Among them, \(\beta\)-phase is well known as the first genuine organic ferromagnet.¹ The long-range ordering occurs around \(T_c \approx 0.6 \text{ K}\) without a static magnetic field. The stability of this phase allows studying well its structure as well as its magnetism. Generally speaking, the intermolecular arrangement of magnetic molecules plays a key role in deciding the sign of the magnetic interaction. In the \(p\)-NPNN family, \(\text{NO–NO}_2\) and \(\text{NO–phenyl}\) contact between neighboring molecules induce ferromagnetic interactions between spins on molecules while \(\text{NO–NO}\) contact induces antiferromagnetic interaction due to a gain of direct transfer energy between singly-occupied-molecular-orbitals (SOMOs).¹,² This is because the wave function of the SOMO mainly exists around an ONCNO fragment in the molecule. For the \(\beta\)-phase, the magnetic coupling in the \(ac\)-plane consists of \(\text{NO–phenyl}\) contact while the coupling along \(b\)-axis consists of \(\text{NO–NO}_2\) contact, leading to the three-dimensional (3D) ferromagnet. By contrast, it is thought that the \(\gamma\)-phase undergoes an antiferromagnetic phase transition around \(T_N = 0.65 \text{ K}\).³ Above \(T_N\), evidence of the one-dimensional ferromagnetic fluctuation is present in the specific heat measurement under magnetic fields. Structurally, molecules along the \(c\)-axis are connected by \(\text{NO–NO}_2\) (ferromagnetic) contact, forming a one-dimensional ferromagnetic chain.³ These chains couple antiferromagnetically through \(\text{NO–NO}\) contact along the \(a\)-axis.³ Therefore, the comparison of the spin structure of the \(\gamma\)-phase with that of the \(\beta\)-phase is expected to give useful information concerning the magneto-structural correlation in magnetic molecules. However, the thermal instability of the \(\gamma\)-phase have prevented us from examining its ground state in more detail. For example, the spin structure has not been known yet.

In this paper, we report ESR absorptions above and below \(T_N\) using low-frequency and low-temperature ESR. We succeeded in observing antiferromagnetic resonance (AFMR) below \(T_N\) for the first time. This observation directly establishes the antiferromagnetic ground state with an orthorhombic anisotropy of \(\gamma-p\text{-NPNN}\). We performed magnetic torque measurements on single crystals using a high sensitive cantilever method.⁵ The torque response shows clear anomaly around a spin-flop (SF) transition and a phase boundary between the antiferromagnetic phase and the full-polarization of spins. We determine the magnetic phase diagram.

2. Experimental

Single crystals of \(\gamma\)-phase of \(p\)-NPNN were grown by the slow evaporation method. An acetonitrile dissolution of \(p\)-NPNN molecules had been kept at 60 °C. Several dark-greenish single crystals, having a typical dimension of \(0.5 \times 0.5 \times 0.2 \text{ mm}^3\), are obtained after the evaporation. Single crystals have plate-like shapes with crystal facets parallel to the \(bc\)-plane. Nakazawa et al. reported the instability of \(\gamma\)-phase below room temperature (RT).⁶ To avoid degeneration to the stable \(\beta\)-phase, we carefully held \(\gamma\)-phase crystals at a constant temperature in a clean atmosphere. Prior to every experiment, we checked the crystals by X-ray diffraction and selected the ones with no twinning and no contamination of other phases. Low-temperature X-ray diffraction measurements using single crystals indicate that no evidence of any structural phase transition is present down to 25 K.⁶ The crystal data at 25 K are triclinic space group \(\text{PI}, a = 8.985(1) \text{ Å}, b = 11.984(2) \text{ Å}, c = 6.4167(5)\)
\[\hat{A}, \alpha = 97.015(7)^\circ, \beta = 104.953(8)^\circ, \gamma = 81.914(2)^\circ, V = 658.3(1) \text{Å}^3, \text{and } Z = 2.\]

Fig. 1 shows the NPNN molecule, the low-temperature structure and the intermolecular contacts. NO–NO\(_2\) and NO–phenyl contacts are indicated by the solid and dotted lines, respectively. The right figure shows the schematic map of magnetic interactions in the bc-plane, where p-NPNN molecules are depicted by closed ellipses.

The magnetic phase diagram of γ-p-NPNN was presented by magnetic susceptibility measurements and specific heat measurements (see Fig. 2).\(^1\) It has been proposed that the long-range ordered phase below \(T_N = 0.6\) K is antiferromagnetic, but no other confirmation on the spin structure has been given. To observe ESR absorptions in this ordered phase and in the vicinity of \(T_N\), a low-magnetic field (low-frequency) should be desirable. At the usual X-band frequency, we could not observe any ESR absorptions which can be identified as AFMR or ferromagnetic resonance (FMR) below \(0.5\) K because the used magnetic field at X-band is larger than the phase boundary at \(0.5\) K. In Fig. 2, the EPR field at X-band is defined by an arrow \(X\).

Accordingly, we constructed new ESR cavities available for the low-frequencies and low-temperatures below \(T_N\). One of them is a LC circuit resonator, where \(L\) is an inductance of pick-up coil and \(C\) is a capacitance. The LC circuit resonator is tuned at the resonance frequency of \(~300\) MHz, which corresponds to the EPR resonance field around 100 Oersted, by adjusting the capacitance of the parallel condenser. Samples are placed at the center of the pick-up coil with a diameter around 2 mm. The large filling factor of the coil allows us to observe AFMR signals at low temperatures with a high accuracy. The oscillating magnetic field (\(H_1\)) generated by the coil is perpendicular to the static magnetic field. All LC resonators including samples are directly cooled by liquid \(^3\)He.

Another type of cavity is a bridged loop-gapped (LG) resonator.\(^7,8\) The bridged LG resonator was used at the region up to \(1\) GHz. The schematic diagram of the LG resonator is shown in Fig. 3. The LG resonator part in the figure is a Cu cylinder, and it has a narrow gap. By tuning...
the capacitance at the gap, the resonance frequency varies quasi-continuously from 700 MHz to 3 GHz. A microwave coaxial cable is linked by the coupling loop at the top part of the LG resonator. An ideal coupling is established by adjusting the length \( t_1 \) in the figure. The change in length \( t_2 \) varies the resonance frequency of LG resonator precisely. A small-diameter double-walled quartz dewar is inserted in the LG resonator and samples located inside the dewar are directly immersed in liquid \(^{3}\text{He}\). The unloaded quality factor of the resonator is approximately 2300 at 1.4 K and 3 GHz. The static magnetic field was controlled by the Bruker ER-032M and applied in the horizontal plane. The temperature of samples was monitored by the vapor pressure of liquid \(^{3}\text{He}\) and by the Cernox resistance thermometer inside the dewar. The lowest available temperature is about 0.45 K. ESR absorption signals were directly obtained by monitoring the reflection intensity from the resonator using a scalar network analyzer (Agilent Technology, 8719ET).

We measured magnetic torque responses using commercial piezo-resistive microcantilever (Seiko instruments). This technique had been developed by Ohmichi et al. for dHvA measurements.\(^{5}\) A sample is attached at the tip of the cantilever using an epoxy glue. The inset photo of Fig. 8 shows the cantilever with the NPNN single crystal. A resistance bridge circuit was used and the off-balanced voltage of the bridge circuit was detected by a lock-in-amplifier (Stanford Research System SR830). The magnetic torque signal is proportional to the off-balanced voltage of the bridge circuit. The sample and cantilever are directly cooled by liquid \(^{3}\text{He}\) and the sample temperature was monitored by a Cernox resistance thermometer. The cantilever is mounted on the adjustable sample holder, and its flexing direction is in the horizontal plane. Therefore, the direction of the applied field can be rotated with respect to the crystal axis.

3. Results and Discussion

3.1 Antiferromagnetic resonance

Figure 4(a) shows a temperature dependence of electron paramagnetic resonance (EPR). The rf frequency is about 286 MHz, and the static magnetic field is applied parallel to the \( c \)-axis for EPR measurements. EPR signals broaden with decreasing temperatures, independently from the magnetic field direction, and completely disappear below 0.6 K. At the lowest temperature, no trace of FMR signal, which is observed in \( \beta \)-phase crystals,\(^{9}\) is present. This implies that samples have experienced neither a degeneration to the stable \( \beta \)-phase, nor a degradation into the Curie-like paramagnetic contamination.

After EPR signals disappeared, new ESR absorption signals emerge at different magnetic fields within a specific angular region.\(^{10}\) Figure 5(a) shows the angular dependence of absorptions at 0.45 K, where the magnetic field is applied in the \( bc \)-plane. Angles defining the applied magnetic field direction, \( \theta \) and \( \phi \), relative to crystal axes are shown in the inset of Fig. 5(b). Note that the observed resonance fields are remarkably different from the corresponding EPR fields. At 1.16 GHz, observed ESR absorptions consist of two resonant modes.\(^{11}\) And these modes can be observed in narrow angular regions: \(-25^\circ < \theta < -15^\circ\) and \(0^\circ < \phi < 60^\circ\) at 284 MHz, and \(-55^\circ < \theta < 15^\circ\) at 1.16 GHz, respectively. As shown in Fig. 5(b), a typical angular dependence of AFMR around the spin-easy axis was clearly observed within the \( bc \)-plane (\( \phi = 0^\circ \)). At \( \theta_{\text{easy}} = -20^\circ \pm 10^\circ \) and \( \phi = 0^\circ \), the maximum separation between two AFMR modes is obtained and the angular dependence shows a symmetric ellipse around \( \theta_{\text{easy}} \). The resonance fields of lower-field signals show a negative slope as a function of the frequency. These results are consistent with our assumption on the spin-easy axis. Note that the spin-easy axis is approximately in [011] direction.

Next, we analyze the AFMR in terms of the mean-field approximation.\(^{12}\) Specific heat measurements under the magnetic field showed the existence of one-dimensional ferromagnetic fluctuation above \( T_N \). The overall temperature dependence of the specific heat is well understood by the one-dimensional ferromagnetic Heisenberg model with interchain couplings.\(^{11}\) As shown in Fig. 1, the one-dimensional ferromagnetic chain runs along the \( c \)-axis. Therefore, on our assumption that intrachain spins are strongly coupled, we applied a four-sublattice model with an orthorhombic anisotropy in order to investigate AFMR modes. Figure 6 shows the schematic diagram of the four-sublattice model. Spins along the \( c \)-axis form ferromagnetic chains. The system can also be seen as ferromagnetic planes coupled
antiferromagnetically, because the in-plane coupling \( J_{13} \) along \( b+c \) is ferromagnetic and the inter-plane coupling \( J_{14} \) along \( a \) is antiferromagnetic,\(^1\) which are shown by dotted and dot-dashed lines.

Using this model, a total free energy can be formulated within the mean-field approximation as follows:

\[
F = - \sum_{i=1}^{4} M_i \cdot H_0 \\
+ A(M_1 \cdot M_2 + M_3 \cdot M_4) + B(M_1 \cdot M_3 + M_2 \cdot M_4) \\
+ \frac{K_1}{2} \sum_{i=1}^{4} \frac{M_i^2}{M_0} + \frac{K_2}{2} \sum_{i=1}^{4} \left( \frac{M_i}{M_0} \right)^4, \\
A = - \frac{4}{N} \left| J_{13} \right| \frac{1}{(g \mu_B)^2}, \\
B = \frac{4}{N} \left| J_{14} \right| \frac{1}{(g \mu_B)^2},
\]

where \( M_i = \langle N/4 \rangle g \mu_B S_i \), \( H_0 \) is the static magnetic field, \( A \) and \( B \) are the molecular field coefficients, \( K_1 \) and \( K_2 \) are the orthorhombic anisotropy parameters, and \( M_0 \) is the magnitude of the sublattice moment. Figure 7 shows the obtained frequency-field diagram of AFMR. Solid lines show typically observable modes while dotted lines show the unobservable ones in ESR measurements. The high frequency modes have no absorption intensity due to the out-of-phase motion of sublattice moments between the ferromagnetic layers. Consequently, the four sublattice model can be well described by the two-dimensional ferromagnetic layers coupled antiferromagnetically, in other words, two sublattice model. To analyze the experiments, we assume the relation between the intra- and inter-plane interaction, \( |J_{13}/k_B| + |J_{14}/k_B| = 0.2 \text{K} \).\(^1\) Considering that the \( \alpha_\theta \)-mode should soften at the saturation magnetic field which will be discussed in what follows, we could evaluate following parameters:

\[
J_{13}/k_B = 0.127 \text{K}, \quad J_{14}/k_B = -0.073 \text{K}, \\
K_1/M_0 = 120 \text{Oe}, \quad K_2/M_0 = 230 \text{Oe}.
\]

The SF field is also estimated to be 520 Oe. This value satisfactorily agrees with magnetic torque measurements.

### 3.2 Magnetic torque measurements

Figure 8 shows the magnetic field dependence of magnetic torque signals at 0.45 K, where the magnetic field is applied parallel in the \( bc \)-plane. The definition of \( \theta \), shown in the inset of Fig. 8, is the same as that in Fig. 5. The torque signal at 1.45 K is also shown in the inset, and depends parabolically on the magnetic field. No clear angular variation and no clear anomaly were found at this temperature. On the other hand, at \( T = 0.45 \text{K} \), magnetic torque signals show a peculiar angular dependence. A sharp anomaly around \( H_{SF} \) (~520 Oe) is observed in the vicinity of \( \theta \approx -35^\circ \) while a step like anomaly observed around \( H_c \) (~2.1 kOe) has a weak angular dependence. No other anomaly is found up to 7 kOe. These angular dependences resemble well that of antiferromagnetic torque responses in \( \lambda-(\text{BEDT})_2\text{FeCl}_4 \), which exhibits an antiferromagnetic ordering below 8 K.\(^1\) In the case of \( \lambda-(\text{BEDT})_2\text{FeCl}_4 \), the lower field anomaly corresponds to the SF transition. As shown in the previous section, our low-frequency ESR
measurements support this scenario and typical AFMR signals along the spin easy axis are clearly observed around this direction. Accordingly, we conclude that the lower field anomaly at $H_c$ is the SF transition and that $\theta \sim -35^\circ \pm 10^\circ$ direction is parallel to the spin-easy axis. On the other hand, the anomaly around $H_c$ may be due to the thermal fluctuation of spins.

Figure 9 shows the angular dependence of magnetic torque signals at 0.45 K. The case of two magnetic fields ($H = 200$ Oe $< H_{SF}$ and $H = 2.5$ kOe $> H_c$) are shown. The angular dependence, except for the signal amplitudes, remains unchanged above $H_{SF}$. The magnitude of the torque signals $I$ follows, $\sin(2(\theta - \theta_0))$, in each case. Contribution of higher-order anisotropic terms is negligible. We estimate $\theta_0$ in each case to be $\theta_0^{AF} = -33^\circ$ in the AF phase and $\theta_0 = -20^\circ$ in the F state, respectively. The inset of Fig. 9 shows the magnetic field dependence of the differential of $\theta_0$, $-d\theta_0/dH$. $\theta_0$ shows a rapid change around 2 kOe, which is lower than $H_c$. $\theta_0^{AF}$ in the AF phase corresponds well to the direction where the anomaly of the torque signal is observed around $H_{SF}$, as shown in Fig. 8.

Figure 10 shows the magnetic phase diagram of $\gamma$-$p$-NPNN along the spin-easy direction. The inset of the figure shows the temperature dependence of torque signals, where the magnetic field direction is parallel to the spin-easy axis. Rapid decreases of the torque signals, which are shown by arrows, indicate the onset temperatures of the Néel ordered state under the magnetic field and the closed triangle and square show the transition fields along the spin-easy axis. Open squares and open circles were determined by the specific heat and the ac susceptibility measurements, respectively. Solid and dotted lines are guide for the eye. The inset shows the temperature dependences of torque signals at various magnetic fields.

3.3 Dipolar energy calculations

Both AFMR and magnetic torque experiments have revealed that the ground state of quasi-one-dimensional (Q1D) ferromagnet $\gamma$-$p$-NPNN is antiferromagnetic with the orthorhombic anisotropy. In order to elucidate a major contribution on the spin anisotropy, we calculate the magnetic dipole–dipole energy and compare it with experiments in both phases. Since the SOMO wave function mainly spreads around NO groups of NPNN molecule, we assumed that the spin density is distributed equivalently on ON atoms. This model calculation has reproduced the previous calculation on the dipole energy in the $\beta$-$p$-NPNN. As denoted previously, the sign of magnetic interactions between molecules could be expected by the type of contact between the molecular fragments. NO–NO contact and NO–phenyl contact along the $b + c$ direction should induce ferromagnetic interactions. In the AF phase, we assume that spins in the $bc$-plane align parallel to each other, and antiparallel alignment between the neighboring layers.

Figures 11 and 12 show the calculated dipolar energy in the AF and F phases, respectively. In the maps displayed in the lower panels, the abscissae are the spin direction in the $bc$-plane and the ordinates are the spin direction along the $a^*$-axis. Sinusoidal curves in the upper panels indicate the dipole energies as a function of the spin direction in the $bc$-plane. In the AF phase, the in-plane anisotropy is small and, thus, the spin direction is well confined in the $bc$-plane. The lowest dipole energy is obtained at $\theta = -30^\circ$ in the $bc$-plane. This result satisfactorily reproduces torque experiments, where the spin-easy axis is obtained around $\theta_{AF}$.
Taking account of this, we can expect that the ONCNO fragment is energetically favorable for the isolated F phase. It may suggest the existence of molecular magnetostriction becomes concentrated on N atoms in the F phase, and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. Assuming that the dihedral angle between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase, it may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase.

**Fig. 11.** Calculation of the dipole–dipole energy as a function of spin direction in the AF-phase. The abscissae are the spin direction in the bc-plane. The ordinate in the lower panel is the spin direction along a*-axis. The sinusoidal curve in the upper panel indicates the change of the dipole energy in the bc-plane.

As shown in Fig. 9, accordingly, we conclude that the anisotropy of spins in the AF phase is mainly determined by the dipole–dipole interaction.

In contrast to the AF case, the F phase has a strong anisotropy in the in-plane dipole energy. The lowest dipole energy is obtained at θ = −33° in the bc-plane. This result is slightly different from that of torque experiments; θF ∼ −20°. This significant difference could be resolved by assuming that the dihedral angle between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction. The molecular orbital calculation suggests that a flat arrangement between the phenyl group and the ONCNO fragment decreases, or that the spin density distribution becomes concentrated on N atoms in the F phase. It may suggest the existence of molecular magnetostriction.

**Fig. 12.** Calculation of the dipole–dipole energy in the full-polarization (F) state. The abscissae are the spin direction in the bc-plane. The ordinate in the lower panel is the spin direction along a*-axis. The sinusoidal curve in the upper panel indicates the change of the dipole energy in the bc-plane.

4. Conclusion

We have observed the antiferromagnetic resonance in the low-temperature phase below TN of γ-p-NPP for the first time. The frequency–field relation proves the collinear spin arrangement with an orthorhombic anisotropy. Low-temperature magnetic torque measurements had been performed using the microcantilever technique. The spin-easy axis aligns approximately parallel to the [011] direction in the antiferromagnetic phase. This is almost consistent with the result of AFMR measurement. However, the torque curve in the fully-polarized phase has a different anisotropy. The calculated magnetic dipole–dipole energy indicates its main contribution on the anisotropy in the AF phase. However, the calculation in the F phase fails to reproduce experimental results. This is an open question for the future research.

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4) These consideration on the magnetic interactions has been discussed on the basis of the room temperature structure, because no low-temperature structural study was reported. We have analyzed low-temperature structural structure of γ-phase at 25K and will report in the separate paper.

11) The asymmetric line shapes of AFMR signals remind us powder pattern. It is known that the FMR signals for the $\beta$-p-NPNN also have asymmetric line shapes. Thus, it may be common characteristic on the molecular spin system and may be associated with the non-localization of spins on isolated molecules.


17) M. Okumura: private communication.