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Antiferromagnetic resonance in quasi-one-dimensional ferromagnet γ-*p*-NPNN

K. Kajiyoshi [a,1], T. Kambe [a,*], K. Oshima [a], M. Tamura [b], M. Kinoshita [c]

[a] *Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan*
[b] *Condensed Molecular Materials Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*
[c] *ISSP, University of Tokyo, Kashiwanohara, Chiba 277-8581, Japan*

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Abstract

The low frequency (∼300 MHz) and low-temperature (0.4 K) ESR were performed in the γ-phase of *p*-NPNN, which is considered to be as a quasi-one-dimensional ferromagnet above the antiferromagnetic ordering temperature (0.65 K without a static magnetic field). Below 0.6 K, we succeeded in observing the antiferromagnetic resonance (AFMR) for the first time. The frequency–field relation is well reproduced by the two-sublattice model with orthorhombic anisotropy. In addition, we measured magnetic torque using small single crystal, which has the dimension of $0.25 \times 0.10 \times 0.10$ mm^3. A spin–flop transition and AF-paramagnetic (AF-P) transition are observed at 470 and 2100 G at 0.4 K, respectively. Both AFMR and magnetic torque measurements indicate that the spin-easy axis is almost parallel to the direction to phenyl ring from the ONCNO fragments.

Keywords: γ-*p*-NPNN; AFMR; Magnetic torque measurement

1. Introduction

Four-type polymorphic structures exist in the *para*-nitrophenyl nitronyl nitroxide (being *p*-NPNN) family, which is called α, β, γ and δ [1]. Among them, β-phase is well known as the first genuine organic ferromagnet [2]. The long-range ordering occurs around 0.6 K without a static magnetic field. The stability of this phase allows studying well its structure as well as its magnetism. Generally speaking, the geometrical arrangement between magnetic molecules plays a key role in selecting the sign of the magnetic interaction. In *p*-NPNN family, NO–NO_2 and NO–phenyl contacts between neighboring molecules induce ferromagnetic interaction between the spins on molecules while NO–NO contact induces antiferromagnetic interaction due to a direct overlapping between singly occupied-molecular-orbitals (SOMOs) [1]. This is because the wave function of SOMO mainly exists around ONCNO fragment in the molecule. For the β-phase, the magnetic coupling in the *ac*-plane consists of the NO–phenyl contact while the coupling along *b*-axis consists of the NO–NO_2 contact, leading to the 3D ferromagnet. Contrary to the β-phase, the γ-phase undergoes antiferromagnetic phase transition around $T_N = 0.65$ K [3]. The NO–NO_2 (ferromagnetic) contact runs along *c*-direction, forming a one-dimensional ferromagnetic chain. The NO–NO contact along *a*-axis possibly guides to the antiferromagnetic state. In this paper, we show the antiferromagnetic resonance (AFMR) below T_N for the first time. This observation directly establishes the antiferromagnetic ground state with orthorhombic anisotropy of γ-phase. We also present the magnetic torque measurements of γ-phase in the vicinity of T_N using a piezo-resistive micro-cantilever. These observations enable us to determine the spin–flop

* Corresponding author. Tel.: +81 86 251 8612; fax: +81 86 251 7830.
E-mail addresses: kajiyosi@science.okayama-u.ac.jp (K. Kajiyoshi), kambe@science.okayama-u.ac.jp (T. Kambe).
1 Fax: +81 86 251 7830.

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field (H_{SF}) and the AF-P transition field (H_C) with high accuracy.

2. Experiments

γ-Phase single crystals were grown by the evaporation method. The acetonitrile solution of NPNN has been kept in an incubator at 60°. Several dark-greenish single crystals, having typical dimension of $0.5 \times 0.5 \times 0.2\ mm^3$, are obtained within 24 h. The previous paper reported the instability of γ-phase under the room temperature [3]. To avoid the degeneration to the stable β-phase, we held the γ-phase crystals in a refrigerator. Before performing the experiments, we carefully selected single crystals without twin boundary and contaminations of the other phase by X-ray diffraction.

In the ESR measurements, homemade LC resonator with the resonant frequency of ~300 MHz was used. The resonant frequency ($2\pi f = 1/\sqrt{LC}$) can be tuned from 200 to 300 MHz (EPR resonance field corresponds to about 70–100 G) by adjusting the capacitance of flat condenser. The samples were directly cooled by the ^{3}He. The temperature was monitored by the vapor pressure of ^{3}He gas and by the Cernox resistive thermometer equipped around LC resonator. The lowest temperature attained is about 0.4 K. ESR absorption signals were obtained by monitoring the reflection intensity from the resonator through the scalar network analyzer (Agilent Technology, 8719ET). In this experiment, the radio frequency (RF) is set to be about 286 MHz.

In the magnetic torque measurements [4], we used a piezo-resistive cantilever, which is fabricated by Seiko Instruments Inc. for atomic force microscopy (AFM). The small sample is attached at the tip of cantilever using epoxy, and placed at the center of magnet. The sample mounted on the cantilever is shown in the inset of Fig. 1. The magnetic torque is proportional to the off-balance voltage of the bridge circuit, which detected by the lock in amplifier (Stanford Research System SR830). The sample mounted on cantilever is directly cooled by the ^{3}He. The system is so sensitive to observe a spin–flop transition even if the very small sample, whose dimension was $0.25 \times 0.10 \times 0.10\ mm^3$, was used. The magnetic field applied to the *bc*-plane in the torque measurements.

3. Results and discussion

3.1. ESR

The EPR signals are broadened with decreasing temperature, independently from the magnetic field direction, and disappeared below 0.6 K. At the lowest temperature, no trace of the ferromagnetic resonance,

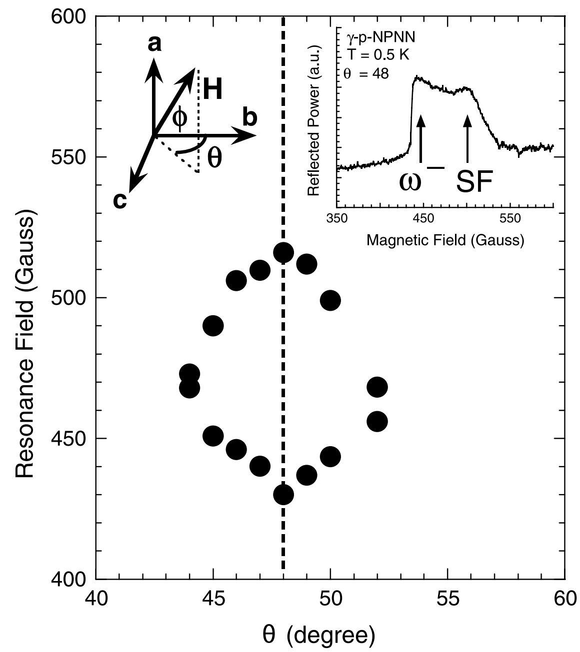

Fig. 1. Angular dependence of the resonance field of ω^- and SF-mode. The inset figure shows the typical AFMR signal. The resonance positions of ω^- and spin–flop (SF)-mode are depicted by the arrows. The angles, θ and ϕ are shown in the inset.

which was observed in the β-phase crystals, is obtained. After EPR signals disappeared, the AFMR signals emerge in different magnetic field. The observed AFMR signal is decomposed by two resonant modes: the lower-field edge of AFMR signal corresponds to the ω^- mode and the higher-field edge corresponds to the spin–flop (SF) mode. Fig. 1 shows the observed AFMR signal and the angular dependence of the ω^- and SF-mode. The angles for applied magnetic field, θ and ϕ, relative to the crystal axis are defined in the inset. These AFMR signals can be observed in the narrow angular region: $44° < \theta < 55°$ and $0° < \phi < 60°$. The typical angular dependence of AFMR around the spin-easy axis was clearly observed within the *bc*-plane. Around $\theta = 48 \pm 10$ and $\phi = 0°$, the maximum separation between the resonance fields for two AFMR modes is obtained. This result indicates that the spin-easy axis is parallel to this direction. It is noted that the spin-easy axis almost points toward the phenyl ring from the ONCNO fragments.

Fig. 2 shows the frequency (ω/γ)-field (H) relation of the AFMR. The resonance field of low-field edge signal increases with decreasing the RF frequency. The inseparability of signals is possibly because the measured temperature is approximate to the Neel temperature. To investigate the AFMR, we applied the two-sublattice model with orthorhombic anisotropy [5]. This assumption is reasonable because that the magnetic coupling in the *bc*-plane is ferromagnetic and the dominant anisotropy term should be caused by the dipole–dipole