Searching for spontaneous magnetic order in an organic ferromagnet. μSR studies of β-phase *p*-NPNN

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Zero-field muon spin rotation (ZF-μSR) studies in the recently synthesized organic ferromagnet β-phase *p*-NPNN are reported. Our measurements, using a microscopic magnetic probe, provide the first direct observation of spontaneous magnetic order in *p*-NPNN. The behaviour of the system is close to that of an isotropic three-dimensional (3D) Heisenberg spin system.

1. Introduction

The synthesis and characterization of organic ferromagnets, composed purely of light elements, has attracted interest from researchers in both chemistry and physics. Two candidate materials, i.e. *p*-NPNN (*p*-nitrophenyl nitronyl nitroxide radical, $C_{13}H_{16}N_3O_4$) and C_{60}-TDAE, have been identified as such systems [1–5]. To examine candidate compounds, efforts have been made via various techniques, such as magnetization [1,5–7], specific heat [6,7] and ESR measurements [8]. The most fundamental parameter – the spontaneous magnetization in these materials – however, remains uninvestigated so far. In this Letter, we report zero-field muon spin rotation studies of ferromagnetic order in β-phase *p*-NPNN, as the first observation of spontaneous magnetization by a microscopic local magnetic probe. Our results clearly show the existence of magnetic order in *p*-NPNN below 0.67 K. The behaviour of the system closely resembles that of an isotropic three-dimensional (3D) Heisenberg spin system.

2. Experimental

In a ZF-μSR measurement [9], 100% spin polarized positive muons are implanted into a sample of interest, where they quickly come to rest at an interstitial site. In the presence of an internal magnetic field the muon spins undergo Larmor precession, with frequency $\nu_\mu = (\gamma_\mu/2\pi)H_{\rm int}$, where the muon gyromagnetic ratio $\gamma_\mu/2\pi = 13.553$ kHz/G. Due to the parity violation of the weak interaction, the muon decay positron is emitted preferentially along the muon spin direction. A time histogram of positron events reflects the muon spin precession and hence the internal magnetic field of the target specimen. In ferromagnets, the internal magnetic field $H_{\rm int}$ generally consists of dipolar, hyperfine, Lorentz and demagnetization fields; the magnitude of these fields is directly proportional to the spontaneous magnetization M. The temperature dependence of $M(T)$ can be determined precisely via $\nu_\mu \propto H_{\rm int} \propto M$. Although neutron diffraction can also provide extensive information for magnetically ordered systems, μSR is a more sensitive probe of systems with small specimens, small ordered moments, and dilute/random/incommensurate spin arrangements. These advantages helped the recent μSR study of spin density

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waves in the organic magnetic systems $(TMTSF)_2$-X [10].

The specimen of β-phase *p*-NPNN was prepared at the University of Tokyo (ISSP) following the procedures described in ref. [2]. The μSR experiments were performed at the M15 channel of TRIUMF with a polarized positive surface muon beam. Five single crystals (about 200 mg in total weight) were mounted in an Oxford Instruments Model 400 top-loading dilution refrigerator with their *ac* plane normal to the muon beam direction. Stray magnetic fields were reduced to less than 20 mG. We performed two sets of ZF measurements in *p*-NPNN: with the initial muon spin s_μ both parallel and perpendicular to the $\hat{b}$ axis of the crystals.

3. Results and discussion

Fig. 1 shows several typical μSR time spectra in *p*-NPNN with $s_\mu \perp \hat{b}$. The slowly relaxing signal at 0.70 K is characteristic of a random internal field of about 4 G, which we attribute to static nuclear dipolar fields. At $T=0.70$ K, the system is in the paramagnetic phase, however, by $T=0.64$ K an oscillation with $\nu_\mu=0.9$ MHz appears. This observation provides direct evidence for the onset of spontaneous magnetization in this compound. With decreasing temperature, the oscillation frequency increases, reaching a maximum of $\nu_\mu=2.1$ MHz at 0.02 K. The long-lived oscillation observed below T_c indicates that the muons experience a rather homogeneous local field which requires that the ferromagnetic spin network be commensurate with the crystallographic structure. This feature is in clear contrast to the fast relaxation of the precession signal observed in the incommensurate SDW system $(TMTSF)_2$-X [10].

In the configuration where $s_\mu \| \hat{b}$, the amplitude of oscillation is much smaller (about 20% of that in $s_\mu \perp \hat{b}$ configuration), indicating that the internal field is nearly along the $\hat{b}$ axis. This suggests that the spin orientation in different magnetic domains is not aligned randomly and is most likely along the $\hat{b}$ axis.

Fig. 2 shows the temperature dependence of the precession frequency $\nu_\mu(T)$ obtained in *p*-NPNN in zero external field. The Curie temperature is 0.67 K, which is slightly higher than 0.60 K obtained by the heat capacity measurement [6,7]. This difference of T_c may indicate a small variation in the ordering temperature from sample to sample. Such a small difference in T_c (about 50 mK) was also observed

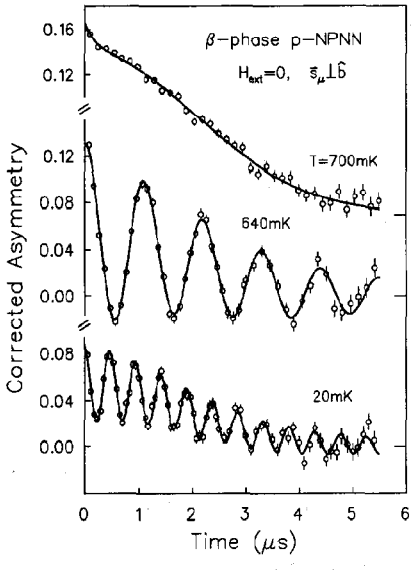

Fig. 1. Zero-field μSR time spectra observed in β-phase single crystals of *p*-NPNN with initial muon spin perpendicular to the crystal $\hat{b}$ axis. The appearance of oscillation below $T_c=0.67$ K is attributed to the onset of the spontaneous ferromagnetic order.

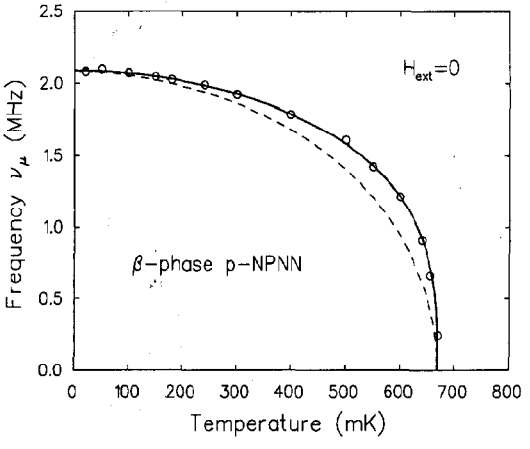

Fig. 2. Temperature dependence of muon precession frequency below T_c in zero external field. The frequency is proportional to the spontaneous magnetization M. The solid line shows a fit of $M(T) \propto [1-(T/T_c)^\alpha]^\beta$ with $\alpha=1.86$ and $\beta=0.32$, and the dashed line represents calculation for isotropic 3D Heisenberg model.

by ac susceptibility measurement on different specimens (see fig. 3 in ref. [6] which shows $T_c \approx 600$ mK and fig. 5 in ref. [7] showing $T_c \approx 650$ mK). Combining the present result of $M(0.44\ \mathrm{K})/M(0) = 0.82$ with $M(0.44\ \mathrm{K}) = 0.5\ \mu_B$/molecule obtained by magnetization measurements [6,7] we find $M(0) = 0.6\ \mu_B$/molecule. The deviation from the expected value of 1 μ_B/molecule may be partly due to systematic uncertainties in the magnetization measurements.

The temperature dependence of $M(T)$ is very similar to that observed in conventional inorganic ferromagnets, such as in Ni [11]. The solid line in fig. 2 shows a fit of $M(T) \propto [1-(T/T_c)^{\alpha}]^{\beta}$ with $\alpha = 1.86$ and $\beta = 0.32$. The agreement between the μSR data (open circle) and the solid line is remarkably good, which allows us to discuss our results in two interesting regions, namely $T \to 0$ and T_c. At temperatures well below T_c, M decreases with increasing temperatures as $M(0) - M(T) \propto T^{\alpha}$, close to the magnon-like behaviour of $M(0) - M(T) \propto T^{1.5}$. Near T_c, $M(T) \propto (T_c - T)^{\beta}$ with the critical magnetization exponent $\beta = 0.32$, in agreement with a value of $\approx \frac{1}{3}$ expected for a 3D Heisenberg system [#1]. Thus, the temperature dependence of $M(T)$ in *p*-NPNN, both at low temperature and near T_c, is consistent with that of a 3D Heisenberg system.

The origin of the anisotropy in *p*-NPNN is not well understood. A rapid saturation of the hysteresis curve [6,7] below 50 G suggests a rather weak anisotropy in the system. To estimate the anisotropy, we employ a simple calculation, considering only the dipolar interaction within the spin network. Using $M = 0.6\ \mu_B$/molecule, the crystal structure from ref. [2] and a spherical domain boundary, we find that the easy axis (which costs the least energy to align the spins without an applied field) is the $\hat{b}$ axis and an anisotropy field H_A of 20 G, consistent with both the μSR and magnetization measurements. This indicates that the dipolar coupling must play an important role in determining the anisotropy in *p*-NPNN. The anisotropy energy $MH_A \approx 1$ mK is much smaller than T_c, and hence the behaviour of the system is close to that of an isotropic Heisenberg system.

A two-dimensional character has been suggested on the basis of the crystal structure of *p*-NPNN [2]. To interpret the μSR results, we constructed an isotropic Heisenberg spin-1/2 Hamiltonian including both the coupling J between four nearest neighbors in the *ac* plane and J' between four nearest neighbors out of plane. The temperature dependence of M is evaluated by using the random phase approximation (RPA). However, no satisfactory fit to the μSR data is obtained by varying J and J'. In general, with a small ratio of J'/J, M tends to decrease rapidly with increasing temperature due to the strong magnon excitation in a low-dimensional system. The dashed line in fig. 2 shows a curve with specific choice of $J = J' = 470$ mK. A slight difference between μSR data and Heisenberg model may be due to the inappropriate mean-field-like RPA approximation near T_c.

An anomalous reduction of the oscillation amplitude A_{osc} and of the total asymmetry with decreasing temperature is evident in fig. 1. The ratio of $A_{osc}(0)/A_{osc}(T_c) = 0.45$. A missing asymmetry in μSR is usually due to the formation of muonium or the appearance of large muon local field, which leads to a rapid relaxation of time spectrum in an extremely short time scale. In either case, the strong interchange between the normal muon (oscillation) signal and fast relaxing signal at such low temperature (below 0.7 K) is unusual. The mechanism for this phenomenon is not clear at the moment.

In summary, the present results clearly demonstrate the appearance of spontaneous magnetic order in *p*-NPNN, which follows the behaviour expected for an isotropic 3D Heisenberg spin system. The observed homogeneous and unique local field at the muon site indicates that the muon occupies a unique crystallographic site in the complicated unit cell of the large *p*-NPNN molecule. This feature helps the use of μSR to distinguish between incommensurate and commensurate spin arrangement in organic systems.

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[#1] Experimental values of β in isotropic 3D systems are summarized in table 16 (for seven compounds, $\beta = 0.31$–0.40) of ref. [12]; a theoretical value of $\beta = 0.367$ for 3D Heisenberg model is listed in table 5.1 of ref. [13].

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