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An Organic Radical Ferromagnet

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The γ-phase crystal of 2-(4'-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-N-oxide is shown to become a bulk ferromagnet below about 0.65 K from the measurements of magnetization, magnetic susceptibility, and heat capacity.

There has been a growing interest in organic ferromagnetism. Some organic polymers have recently been claimed as a ferromagnet even at room temperature,1) though their structure and magnetic properties are not yet well characterized. As for simple organic radicals, however, no compound has so far been reported to exhibit a phase transition to ferromagnetic state. Some time ago, the magnetic properties of (bis(2,2,6,6-tetramethylpiperidin-4-yl-1-oxyl) suberate (or TANOL suberate) were studied in detail.2) This compound was shown to have two-dimensional ferromagnetic coupling on the crystallographic *ac* plane, but the coupling along the *b* axis is antiferromagnetic, resulting in a metamagnet below 0.39 K. Recently, we have studied the magnetic properties of 4-[[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)-phenoxy (or galvinoxyl)3,4) and 2-(4'-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-N-oxide (or p-nitrophenyl nitronyl nitroxide, abbreviated as p-NPNN)5,6)and shown that the ferromagnetic coupling is operative between the adjacent radicals, thereby resulting in the formation of exchange correlated spin domains at low temperatures.6) In this letter, we will show that the γ-phase crystal of p-NPNN7) exhibits a phase transition to a ferromagnetic ordered state at about 0.65 K.

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The γ-phase crystals of p-NPNN were prepared by the method described previously.$^{6)}$ The magnetization at low temperatures and the static magnetic susceptibility in the range of 1.8-300 K were reexamined for a plate-like single crystal with a Quantum Design MPMS SQUID magnetometer. The susceptibilities below 4.5 K were measured at the applied field of 50 mT to suppress the saturation effect as small as possible. The heat capacity was measured between 0.4 and 6 K with an adiabatic heat pulse calorimeter described previously.$^{9)}$

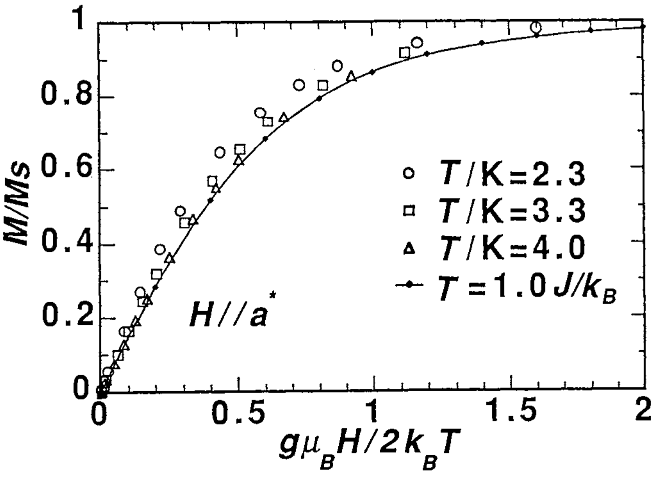

Fig. 1. The field dependence of magnetization of the γ-phase of p-NPNN at 2.3, 3.3, and 4.0 K compared with the theory based on Eq. 1 with $k_BT/J = 1.0$.

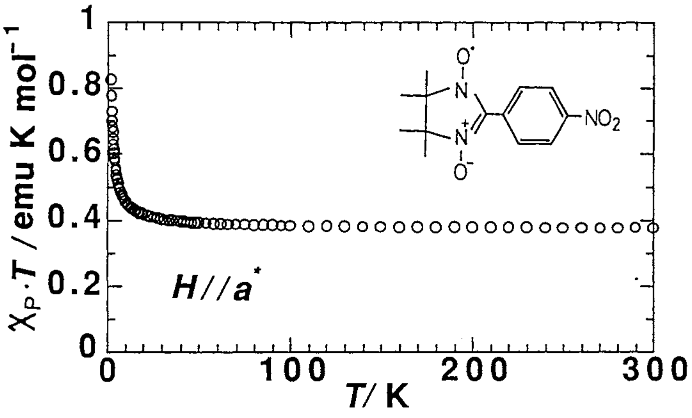

Fig. 2. The temperature dependence of χ_pT of the γ-phase of p-NPNN.$^{10)}$

Figure 1 shows the field dependence of the magnetization of the γ-phase of p-NPNN with the field nearly parallel to the *a* axis. The overall magnetization curve at 2.3 K agrees with that reported previously.$^{6)}$ The magnetization grows up more steeply when the temperature is lowered. This indicates that the intermolecular ferromagnetic interaction manifests itself at lower temperatures. The field dependence of magnetization is also calculated on the basis of the one-dimensional Heisenberg Hamiltonian, Eq. 1, as a function of k_BT/J;

$$H = -J \sum S_i S_{i+1} + 2h \sum S_i^z \ , \quad \text{with} \quad h = g\mu_B H/2, \text{ and } S = 1/2. \tag{1}$$

The magnetization at 4.0 K is a little larger than the theoretical result with $k_BT/J = 1.0$. Thus the present spin system seems to be well described as a one-dimensional Heisenberg ferromagnet around 4 K with the exchange interaction parameter J/k_B being slightly bigger than 4 K.

In Fig. 2 is shown the temperature dependence of the product of susceptibility and temperature, χ_pT. The product of 0.376 emu K mol^{-1} at 300 K is consistent with the Curie constant of S=1/2 spin. As is seen in Fig. 2, the product increases as the temperature decreases and reaches 0.825 emu K mol^{-1} at 1.8 K. The observed products above about 5 K fit well with the theoretical calculation on the basis of Eq. 1 with J/k_B = 4.3 K. This is consistent with the result of magnetization measurements. However, the observed product deviates upwards from the theoretical value below about 4 K. This deviation seems to be precursory indications of a ferromagnetic phase transition and has prompted us to examine the behavior at lower temperatures.

The temperature dependence of the heat capacity, C_p, of the γ-phase of p-NPNN is shown in Fig. 3 in the temperature range of 0.4-6 K. The heat capacity exhibits the λ-shaped anomaly peaking at T_C = 0.65 K. The shape of the anomaly indicates that the transition is of bulk nature, although the associated entropy change estimated from the data in the present temperature range is somewhat less than Rln2 for the ordering of S=1/2 spins.

The ac susceptibility measurements are now in progress. Preliminary results in Fig. 4 show that the ac susceptibility (supposedly continuous to dc susceptibility of Fig. 2) measured at the ac field (123 Hz) of less than 10 μT and at the zero static field becomes very big below T_C compared with that above T_C. This large susceptibility strongly suggests that the ferromagnetic ordering occurs in the present spin system below T_C.

From these, we conclude that the γ-phase of p-NPNN becomes a bulk ferromagnet below about 0.65 K. To our knowledge, this is the first organic ferromagnet which is

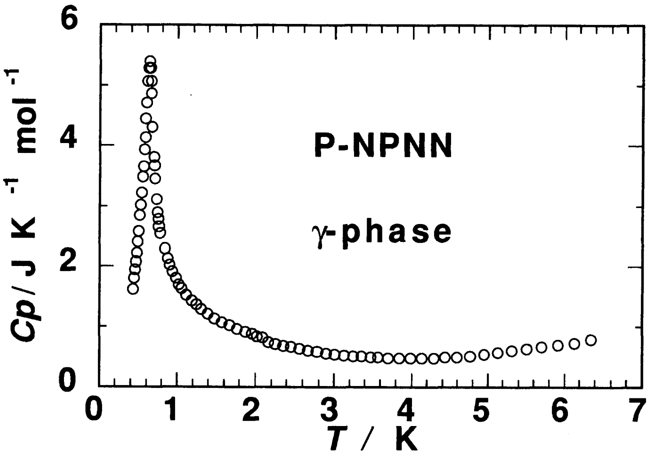

Fig. 3. The temperature dependence of heat capacity of the γ-phase of p-NPNN.

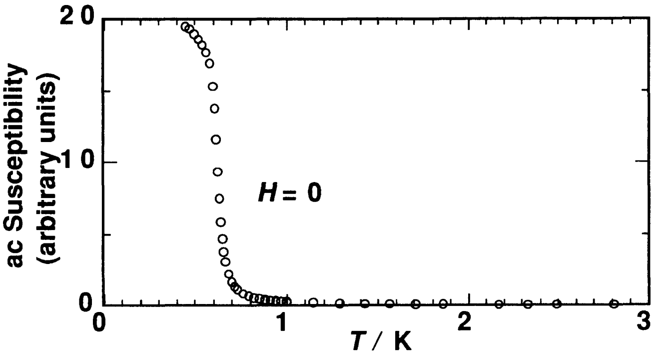

Fig. 4. The temperature dependence of ac susceptibility of the γ-phase of p-NPNN.

composed of a simple radical having well-defined chemical and crystal structure and consisting only of the light elements of H, C, N, and O. The details of the present work will appear shortly.

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10) 1 emu K mol^{-1} = $(1/4\pi)$ cm^3 K mol^{-1}.

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