Discovery of a Quasi-1D Organic Ferromagnet, *p*-NPNN

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We discovered that an organic radical crystal, *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN), is a quasi-1D ferromagnet induced by unpaired electrons on radicals. The magnetization and the susceptibility of the triclinic γ-phase crystal are very well represented by the Bethe-ansatz solution of the $S=\frac{1}{2}$ 1D Heisenberg ferromagnet with nearest-neighbor coupling $J \simeq 4.3$ K. Low-temperature specific heat and ac susceptibility measurements revealed that the crystal undergoes a ferromagnetic transition at 0.65 K. The interchain coupling J' was estimated to be about 0.1 K.

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In the localized spin systems which are described by the Heisenberg model, ferromagnetic substances are quite rare in comparison with antiferromagnetic substances. EuO [1], K_2CuF_4 [2], and TMCuC [3] are known as typical examples of 3D, 2D, and 1D ferromagnetic substances. The search for new ferromagnets has recently been extended to molecular or polymer substances consisting of transition-metal elements and organic ligands [4]. And some organic polymers consisting of light elements have been claimed [5] to be ferromagnets even at room temperature. Their saturation moment, however, was so small (corresponding to only a few percent of monomer equivalence) and their reproducibility was so poor that questions about the reliability have been raised. On the other hand, in simple organic compounds consisting only of light elements such as H, C, N, and O, no ferromagnetic long-range order has been reported until the present. In the course of our studies on ferromagnetic coupling in simple organic radicals [6], we have found that the γ-phase crystal of 2-(4′-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-N-oxide, $C_{13}H_{16}N_3O_4$ (or *p*-nitrophenyl nitronyl nitroxide, abbreviated as *p*-NPNN hereafter) has a ferromagnetic coupling between the unpaired electrons on the radicals [7] (see Fig. 3). Here, we report that the γ phase of *p*-NPNN is well described by the model of $S=\frac{1}{2}$ ferromagnetic Heisenberg chain and the crystal undergoes a ferromagnetic phase transition at $T=0.65$ K due to residual interchain coupling.

Theoretically the 1D Heisenberg ferromagnet with $S=\frac{1}{2}$ has been investigated by many authors [8-12]. Decades ago Bethe [8] demonstrated that the exact many-body wave function of this Hamiltonian can be written down analytically. Using his formalism, one of the authors (Takahashi) derived the coupled integral equations which determine the thermodynamic quantities of this system [9]. The specific heat and magnetic susceptibility at finite temperature can be calculated by this set of equations [10]. It was found that the susceptibility diverges as T^{-2} and that the specific heat behaves as $\sqrt{T}$ at low temperatures. These low-temperature properties are explained also by the modified spin-wave approximation [11]. More recently the thermodynamic properties were calculated by applying the Bethe-ansatz technique to the quantum transfer matrix (not to the Hamiltonian) [12]. Using this method we can calculate the thermodynamic quantities (magnetization curve, magnetic susceptibility, specific heat, correlation length, etc.) precisely up to six or seven significant figures at a given temperature. The Hamiltonian is

$$\mathcal{H} = -J\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{S}_{i+1} - 2h\sum_{i=1}^{N}S_i^z ,$$
$$h=\tfrac{1}{2}g\mu_B H,\quad S=\tfrac{1}{2} . \tag{1}$$

The free energy of this system per spin is given by the equation for a series of complex numbers $\{p_l,\ l=1,2,3,\dots\}$ which is determined by

$$p_l = \frac{4\pi T}{J}\left(l-\frac{1}{2}\right) + \frac{4hi}{J} + \frac{p_l}{1+p_l^2} + \frac{2T}{Ji}\sum_{j=1}^{\infty}\ln[L(p_l,p_j)L(p_l,-\bar{p}_j)] ,$$
$$L(x,y) = \frac{1-(1-ix)^{-1}+iy}{1-(1+ix)^{-1}-iy} , \tag{2}$$

$$f(T,h) = -T\ln 2 - \frac{T}{2}\sum_{l=1}^{\infty}\ln\left(\frac{(1+p_l^2)(1+\bar{p}_l^2)}{[4\pi T(l-\frac{1}{2})/J]^4}\right) . \tag{3}$$

This set of equations should be equivalent to the thermodynamic Bethe-ansatz integral equations [9]. At $l \gg J/T$, p_l approaches $4\pi T(l-\frac{1}{2})/J + \text{const}\times i$. So we can determine p_l's at given T and h by iteration. The magnetization, energy, susceptibility, and specific heat are given by differentiation of the free energy. The differentiations of p_l's are given by a set of linear equations. The numerical calculations of these equations are straightforward. The derivations of Eqs. (2) and (3) in the case $h=0$ were given in Ref. [12] as a special case of *XYZ* chains. The equation of *XXZ* chains in nonzero field as the generalization of Eqs. (2) and (3) will be given in a separate pa-

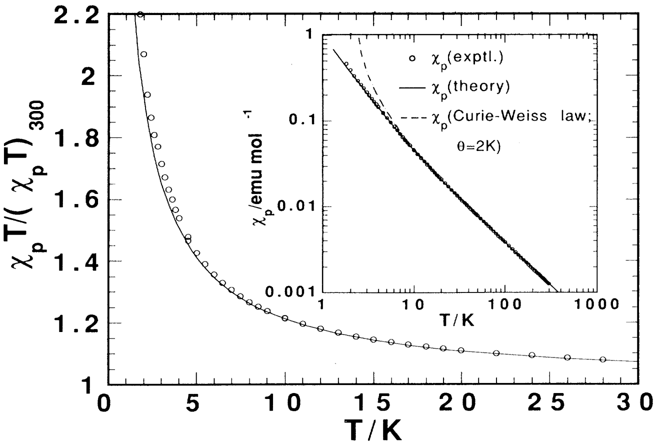

FIG. 1. Low-field magnetic susceptibility multiplied by temperature as a function of temperature at $T \geq 1.8$ K for a single crystal of the γ phase (circles). The product is normalized with the room-temperature value. The solid line is the theoretical line for a ferromagnetic Heisenberg chain with $J=4.3$ K. In the inset the above are compared up to 300 K with the Curie-Weiss law with $\theta=2$ K.

per [13].

The crystal structure of the γ phase of p-NPNN is described briefly in Ref. [7]. The γ phase of p-NPNN crystallizes in the triclinic $P\bar{1}$ system ($a=9.193$, $b=12.105$, $c=6.471$ Å, $\alpha=97.35$, $\beta=104.44$, $\gamma=82.22°$, $V=687.6$ Å^3, and $Z=2$). The unpaired electron is delocalized over the p-NPNN molecule (mainly on the O-N-C-N-O group), but confined within the molecule, thereby rendering the crystal an insulator. The principal g factors of the crystal are determined to be $g_1=2.0117$, $g_2=2.0051$, and $g_3=2.0038$ from the EPR experiments at room temperature. The magnetization and dc susceptibility were measured with a Quantum Design MPMS magnetometer. All the magnetic measurements were performed on a single crystal of about 15 mg in weight, but the specific-heat measurement was done on several pieces of small single crystals. No anisotropic effect was recognizable in the dc susceptibility except for the diamagnetic contribution.

In Fig. 1 is shown the temperature dependence of the product of the paramagnetic susceptibility and temperature $\chi_p T$, normalized by the product at 300 K. The product at 300 K $(\chi_p T)_{300}$ is 0.377 emu K mol^{-1}, which is consistent with the Curie constant for $S=\frac{1}{2}$ per radical. In Fig. 1 the observed product is compared with that calculated on the basis of Eq. (1) with $J=4.3$ K. The observed products agree well with the calculation as shown in the figure. The agreement is much better in the whole temperature range between 1.8 and 300 K than a usual mean-field approximation where χ_p strongly diverges at $T \simeq 2.0$ K (see the inset of Fig. 1). We can therefore conclude that the γ-phase crystal of p-NPNN is a quasi-one-dimensional Heisenberg ferromagnet with $S=\frac{1}{2}$.

The field dependence of the magnetization of the γ phase of p-NPNN is shown in Fig. 2 at several temperatures together with the theoretical curves, where the saturation magnetization M_s of 5613 emu mol^{-1} is also consistent with an $S=\frac{1}{2}$ system of $g \simeq 2.01$. The observed magnetizations at $T=1.8$, 2.3, and 4.0 K fit rather well with those calculated with $T/J=0.419$, 0.535, and 0.936 ($J=4.3$ K), but slightly deviate upwards. This is consistent with the results of susceptibility measurements just described, where J is estimated to be 4.3 K.

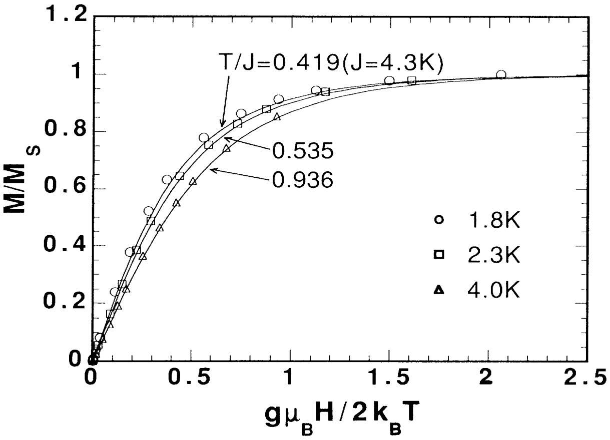

FIG. 2. Magnetization of the γ-phase crystal as a function of $h/k_B T$ at 1.8, 2.3, and 4.0 K for the same crystal used in Fig. 1. Solid lines are the theoretical curves with $J=4.3$ K at corresponding temperatures.

The observed susceptibility in Fig. 1 shows slight enhancement compared with the calculated one below about 6 K. This enhancement is probably due to the effect of interchain interaction. As a matter of fact, the substance exhibits a phase transition at $T_c=0.65$ K. This was revealed by low-temperature specific heat under constant pressure C_p, and ac susceptibility measurements. The specific heat was measured between 0.4 and 6 K with an adiabatic heat-pulse calorimeter, the details of which were described elsewhere [14].

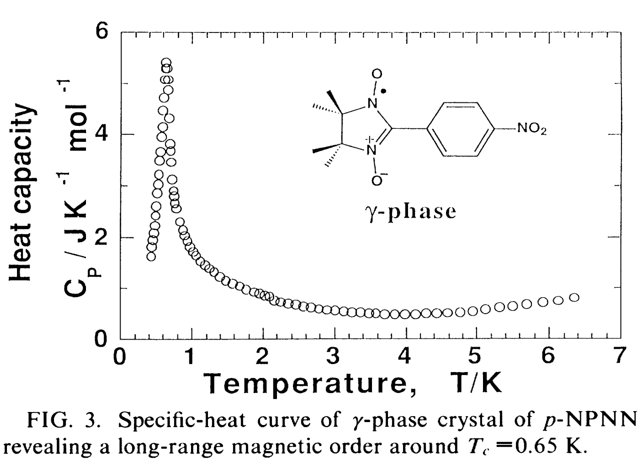

FIG. 3. Specific-heat curve of γ-phase crystal of p-NPNN, revealing a long-range magnetic order around $T_c=0.65$ K.

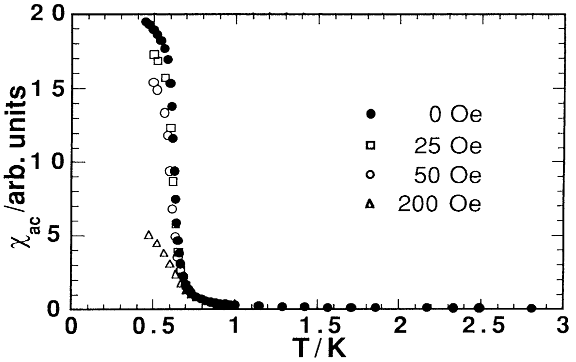

FIG. 4. ac susceptibility of the γ-phase single crystal under the static magnetic field of 25, 50, and 200 Oe, perpendicular to the ac field of 100 mOe.

Figure 3 shows the λ-like phase transition at T_c. The magnetic entropy estimated from the data in the present temperature range is somewhat less than $R\ln 2$, but confirming the bulk nature of the transition for the $S=\frac{1}{2}$ spins. In order to gain information about the magnetic state below T_c, the ac susceptibility has been measured in an ac field of about 100 mOe at 123 Hz.

In Fig. 4 is shown the temperature dependence of ac susceptibility of the γ phase of *p*-NPNN measured at zero and low static fields (25, 50, and 200 Oe) perpendicular to the ac field. The zero-field susceptibility becomes very large at T_c and the almost diverging susceptibility strongly suggests that ferromagnetic long-range order is achieved in this substance below T_c. This is probably the first ferromagnetic genuine organic compound containing only light elements and having well-defined structure. The ac susceptibility below T_c is very much suppressed when small static fields are applied. This probably means that the substance has very small anisotropy against magnetic fields. This fact is consistent with the nearly free spin *g* factors for the three principal directions determined from EPR experiments.

From the mean-field theory, the susceptibility of the quasi-1D system is given by

$$\chi=\frac{\chi_0}{1-\frac{1}{2}J'z\chi_0},$$

where χ_0 is the susceptibility of pure 1D Heisenberg model ($\chi_0=-\partial^2 f/\partial h^2$), J' is the interchain coupling constant, and z is the number of interchain bonds per spin. At $T=0.65\text{ K}=0.151J$, theoretical calculation gives $\chi_0 T=3.30$. Assuming that the zero-field ac susceptibility at 0.65 K diverges we obtain $J'z/2=0.65/3.30\simeq 0.2$ K. From this, we estimate roughly the interchain coupling constant to be $J'\simeq 0.1$ K assuming $z=4$. We therefore conclude that the γ phase of *p*-NPNN is a quasi-one-dimensional ferromagnetic substance with $J'/J\sim 0.02$. Further detailed experiments are under way to clarify more precisely the nature of magnetism evoked by the delocalized unpaired π electrons in this substance.

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