Low Temperature Static Magnetization of an Organic Ferromagnet, β-*p*-NPNN

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Abstract

A ^{3}He refrigerator mountable to a commercial SQUID magnetometer has been developed, which enables us to measure static magnetizations of a sample at temperatures below 2 K conveniently. The design and usage of the system are outlined. We have applied this to study static magnetic properties of an organic ferromagnet, β-*p*-NPNN, and have confirmed that the saturation magnetization is 1 μ_B per molecule. No hysteretic behavior has been detected, when the field was applied along the easy axis. This indicates that β-*p*-NPNN is a very soft magnet, as expected for an isotropic Heisenberg magnet based on organic radicals.

Keywords: *p*-NPNN, organic ferromagnet, magnetization curve, ^{3}He, saturation moment, coercive force

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An organic radical molecule *p*-NPNN [1-3] (2-(4´-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl 3-*N*-oxide) is known to crystallize in four different phases, α-, β-, γ- and δ-phases, depending on the conditions for crystal growth. Among them, the orthorhombic β-*p*-NPNN was found to exhibit bulk ferromagnetism below T_c = 0.6 K for the first time as a well-characterized organic crystal [4,5]. The characterization of the ferromagnetic ordering was carried out by means of specific heat, ac susceptibility (χ_{ac}), magnetization (*M-H*) curve [4,5] and μSR measurements [6]. From the specific heat, χ_{ac} and μSR results, it has been concluded that β-*p*-NPNN is a simple three-dimensional (3D) spin-1/2 Heisenberg ferromagnet [4,5]. The pressure effect on the specific heat and χ_{ac} has revealed that β-*p*-NPNN undergoes a dimensional crossover to a 2D ferromagnet and it becomes a layered antiferromagnet above 0.65 GPa [7,8]. On the other hand, the *M-H* curve up to 400 Oe at 0.44 K obtained by a dynamical induction method [5], exhibited an unusual feature. The saturation magnetization, M_{sat}, estimated from this *M-H* curve was only about half of the value for an S = 1/2 Heisenberg ferromagnet, $M_{sat}(1/2) = N_A g S \mu_B = 5.58 \times 10^3$ erg Oe^{-1} mol^{-1} [5]. Although a possibility that the small M_s may be related to the delocalized nature of the π spins was suggested [5], it has been desired to check the M_{sat} value by a static measurement. The induction method in principle cannot give very accurate M and H values, because of the ambiguities in the filling factor of the sample in the pick-up coil and in the swept field, even if corrected for these effects. We report here the result of static magnetization measurements of β-*p*-NPNN below T_c, using a recently developed ^{3}He-refrigerator mountable to a Quantum Design SQUID magnetometer, MPMS [9].

Slow evaporation of a benzene solution of *p*-NPNN gave single crystals of β- *p*-NPNN as hexagonal rods with the typical width of 1-2 mm. The pieces of the single crystal, ca. 4 mm in length, were fixed on a small non-magnetic plate. The specimen was installed in the ^{3}He-refrigerator, so as to align the *b*-axis (the easy axis [6]) in the field direction of the magnetometer. The applied field, H_a, was corrected for the demagnetization effect to give the field seen by the sample, $H_{eff.}$ Only a rough estimation of demagnetization factor, N, was possible, because the shape is different piece by piece and is not ellipsoidal. However, the value of N does not affect any conclusion in this work. We applied N of approximately 0.4, to calculate, $H_{eff.} = H_a - 4\pi N M_V$, where M_V denotes the magnetization per unit volume.

While the new measurement system was being conceived, we always kept one thing in mind; "Do not alter the MPMS." We have succeeded in designing a system that is easily attachable and detachable. Our MPMS is equipped with the ^{3}He cryostat only when temperatures lower than 1.8 K is necessary; otherwise it works just as a normal MPMS. The ^{3}He cryostat has been designed to be slim enough to fit into the sample space of Quantum Design's MPMS. The schematic drawing of the cryostat is shown in Fig. 1. It is the "Sample in liquid"-type cryostat, meaning that the sample is soaked in the liquid ^{3}He. The lower end of the main pipe has a vacuum jacket to insulate the inside of the cryostat from the outside environment, which is actually the sample space in an ordinary usage of the MPMS and maintained at 1.6 K during the ^{3}He-temperature operation. Here the base temperature of the MPMS somewhat lower than the usual (around 1.8 K) is achieved by an auxiliary rotary pump, facilitating more efficient condensation of ^{3}He gas.

The principle of the measurement is that we scan the whole cryostat, including the sample, through the pickup coil. In a way it is similar to magnetization measurements with a pressure cell. This method is advantageous in that the sample temperature is very stable during the scan. The problem is that the cryostat contributes to the background. It can be subtracted, however, unless it is too large. The current version has been designed for an RSO (Reciprocating Sample Oscillation) -type drive, although a version that is compatible with a standard DC-type drive is also possible. The present cryostat is supported at its neck by the top part of the moving rack of the RSO unit. On top of the drive we mount a box as a sample-space airlock, and a bellows inside the box interconnects between the ^{3}He cryostat and a flange, which is the port to a gas-handling system.

To hold a sample in position, we use the drinking straws that are used with the MPMS. Since the sample is thermally insulated from the outside of the cryostat, the temperature has to be measured *in situ*. To reduce the background from the thermometer, we have adopted a bare-chip Cernox (Lake Shore Cryotronics, Inc.) sensor, which gives a fairly small moment of 1×10^{-4} emu at 1.6 K and 1 T. It is accommodated in a polyimide tube and placed just above the sample. The total background from the current cryostat is about 6×10^{-4} emu at 0.5 K and 1 T. This is small enough to be neglected in the case reported herein and in most other cases. If necessary, we can subtract the background by measuring it separately.

The usage of the new apparatus is as the following (see the pictures in Fig. 1). The normal MPMS has an O-ring seal made of acryl on the top opening of the RSO drive unit. We replace the seal with an O-ring compression fitting for a more secure connection. After warming up the sample space of the MPMS to around room temperature and venting with He gas, we fix the box on top of the RSO unit by inserting the bottom pipe of the box into the O-ring fitting. Then the ^{3}He cryostat is installed into the MPMS's sample space, and all the connections are made. When the box has been covered and the inside of the ^{3}He cryostat has been evacuated, the system is ready to be cooled down.

Using ^{3}He gas as heat-exchange medium inside the cryostat, we first cool down the MPMS to around 5 K. Then the auxiliary rotary pump lowers the temperature to 1.6 K, at which ^{3}He gas is condensed. Finally the liquefied ^{3}He is pumped out to go below 0.5 K. We can reach 0.48 K within 30 min or so after starting to pump the liquid.

Figure 2 shows the *M*-*H* characteristic of β-*p*-NPNN below and above T_c. The data above T_c, which were measured by a usual method without the ^{3}He-refrigerator, are consistent with those reported previously [4,5]. The saturation of the paramagnetic moment at the value close to $M_{sat}(1/2)$ was observed at 2 K. The static *M*-*H* curves below T_c clearly show that the ferromagnetic moment also saturates at $M_{sat}(1/2)$. Therefore, we conclude M_{sat} of β-*p*-NPNN is $M_{sat}(1/2)$ as expected for an ordinary spin-1/2 Heisenberg ferromagnet.

Another characteristic is the absence of hysteresis as shown in Fig. 3; the magnetization is almost reversible and the coercive force and residual magnetization are too small to be detected, unlike the previous result [4,5]. The small hysteresis observed by the dynamical method might have been an artifact due to the difference in the data-acquisition timing for *M* and *H*. Another thing that we would like to point out is that the field was applied along the easy axis in the present measurements to suppress the irreversible rotation of magnetization against the small dipolar anisotropy, whereas the field had not been along the easy axis in the previous ones. Thus β-*p*-NPNN is concluded to be a considerably soft magnet at least for the easy axis. This behavior is expected for an isotropic Heisenberg spins of the organic radicals, and is consistent with the specific heat [5] and μSR [6] results.

In the ferromagnetic state, *M* rises rapidly below the applied field $H_a \approx 200$ Oe. It is also noted that *M* is still increasing slowly even in the high-filed regime, $H_a > 1$ kOe, until it saturates near $H_a = 10$ kOe. This means that $H_a = 400$ Oe was too low to determine M_s. Since the magnetic anisotropy of β-*p*-NPNN is significantly small, the slow saturation can be related to the thermal fluctuation effect of a soft isotropic ferromagnet, rather than to the rotation of domain magnetization or to the domain wall displacement of hard magnets. If this is the case, the initial increase of M at low fields is regulated by the spontaneous magnetization, M_{sp}, which corresponds to the order parameter. This is followed by slow increase of M in the range, $M_{sp} < M < M_{sat}$, in the high field regime. The spontaneous magnetization $M_{sp}(T)$ decreases from $M_{sp}(0) = M_{sat}$ to zero as $T = T_c$ is approached. From the μSR measurement [7], $M_{sp} \approx 0.8\ M_{sat} = 4.5 \times 10^3$ erg Oe^{-1} mol^{-1} is inferred at $T = 0.48$ K ($T/T_c = 0.8$). This agrees with the initial rise of M observed in this work. In this way, the M-H characteristic of β-*p*-NPNN is understood in terms of the thermal fluctuation.

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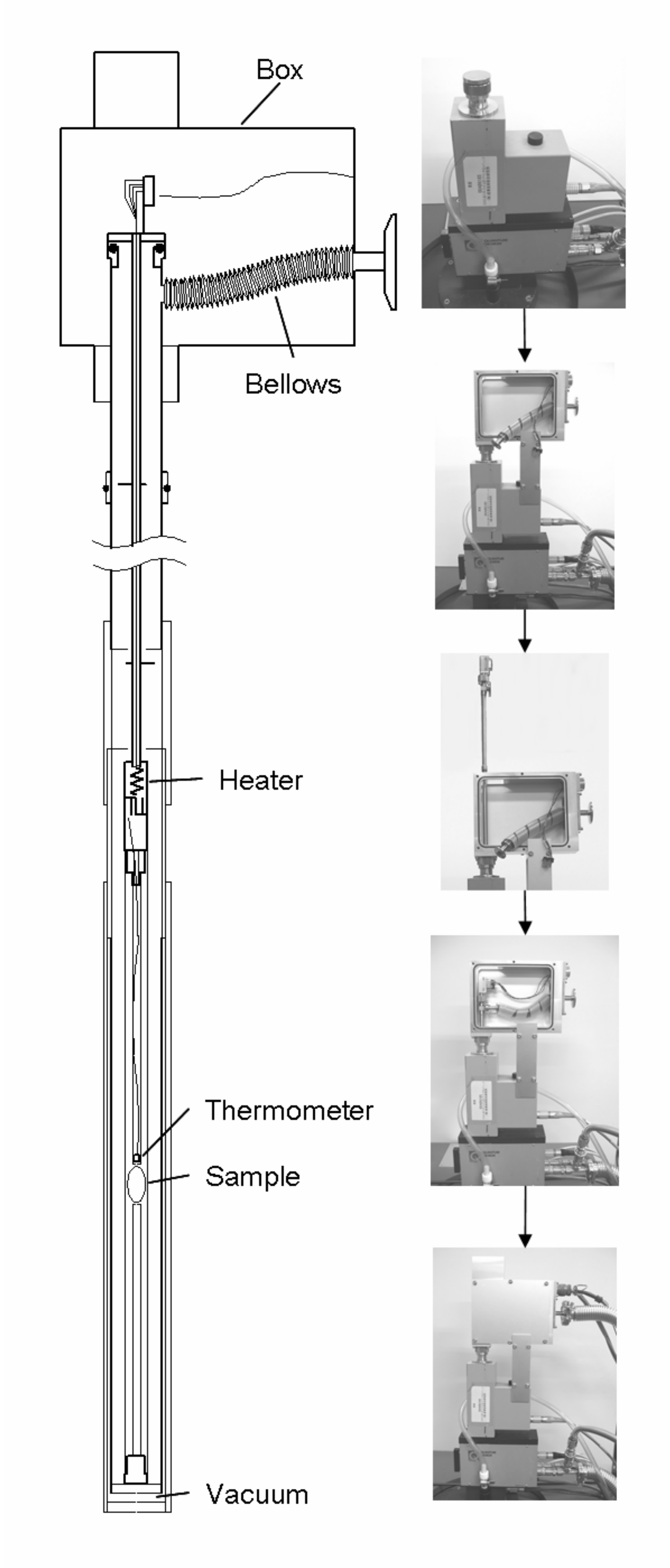
Figure Captions

Fig. 1. (Left) Schematic drawing of our ^{3}He cryostat. (Right) Pictures showing the set-up procedure of the ^{3}He cryostat.

Fig. 2. Magnetization of β-*p*-NPNN below and above T_c plotted versus H/T. The inset shows the overall *M*-*H* characteristic in the ferromagnetic state. Demagnetization correction is not made for the data in this figure.

Fig. 3. Low field *M*-*H* curve of ferromagnetic β-*p*-NPNN at 0.48 K. The closed symbols show the data corrected for demagnetization effect, while open ones are without the correction. Both upward and downward field sweep data are shown. No hysteretic behavior is found.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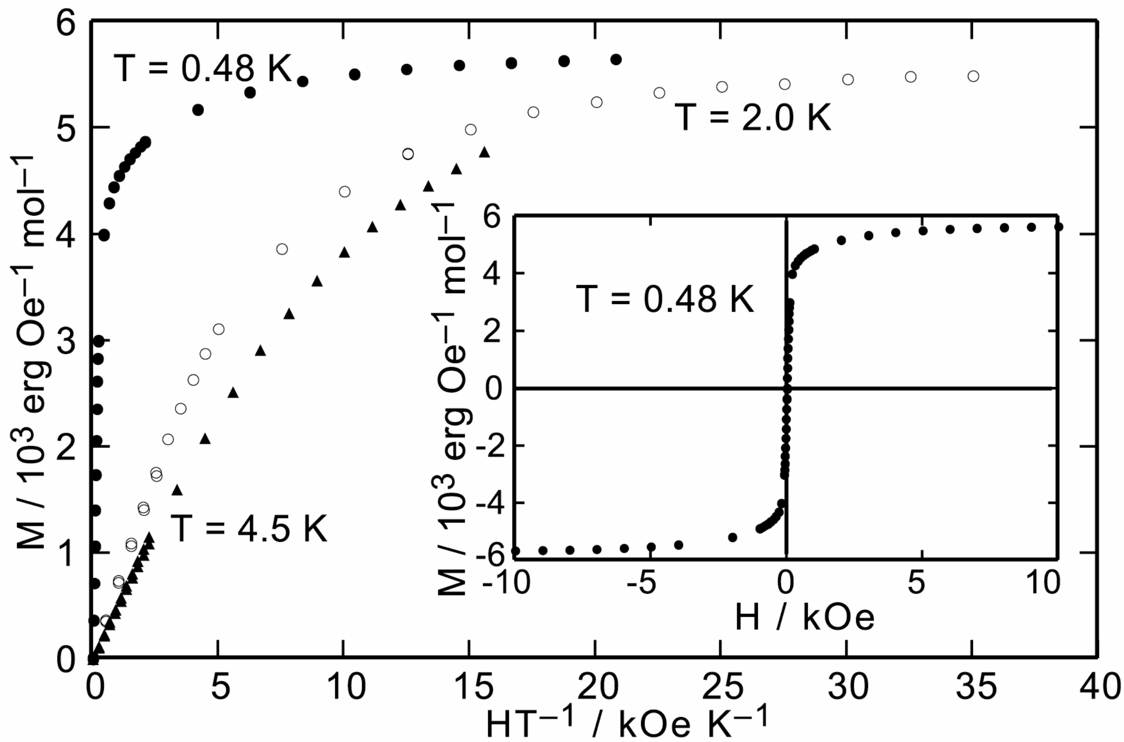
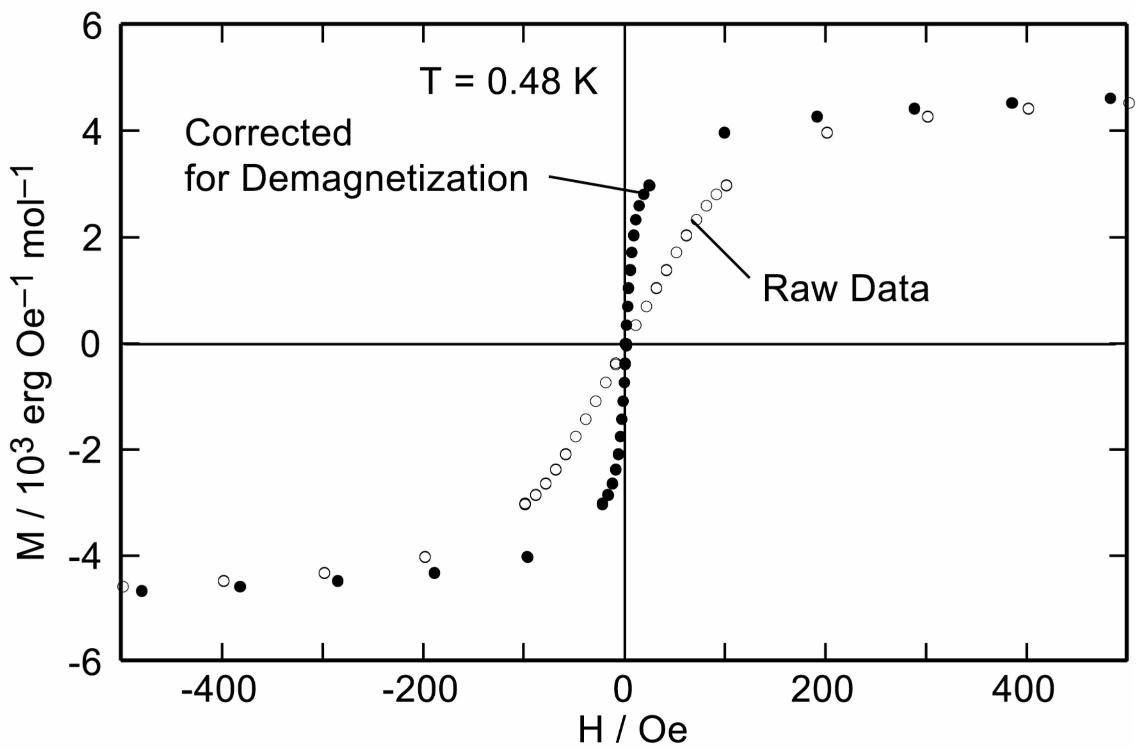


T = 0.48 K
T = 2.0 K
T = 4.5 K
M / 10^3 erg Oe^−1 mol^−1
HT^−1 / kOe K^−1
0
5
10
15
20
25
30
35
40
1
2
3
4
6
T = 0.48 K
H / kOe
-10
-5
-2
-4
-6


T = 0.48 K
Corrected
for Demagnetization
Raw Data
M / 10^3 erg Oe^-1 mol^-1
H / Oe
6
4
2
0
-2
-4
-6
-400
-200
0
200
400