Pressure effects on an organic radical ferromagnet: 2,5-difluorophenyl-α-nitronyl nitroxide

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Raising a transition temperature (T_c) in organic radical ferromagnets is a desire for material scientists. We investigated the pressure effects on an organic radical ferromagnet 2,5-difluorophenyl-α-nitronyl nitroxide (2,5-DFPNN), which has a ferromagnetic transition at 0.45 K. The hydrostatic pressure effects were investigated through measurements of ac magnetic susceptibility (χ) up to $P=1.7$ GPa, heat capacity (C_p) up to $P=1.5$ GPa, and powder x-ray diffraction up to $P=4.7$ GPa. Furthermore, ac magnetic susceptibility under nonhydrostatic pressure was also measured in the pressure region up to 10.0 GPa. As for 2,5-DFPNN, we observed the pressure-induced enhancement of T_c as $dT_c/dP=7.9\times10^{-2}$ K/GPa [$T_c(P=1.5$ GPa) $=0.57$ K], while other prototypes, the β phase of p-NPNN and p-Cl-C_6H_4-CH=N-TEMPO show the negative pressure effects. The results for the C_p and the crystal structural analysis suggest that the magnetic dimension of the short-range order developing above T_c transforms from one dimension (a axis) to two dimensions (ac plane) under high pressure. This increase of the magnetic dimension probably promotes to increase T_c. The ferromagnetic signal of χ, however, decreases with increasing pressure, and finally disappears for $P \geqslant 5.0$ GPa. The decrease seems to originate from the decrease of the ferromagnetic interaction along the b axis. Similar instability of organic ferromagnetic long range order against pressure has been observed for the β phase of p-NPNN and p-Cl-C_6H_4-CH=N-TEMPO.

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I. INTRODUCTION

Organic radical crystals consisting of only light elements such as H, C, N, O, etc., favor columnar molecular stacking reflecting the planar molecular structure, and often show low-dimensional magnetic properties. The magnetic origin on them is an unpaired electron, and the intermolecular interaction depends on the overlaps of molecular orbitals (MO's). The most amount of spin density concentrates on a part of the molecule around which a single occupied molecular orbital (SOMO) spreads. The residual spin density is distributed over the whole molecule via anti-SOMO's such as a highest occupied MO (HOMO) and/or a lowest unoccupied MO (LUMO). The symmetric molecular stacking allows large SOMO-SOMO overlap, which brings about antiferromagnetic intermolecular interaction. On the other hand, the antisymmetric one encourages the overlaps between SOMO and anti-SOMO rather than SOMO-SOMO overlap. The overlaps between SOMO and anti-SOMO induce ferromagnetic intermolecular interaction. Generally, in organic radical crystals, the antiferromagnetic intermolecular correlation is often realized, due to the symmetric molecular stacking. On the other hand, the disappearance of the orbital angular momentum realizes the isotropic spin system there, and their magnetism has actively been studied from interests in both fields of materials science and quantum spin system.[1]

In organic radical crystals, an appearance of the ferromagnetic long-range order (LRO) is a very rare case, since it is very difficult to realize the antisymmetric molecular stacking along every crystal axis. In 1991, a ferromagnetic LRO was found in the β phase of p-nitrophenyl nitronyl nitroxide ($C_{13}H_{16}N_3O_4$, abbreviated as the β phase of p-NPNN).[2] For a decade, some syntheses of organic radical ferromagnets have succeeded.[3–6] However, their mechanism has not been completely understood. Furthermore, the significant quantum effects due to low dimensionality and the isotropic spin symmetry suppress the LRO into very low temperatures, together with strict condition of the molecular stacking for them. The real transition temperatures of the ferromagnetic LRO (T_c's) have not reached even 1.0 K, except for 1.48 K of N,N'-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane (abbreviated as dupeyredioxyl).[3] It has been a desire for mate-
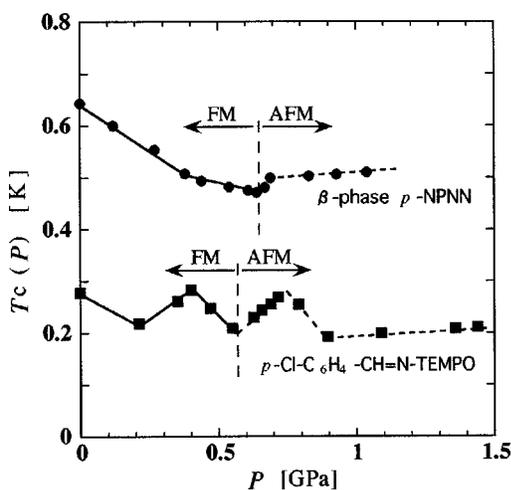
FIG. 1. Pressure dependence of transition temperature (T_c) in two typical organic radical ferromagnets, the β phase of p-NPNN [$T_c(P=0)=0.61$ K] (Refs. 7–9) and p-Cl-C$_6$H$_4$-CH=N-TEMPO [$T_c(P=0)=0.28$ K] (Ref. 10). The solid and dotted lines stand for the ferromagnetic (FM) and antiferromagnetic (AFM) regions, respectively.

rial scientists to raise the T_c (up to a liquid-nitrogen temperature), and a variety of research has still been tried.

As for the study on the interaction mechanism of organic radical ferromagnets, there are mainly two approaches: (1) systematical synthesis of many promising derivatives and (2) continuous observation of magnetic properties of a certain prototype derivative under pressure. In the former chemical approach, the magnetostructural correlation has been investigated for various series of derivatives. However, this approach is not adequate to pursuing the crucial knowledge for the magnetic interaction systematically, since the crystal structure drastically changes by a small substitution. On the other hand, the latter physical approach enables to control the structure and the magnetic properties systematically, changing the overlaps of MO's continuously.[7–10] We have investigated the pressure effects on two prototypes, the β phase of p-NPNN [$T_c(P=0)=0.61$ K],[7–9] and 4-(p-chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl [C$_{16}$H$_{22}$ClN$_2$O, p-Cl-C$_6$H$_4$-CH=N-TEMPO, T_c ($P=0)=0.28$ K],[10] and observed the pressure dependences of T_c as shown in Fig. 1. In the above two compounds, there are the following three common characteristics under pressure: (1) the ferromagnetic LRO transforms into the antiferromagnetic one at around $P=0.7$ GPa (see Fig. 1), (2) the T_c under pressure does not exceed the initial value (see Fig. 1), and (3) the dimension of the short-range order (SRO) developing above T_c decreases by applying pressure [the β phase of p-NPNN, three dimensions (3D)$\rightarrow$two dimensions (2D), p-Cl-C$_6$H$_4$-CH=N-TEMPO: 2D$\rightarrow$1D]. These pressure effects have been explained by considering the pressure-induced rotations of nitrophenyl moiety (in the case of the β phase of p-NPNN)[11] and methyl moiety (in the case of p-Cl-C$_6$H$_4$-CH=N-TEMPO),[10] respectively. These results suggest that the pressure can bring about the intramolecular deformation as well as the intermolecular shrinkage.
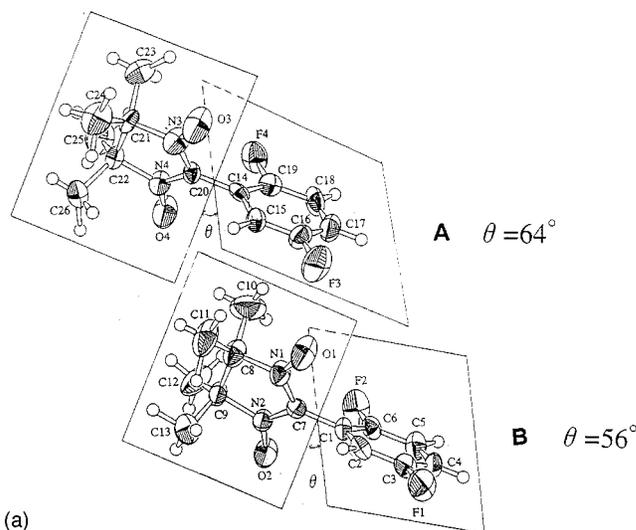
(a)
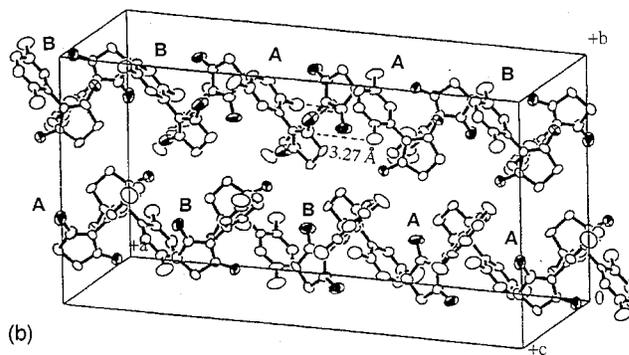
(b)

FIG. 2. (a) Molecular structure of 2, 5-DFPNN. (b) The schematic molecular stacking in the unit cell. The unit cell consists of two rotational isomers (A and B), which are stacked as -A-A-B-B-A-A- along the a axis.

Our question is whether the above three pressure-induced phenomena are common characteristics of organic radical ferromagnets or not. In this paper, we report the pressure effects on a typical organic radical ferromagnet, 2,5-difluorophenyl-α-nitronyl nitroxide (C$_{13}$H$_{15}$N$_2$O$_2$F$_2$, abbreviated as 2,5-DFPNN), whose T_c at ambient pressure is 0.45 K.[6]

In Sec. II, explanations about the sample and experimental apparatus will be mentioned. In Sec. III, the experimental results under hydrostatic pressure, such as the thermal and magnetic measurements up to $P=1.7$ GPa using a clamp cell of piston cylinder type and structural analysis experiments up to $P=4.7$ GPa using a diamond anvil cell (DAC), will be shown and analyzed. In Sec. IV, the magnetic measurements under nonhydrostatic pressure up to $P=10.0$ GPa using a DAC will be shown. In Sec. V, a model to explain the pressure effects on 2,5-DFPNN will be discussed, and finally a way to increase T_c effectively will be proposed.

II. EXPERIMENT

A. Sample

The preparation of 2,5-difluorophenyl-α-nitronyl nitroxide (2,5-DFPNN) has been described in Ref. 6. Figure 2

shows the molecular structure (a) and an overview of the molecular stacking in the unit cell (b). Most amount of spin density concentrates on two NO moieties of five-membered ring, around which SOMO spreads. The crystal structure belongs to orthorhombic with the space group Pbca, and the lattice parameters are $a = 30.199(9)$ Å, $b = 15.604(6)$ Å, and $c = 11.096(6)$ Å.[6] The unit cell of 2,5-DFPNN consists of two rotational isomers as follows: one with dihedral angle between the plane of phenyl ring and the mean plane of five-membered ring to be 64° (rotamer A) and the other to be 56° (rotamer B). These rotational isomers form a columnar structure along the a and b axes and, along the a axis, they are located in an alternated stack such as -A-A-B-B-A-A-. Along the c axis, the zig-zag columns with perpendicular orientation of each molecular axis are formed. The antisymmetrical molecular stacking along every crystal axis brings about a possible magnetic interaction for the ferromagnetic LRO. The structural analysis shows that a ferromagnetic interaction along the a axis is predominant due to a short contact between fluorine (F) atom and nitrogen (N) atom of radical center. The experimental results for the heat capacity and magnetic susceptibility at ambient pressure indicate that a ferromagnetic transition occurs at 0.45 K, above which one-dimensional SRO with the intrachain interaction $J/k_B = 0.70$ K develops.[6]

B. High pressure experiment using clamp cell

By means of a clamp cell of piston cylinder type, the heat capacity and ac magnetic susceptibility for the polycrystalline sample of 2,5-DFPNN were measured under hydrostatic pressure up to 1.74 GPa. The clamp cell made of Cu-Be with the inner and outer diameters 4–12 mm was set in the ^{3}He-^{4}He dilution refrigerator. As for a pressure-transmitting medium to produce hydrostatic pressure, an Apiezon-J grease with proper viscosity and good thermal conductivity was used.[12] A Teflon cell to hold the sample (91.7 mg) and Apiezon-J grease (36.4 mg) was inserted into a sample space in the clamp cell, in order to seal pressure effectively. Prior to this experiment, we have investigated a relation between load at room temperature and the actual pressure at liquid-^{4}He temperature by measuring pressure dependence of superconducting transition temperature of Al.[13] The experimental accuracy of estimating pressure is about 0.02 GPa.

The heat capacity was measured with adiabatic heat-pulse method. To extract the magnetic heat capacity (C_p) of 2,5-DFPNN from the observed heat capacity, the pressure effects on heat capacities of the Apiezon-J grease,[12] the lattice contribution of 2,5-DFPNN, and the Teflon cell have been considered. The lattice contribution, for example, was estimated so that total magnetic entropy for $S = \frac{1}{2}$ [$Nk_B \ln(2S+1) = Nk_B \ln 2$] was preserved in the high-temperature limit. Generally, it decreases with increasing pressure, due to the increase of Debye temperature.

The in-phase (χ') and out-phase components (χ'') of the ac magnetic susceptibility were measured using an ac resistance bridge (Linear Research Inc., model LR-700) in the temperature region from 0.25 to 5.0 K. In the ac bridge, the frequency of the ac current was fixed to be 15.9 Hz, and the

measurement was performed under ac magnetic field of 0.1 Oe peak-to-peak. For some pressures, the external magnetic field (H) dependences of χ' up to 250 Oe were measured at the lowest temperature for each measurement, and the magnetization (M) curve was obtained by integrating χ' against H.

C. High pressure experiment using a DAC

The powder structural analysis experiments up to $P = 4.7$ GPa and the measurements of ac magnetic susceptibility up to $P = 10.0$ GPa were performed, using a DAC. The tip diameter of diamond anvils used in each experiment was 0.6 and 1.0 mm, respectively. The gaskets were made of nonmagnetic hardened Cu-Be. In the sample space made by drilling the gasket, powdered sample of 2,5-DFPNN and two pieces of ruby were set with a liquid pressure-transmitting medium, fluorine oil. The pressure was estimated from the shift of the R_1 line of ruby fluorescence at room temperature.[14] The experimental accuracy of estimating pressure is about 0.2 GPa.

For the crystal structure analysis under pressure up to 4.7 GPa, the powder diffraction pattern was measured in the range $2\theta < 45°$ at room temperature, using the MPD system with a two-dimensional cylindrical imaging plate detector on BL-1B at the photon factory (PF), Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK).[15] The x-ray wavelength was 0.6905(4) Å calibrated with a CeO_2 powder diffraction pattern. The lattice constants were estimated by using a program for the pattern fitting (MAC science). The R_{wp} factor at $P = 0$, 0.4, 1.9, and 4.7 GPa was 11.0, 13.7, 8.0, and 4.0 %, respectively.

In the measurement of ac magnetic susceptibility, a primary coil (10 turns of Cu wire with diameter 0.05 mm) with the 6 mm inner diameter and secondary one (20 turns) with the 10 mm inner diameter were placed around diamond anvils. In the sample space, however, the pressure transmitting medium enough to realize the hydrostatic pressure could not be held, because the sample was full stuffed there to observe the signal as much as possible. The applied pressure might be not hydrostatic but slightly uniaxial-like. The magnetic signal of the sample of about 0.2 mg was measured within accuracy of 10^{-7} emu under the ac magnetic field applied of 0.2 Oe peak-to-peak and 15.9 Hz, using the ac resistance bridge mentioned in the above subsection. In order to decrease the noise in the measurements, there was no GPIB connection between the ac bridge and a computer. As for the out-phase susceptibility, we could not detect it due to the noise comparable to the signal of the sample. We set a plastic plate at a part for transmitting the load in DAC, in order to lessen the change of pressure due to the thermal shrinkage. Prior to the measurements of 2,5-DFPNN, we have checked that there was not large change of pressure between room temperature and liquid-^{4}He temperature by investigating the pressure effects on the superconducting transition temperature of Pb.
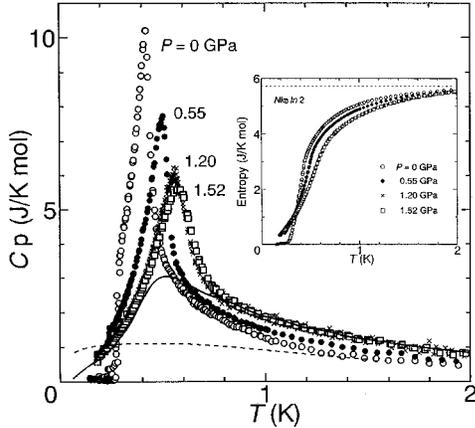
FIG. 3. Pressure dependence of the magnetic heat capacity (C_p) and the magnetic entropy of 2,5-DFPNN in the hydrostatic pressure region up to 1.52 GPa. The dotted and solid curves express the theoretical curves of $S = \frac{1}{2}$ one-dimensional Heisenberg ferromagnetic system (Ref. 16) with intrachain interaction $J/k_B = 0.70$ K and $S = \frac{1}{2}$ two-dimensional (square-lattice) one (Refs. 18, and 19) with intraplane interaction $J_{2D}/k_B = 0.70$ K, respectively. The dotted line in the inset represents the total magnetic entropy $Nk_B \ln(2S+1)$ for $S = \frac{1}{2}$.

III. EXPERIMENTAL RESULTS UNDER HYDROSTATIC PRESSURE

A. Thermal measurement

Figure 3 shows pressure dependences of the magnetic heat capacity (C_p) and magnetic entropy of 2,5-DFPNN in the temperature region below 2.0 K. As for the result of C_p at ambient pressure, there is a sharp anomaly due to the ferromagnetic LRO at around $T = 0.42$ K. This anomaly is not perfectly three-dimensional, and accompanies a plateau characteristic of $S = \frac{1}{2}$ 1D Heisenberg ferromagnetic system. In this system, the magnitude of C_p in the plateau does not depend on the intrachain interaction (J), but its position shifts toward high temperatures with increasing J. At ambient pressure, the temperature dependence of C_p for $T > 1.0$ K can be reproduced by a theoretical curve of the above 1D system[16] with $J/k_B = 0.70$ K. This analytic result is consistent with the previous report by Nakatsuji *et al.*[6] Given the crystal structure of 2,5-DFPNN, the one-dimensional SRO seems to develop along the a axis. From Oguchi's theory,[17] the order of interchain interaction (J') has been estimated to be $J'/J \simeq \frac{1}{5}$, using a relation of $k_B T_c / J \simeq 0.45/0.70$.[6]

Applying pressure makes the anomaly of C_p shift toward high temperatures. The pressure dependence of T_c estimated from the peak position of C_p is plotted in Fig. 4. The T_c is enhanced up to 0.57 K at $P = 1.52$ GPa. The quantitative analysis of C_p for $T > T_c$ suggests that the magnetic dimension of SRO changes from 1D to 2D by pressure. For $P \geqslant 1.20$ GPa, the decay of C_p above T_c is reproduced by the result of Monte Carlo simulation for $S = \frac{1}{2}$ 2D (square lattice) Heisenberg ferromagnetic system with the intraplane interaction $J_{2D}/k_B = 0.70$ K.[18,19] This result suggests that a 2D intermolecular correlation is strengthened under pressure. The
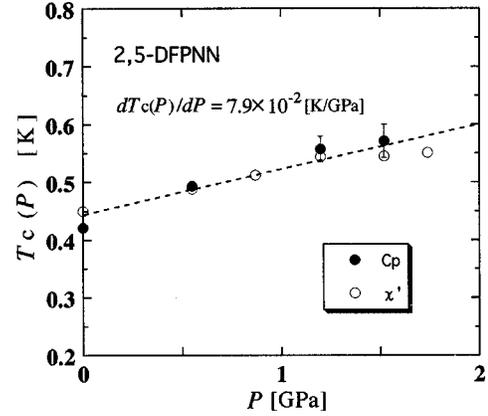
FIG. 4. Pressure dependence of the ferromagnetic transition temperature (T_c) of 2,5-DFPNN estimated from the heat capacity C_p (●) and the in-phase ac susceptibility χ' measurements (○). The dotted line expresses $T_c(P) = 7.9 \times 10^{-2}\, P + 4.5 \times 10^{-1}$.

detailed intermolecular network for $P \geqslant 1.20$ GPa will be discussed in the Sec. III C, based on the crystal structural data under pressure. Similar crossover of the dimension of SRO has been observed in the β phase of p-NPNN (3D→2D) (Ref. 7) and p-Cl-C$_6$H$_4$-CH=N-TEMPO (2D→1D).[10] In the above two compounds, the dimension of SRO decreases by pressure, and the T_c values initially decrease with increasing pressure as shown in Fig. 1. The relationship between the pressure effects on T_c and the change of the dimension of SRO will be discussed in Sec. V.

B. Magnetic measurement

Figure 5 shows pressure dependences of χ' and χ'' of 2,5-DFPNN in the pressure region up to 1.74 GPa. At ambient pressure, the rapid increases of χ' and χ'' are detected below 0.5 K, and these results are consistent with the report of Nakatsuji *et al.*[6] In a series of measurement under pressure, the temperature, at which $d\chi'/dT$ has the largest value, is consistent with the T_c estimated in the measurements of C_p and, hereafter, it will be evaluated as T_c in χ'. The T_c for χ' at ambient pressure is estimated to be 0.45 ± 0.01 K. The temperature dependence of χ' below T_c is different from that of χ'', which tends to diverge below 0.3 K. There is, however, no anomaly of C_p below 0.3 K as shown in the above subsection, and we have not yet understood the origin of its divergence of χ''. Applying pressure makes the ferromagnetic signals of χ' and χ'' shift toward high temperatures, and the T_c is enhanced with increasing pressure. On the other hand, the magnitudes of χ' and χ'' tend to be suppressed by pressure.

Figure 4 shows the pressure dependence of T_c estimated from the results of χ', together with that from C_p. The T_c increases linearly against pressure with the slope of $dT_c/dP = +7.9 \times 10^{-2}$ K/GPa (see the dotted line of Fig. 4). This pressure-induced enhancement of T_c has been never seen in the β phase of p-NPNN (Refs. 7–9) and p-Cl-C$_6$H$_4$-CH=N-TEMPO.[10] Figure 6 shows the pressure dependence of the magnetization (M) of 2,5-DFPNN in the magnetic field (H) region
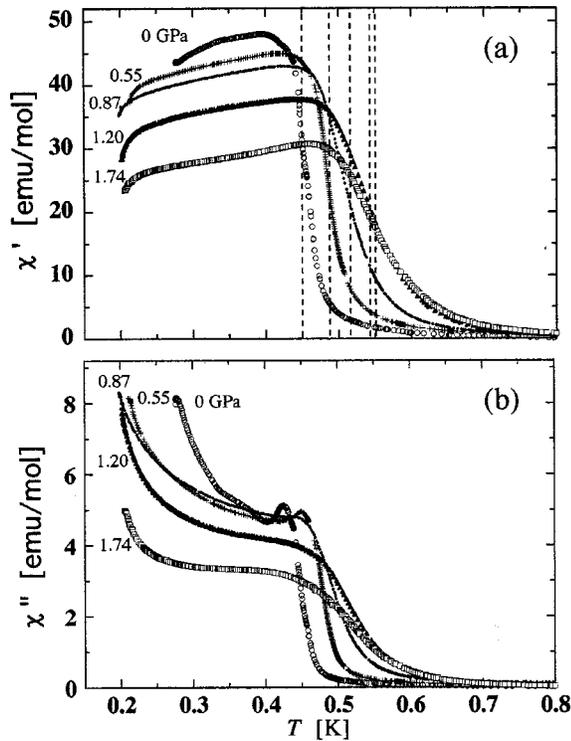
FIG. 5. Pressure dependences of in-phase component χ' (a) and out-of-phase one χ'' (b) of ac magnetic susceptibility for 2,5-DFPNN under hydrostatic pressure up to $P = 1.74$ GPa. The transition temperature (T_c) to the ferromagnetic long-range order at each pressure is shown by dotted line, and it shifts toward high temperatures with increasing pressure.

below 250 Oe at a temperature below T_c. In the considered pressure region, a ferromagnetic M-H curve is observed, whereas a spin-flop transition characteristic of antiferromagnetic transition is not detected. This result indicates that the ferromagnetic LRO of 2,5-DFPNN survives in a pressure region wider than those of the β phase of p-NPNN (Refs. 8, and 9) and p-Cl-C_6H_4-CH=N-TEMPO,[10] whose LRO's transform from ferromagnetic to antiferromagnetic at around $P = 0.7$ GPa. However, the magnetic moment of 2,5-DFPNN at each magnetic field decreases with increasing pressure, and these pressure effects will be discussed in Sec. V.

As for χ and M under pressure, we notice the following phenomena: (1) a pressure-induced enhancement of T_c and (2) a pressure-induced suppression of magnetic moment. The question is how these two contradictory phenomena appear together. Thus, the structural analysis experiments were performed in the pressure region up to 4.7 GPa to discuss the changes of the molecular stacking under pressure.

C. Structural analysis

Powdered x-ray diffraction experiments of 2,5-DFPNN have been performed at room temperature in the pressure region up to 4.7 GPa. As the pressure increases, a series of diffraction pattern shifts toward high angles without changing their shape. This implies that the original crystal symmetry is preserved in the considered pressure region.
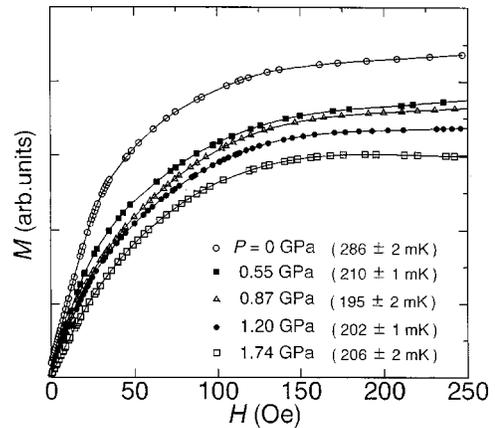
FIG. 6. Pressure dependence of the magnetization (M) curve of 2,5-DFPNN up to magnetic field (H) 250 Oe in the hydrostatic pressure region below $P = 1.74$ GPa. Each measurement was performed at the lowest temperature in each measurement, which was sufficiently below each T_c.

Figure 7 shows the pressure dependences of the lattice constants (a, b, and c) and of the volume of the unit cell (V), which have been estimated using a program for the pattern fitting. The result indicates that the compressibility of this compound is anisotropic, and the shrinkage along the c axis is larger than along the two other axes, especially in the low pressure region below 1 GPa. At ambient pressure, the molecular stacking along every crystal axis are antisymmetric, and they are suitable to the realization of the ferromagnetic LRO. Taking the molecular stacking at ambient pressure into consideration, the intermolecular interaction along the a axis is expected to be the largest at ambient pressure, and actually the one-dimensional characteristics has been observed in C_p for $T > T_c$. The remarkable shrinkage along the c axis under pressure suggests that ferromagnetic correlations might expand from 1D (along the a axis) to 2D (on the ac plane) with increasing pressures. This scenario can explain the increase
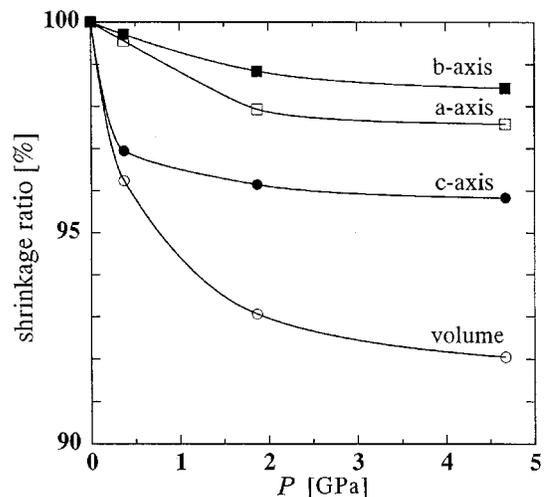
FIG. 7. Pressure dependences of the lattice constants (a, b, and c) and the volume of unit cell (V) of 2,5-DFPNN. The solid curves are the guides for the eye.
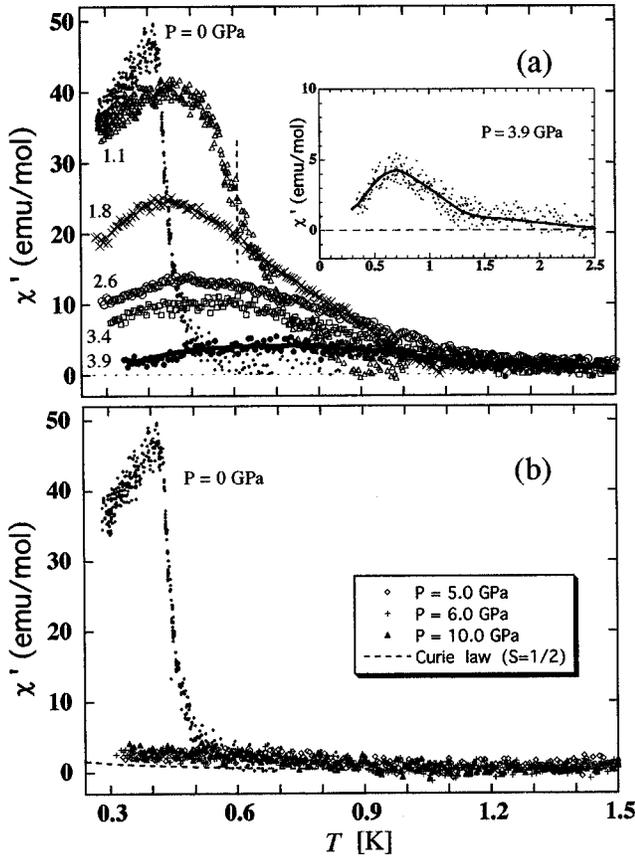
FIG. 8. Pressure dependence of in-phase ac magnetic susceptibility (χ') of 2,5-DFPNN under nonhydrostatic pressure: (a) for $P \leqslant 3.9$ GPa, and (b) for $P = 0$, 5.0, 6.0, and 10.0 GPa. The dotted line in (a) shows the imaginary T_c at $P = 1.1$ GPa. The dotted curve in (b) expresses the Curie's law for $S = \frac{1}{2}$.

of the dimension of SRO seen in C_p. The shrinkage of V is 7.9% at $P = 4.7$ GPa, and that at $P = 1$ GPa is probably 5–6%. The compressibility of 2,5-DFPNN is smaller than that of the β phase of p-NPNN,[8,9] and it suggests that 2,5-DFPNN is stronger against pressure than the β phase of p-NPNN.[8,9] How structural changes can induce the change of magnetism observed in this section will be discussed in detail in Sec. V.

IV. MAGNETIC MEASUREMENT UNDER NONHYDROSTATIC PRESSURE

In order to investigate whether the T_c goes on increasing by pressure for $P > 2$ GPa or not, χ' was measured in the pressure region up to 10.0 GPa using DAC. Figure 8 shows the pressure dependence of χ' for 2,5-DFPNN up to 10.0 GPa [(a) $P \leqslant 3.9$ GPa, (b) $P = 0$, 5.0, 6.0, and 10.0 GPa]. In the pressure region of $P \leqslant 3.9$ GPa, the ferromagnetic behavior is detected, and the ferromagnetic signal shifts toward high temperatures by pressure, decreasing its magnitude. Similar behavior has been also seen under hydrostatic pressure up to 1.74 GPa (see Fig. 5), but the magnitude of the shift is larger than that under hydrostatic pressure. In this experiment, there is a problem of the nonhydrostatic pres-

sure, and therefore we cannot evaluate T_c quantitatively. However, if T_c is decided as Fig. 5, the T_c value for $P = 1.1$ and 3.4 GPa exceeds 0.6 and 0.8 K, respectively. As for the susceptibility at $P = 3.9$ GPa, there is the cusp at around 0.7 K, below which it largely decreases. This temperature dependence is the characteristic of the antiferromagnetic LRO, and we suppose that the ferromagnetic LRO may disappear at around $P = 4$ GPa.

For $P > 5.0$ GPa, the ferromagnetic signal cannot be detected within the present experimental accuracy, as seen in Fig. 8(b). The magnitude of the susceptibility for $P \geqslant 5.0$ GPa decreases down to the same magnitude as the Curie's law for $S = \frac{1}{2}$.

V. DISCUSSION

In this section, we discuss the interaction mechanism on the enhancement of T_c and the suppression of ferromagnetic signal under pressure, taking the anisotropic shrinkage under pressure into consideration. At first, for understanding of the pressure effects on T_c and the magnetic dimension of SRO, it is helpful to recall the crystal structure at ambient pressure. As mentioned in Sec. II, the molecules of 2,5-DFPNN form the antisymmetric stacks along the three crystal axes, and it makes us expect the occurrence of ferromagnetic LRO. The ferromagnetic intermolecular interaction along the a axis seems to be the largest of three principal axes. The measurement of the heat capacity under pressure indicates that the dimension of SRO seems to transform from 1D into 2D for $P \geqslant 1.20$ GPa. The structural analyses under pressure show that the shrinkage of the intermolecular distance along the c axis is more pronounced than the other two, especially below 1 GPa. These results suggest that the ferromagnetic network on the ac plane might be strengthened under pressure.

Based on the mean field theory in the quasi-1D magnetic system, the magnetic ordering temperature is known to depend on square root of the product of intrachain and interchain interactions. In the case of the quasi-2D one, the magnetic ordering temperature strongly depends on the two-dimensional intraplane interaction. The enhancement of the magnetic dimension of SRO can bring about the increase of T_c. In the case of 2,5-DFPNN, the enhancement of T_c probably originates from the development of the ferromagnetic interactions on the ac plane. However, as the pressure increases, the ferromagnetic signal becomes smaller as seen in Figs. 5, 6, and 8. This suggests that the ferromagnetic LRO of 2,5-DFPNN is not perfectly stable under pressure and actually another factor such as the pressure effects of the interplane interaction may also has to be considered.

Here, we also discuss the pressure effects on the shortest contact of interatomic distances between neighboring molecules. The shortest contact at ambient pressure is between the N atom of rotamer A and F atom of the adjacent rotamer A along the a axis, and the distance at ambient pressure is 3.27 Å [see Fig. 2(b)]. At around $P = 4.7$ GPa, there is the shrinkage of about 2.4% along the a axis, and the above N-F distance may become 3.19 Å, which is 106% of the sum of these Van der Waals radii (1.55 Å + 1.47 Å = 3.02 Å). The data of the structural analysis suggest the volume of the unit

cell hardly decrease for $P>2$ GPa, around which the magnitude of χ' rapidly decreases as seen in Fig. 8. The effects of the Van der Waals forces should become important under high pressure. There, the molecules cannot shrink uniformly and, for $P>2$ GPa, the intramolecular structure might change distorting the molecular frame slightly. The ac susceptibility at $P=3.8$ GPa shows the antiferromagnetic cusp at around 0.7 K. As the pressure increases, the ferromagnetic interaction along the b axis may approach to the antiferromagnetic one. The promising LRO at $P\simeq3.8$ GPa is an antiferromagnetic stack structure of ferromagnetic planes. The direct proof about this assumption has not been able to be detected in the present experiments, because it is very difficult to decide the position of light atoms such as H, C, N, O, and F by the powdered x-ray diffraction experiment. However, these scenario could explain that the ferromagnetic state of 2,5-DFPNN becomes unstable under high pressure.

A series of experiment of the pressure effects on the β phase of p-NPNN, p-Cl-C$_6$H$_4$-CH=N-TEMPO and 2,5-DFPNN suggest that the ferromagnetic LRO in organic radical crystals becomes unstable by the change of balance between ferromagnetic and antiferromagnetic interactions under pressure. Recently, we have also observed the decreases of both T_c and the magnetic moment for another prototype, dupeyredioxyl $[T_c(P=0)=1.48$ K$].$[20] Thus, the instability of the ferromagnetic LRO under pressure is probably common character of the "soft" organic radical crystals. However, if the intermolecular distance along an direction can be intentionally shrunk, for example, using a technique of uniaxial pressure, the transition temperature of organic radical ferromagnets might be enhanced more effectively. In the case of 2,5-DFPNN, the pressurization only along the c axis probably brings about more effective enhancement of T_c.

VI. CONCLUSION

We studied the pressure effects on a typical organic radical ferromagnet 2,5-difluorophenyl-α-nitronyl nitroxide (2,5-DFPNN) with T_c $(P=0$ GPa$)=0.45$ K in the pressure region up to 10.0 GPa, through the measurements of the ac magnetic susceptibility, heat capacity and powdered x-ray diffraction. The transition temperature T_c is enhanced linearly against pressure as $dT_c/dP=7.9\times10^{-2}$ K/GPa, and reaches 0.57 K at $P\simeq1.5$ GPa. This enhancement of T_c was observed in organic radical ferromagnets. The ferromagnetic state of 2,5-DFPNN is more stable than those of the β phase of p-NPNN and p-Cl-C$_6$H$_4$-CH=N-TEMPO against pressure. We consider that the enhancement of T_c originates mainly from the development of the two-dimensional ferromagnetic interaction on the ac plane. The ferromagnetic signal, however, decreases by the pressure, and almost disappears for $P\gtrsim5.0$ GPa. We assume that the decrease of the ferromagnetic interaction along the residual b axis might bring about the suppression of ferromagnetic signal. From a series of study about the pressure effects on organic radical ferromagnets, however, we summarize as follows: the instability of the ferromagnetic long-range order under pressure is the common characteristic of the "soft" organic radical crystals. In the case of 2,5-DFPNN, if an intermolecular distance only along the c axis can be intentionally shrunk to increase the dimension of the short range order, the T_c may be enhanced more effectively.

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