Pressure effects on intermolecular interactions of the organic ferromagnetic crystalline β-phase p-nitrophenyl nitronyl nitroxide

Kazuyoshi Takeda and Kensuke Konishi*

Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka 812-81, Japan

Masafumi Tamura[†] and Minoru Kinoshita[‡]

The Institute for Solid State Physics, The University of Tokyo, Minato-ku, Tokyo 106, Japan

(Received 25 September 1995)

The pressure effects on intermolecular magnetic interactions in a prototype and genuine organic ferromagnet, β-phase crystal of p-nitrophenyl nitronyl nitroxide, have been studied by the simultaneous measurements of magnetic susceptibility and heat capacity under the hydrostatic pressure of the range 0–7.7 kbar. A reduction of the Curie temperature from 0.61 K at an ambient pressure to 0.35 K at 7.2 kbar has been observed. This makes a significant contrast to the pressure-induced enhancement of the Néel temperature of organic antiferromagnets. The reduction of exchange interactions in the present compound is verified by the estimation of the ground-state energy under the pressures. Another remarkable feature of the results is a lowering of magnetic lattice dimensionality under pressure; the heat capacity curve under the pressure $P = 7.2$ kbar shows the short-range-ordering behavior expected of a low-dimensional Heisenberg ferromagnetic above the Curie temperature. This suggests that the interactions between the adjacent ac planes are relatively weakened to other interactions in the compressed crystal. These observed results are interpreted in terms of the virtual charge transfer mechanism rather than pressure effects on the dipolar interactions.

I. INTRODUCTION

A movement to search out bulk ferromagnetic organic materials consisting exclusively of light elements such as H, C, N, and O is becoming quite active in recent years, in both fields of molecular physics and material science. Following the discovery of the example of organic ferromagnet, the β-phase crystal of p-nitrophenyl nitronyl nitroxide (β-p-NPNN; $C_{13}H_{16}N_3O_4$),[1] several examples have been reported within a couple of years.[2-5] The essential condition for introducing ferromagnetic coupling between radical molecules is becoming clear in some cases, where the intermolecular charge transfer is possible via different molecular orbitals.[6,7] In experimental researches for controlling the charge transfer between molecules, a variety of derivative crystals of several promising radicals have been systematically prepared, by which intermolecular interactions are varied between ferro- and antiferromagnetic ones.[3-5,8] Another method to control the overlapping of molecular orbitals is to apply pressure to a radical crystal, so that its magnetic properties are continuously examined as a function of compressed topological configuration of radical molecules. However, the investigation of pressure effects on magnetic organic radical crystals has rarely been reported. In our previous study on genuine organic antiferromagnets, we found that their Néel temperatures or exchange interactions increase more than 50% under a hydrostatic pressure up to $P \simeq 7$ kbar.[9-11]

In the present work, we will describe the pressure effects on magnetic and thermal properties for the ferromagnetic organic radical crystal, β-p-NPNN. The ferromagnetism of β-p-NPNN at an ambient pressure has been well characterized by the measurements of magnetic susceptibility, magnetization, heat capacity,[1] zero-field muon spin rotation,[12] neutron diffraction,[13] and ferromagnetic resonance.[14] Even so, detailed mechanism of the ferromagnetic couplings remains an open question. Theoretical calculation of the magnetic interactions has suggested the existence of ferromagnetic exchange interactions in this system, giving qualitative agreement with the observed Curie temperature ($T_c = 0.6$ K).[15] From experimental point of view, pressurization of this compound will also give a crucial information about a question whether the ferromagnetism of β-p-NPNN originates in dipolar couplings[16] or in exchange interactions.

II. EXPERIMENT

The molecular structure of β-p-NPNN is shown in Fig. 1(a), together with other two molecules which bring about ferromagnetic interactions in solid state. The nitroxide radical crystal 1(b) exhibits the highest Curie temperature ($T_c = 1.48$ K) of the genuine organic radical ferromagnets ever reported[2] and the verdazyl radical 1(c) shows a characteristic feature of isotropic Heisenberg ferromagnet in one dimension at temperatures $T > T_c$.[17]

The crystals of β-p-NPNN were prepared by the method described previously.[1] The crystal belongs to the space group

(a) $T_C = 0.61$ K   (b) $T_C = 1.48$ K   (c) $T_C = 0.67$ K
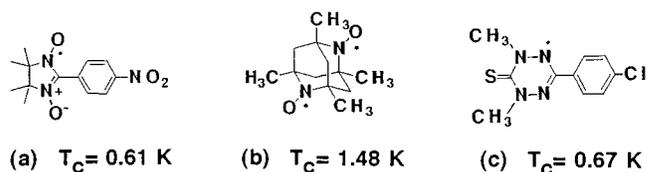
FIG. 1. Molecular structures of some genuine organic ferromagnetic radical crystals.

(a)

(b)   (c)
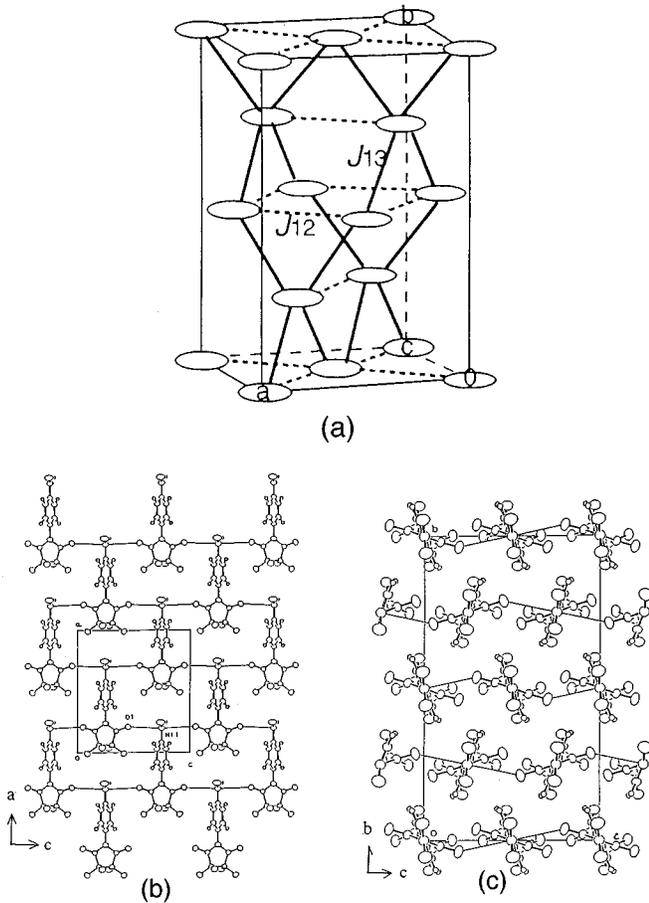
FIG. 2. (a) Schematic drawing of the crystal structure of β-p-NPNN. Each ellipsoid represents the radical molecule. The possible exchange paths are denoted with J_{12} and J_{13}. Molecular arrangement on the ac plane (b) and the bc plane (c) (Ref. 18).

of $F2dd$, and we use here the axis definition of $a = 12.374$, $b = 19.350$, and $c = 10.960$ A.[18] The crystal structure is schematically shown in Fig. 2.

The ac susceptibility and the heat capacity were measured simultaneously under the hydrostatic pressure by the use of a cryostat with the CuBe pressure clamp cell (Fig. 3). The temperature lower than ^{3}He temperatures was achieved by the adiabatic demagnetization of the sample itself. The polycrystalline sample of β-p-NPNN (0.389 g) and the pressure transmission oil (0.344 g of Apiezon-J oil) were placed in the pressure cell together with a small tip of Sn metal. The pressure was calibrated against the pressure dependence of the superconducting transition temperature of Sn[19] An example of this calibration is given in Fig. 4, where the transition temperature is detected by the temperature dependence of the susceptibility of Sn. We can determine the value of the hydrostatic pressure P within the experimental error of 0.1 kbar. The susceptibility was measured at 200 Hz and peak-to-peak field of about 0.5 Oe. The measurements were carried out at the pressure $p = 0.001 (=P_o)$, 2.5, 5.4, 7.2, and 7.7 kbar. The value of the susceptibility (χ) and the heat capacity (C_p) were quite reproducible for pressure cycles of $P \leftrightarrow P_o$.

(1)   (2)
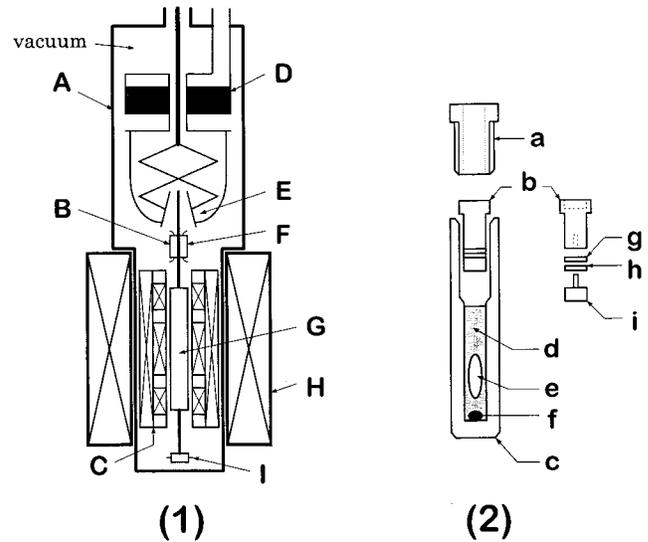
FIG. 3. (1) Schematic structure of the cryostat for the simultaneous measurement of magnetic susceptibility and heat capacity under the hydrostatic pressure. A, adiabatic tube; B, thermometer 1; C, coil system for ac susceptibility; D, liquid ^{3}He pot; E, mechanical heat switch; F, thermometer 2; G, pressure clamp cell; H, superconducting magnet; I, heater and subheater. (2) Pressure clamp cell. a, locking nut; b, piston; c, cylinder; d, pressure transmission oil; e, sample; f, Sn; g, Cu seal; h, Teflon seal; i mushroom plug.

III. EXPERIMENTAL RESULTS

Figure 5 shows the results of the simultaneous measurements of magnetic susceptibility and heat capacity of β-p-NPNN at an ambient pressure (P_o). The signal ratio of heat capacity of the sample itself to the total heat capacity, including the pressure cell, Apiezon-J oil and so on, is about 40% around 1 K, and it increases acceleratedly at lower temperatures. The lattice heat capacity is negligibly small in this temperature region. The sharp heat capacity peak of λ type appears at 0.61 ± 0.02 K and the susceptibility shows an abrupt increase around this temperature. The overall behavior of C_p and χ is essentially in agreement with that reported previously.[1] This proves that the crystals are stable enough
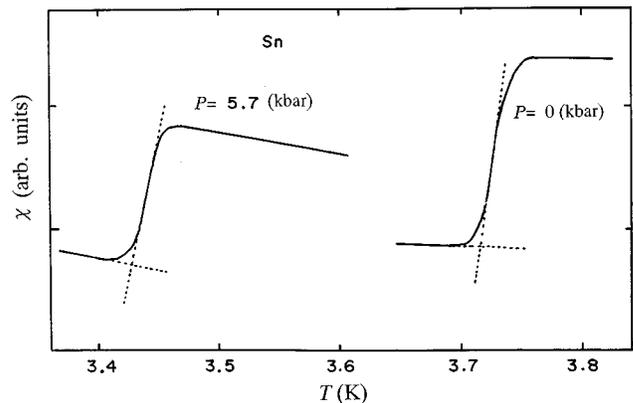
FIG. 4. An example of the pressure calibration from the superconducting transition temperature detected by the susceptibility measurement of Sn.
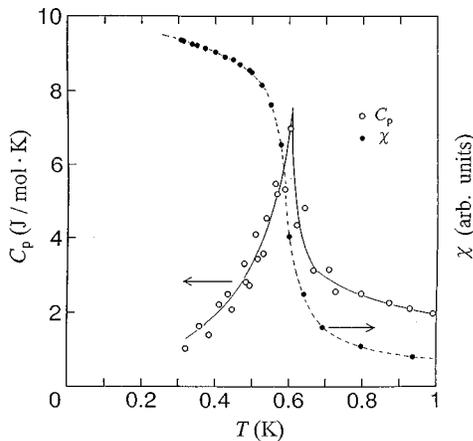
FIG. 5. Results of the simultaneous measurements of magnetic susceptibility and heat capacity of β-p-NPNN at an ambient pressure (P_o).

even in the pressure transmission oil. In this paper, the Curie temperature $T_c(P)$ is defined as the temperature where the heat capacity gives the sharp peak of λ type.

As the pressure increases, these anomalies in C_p and χ clearly shift to the lower temperature side as seen in Fig. 6. In addition, the λ-type heat capacity peak becomes lower
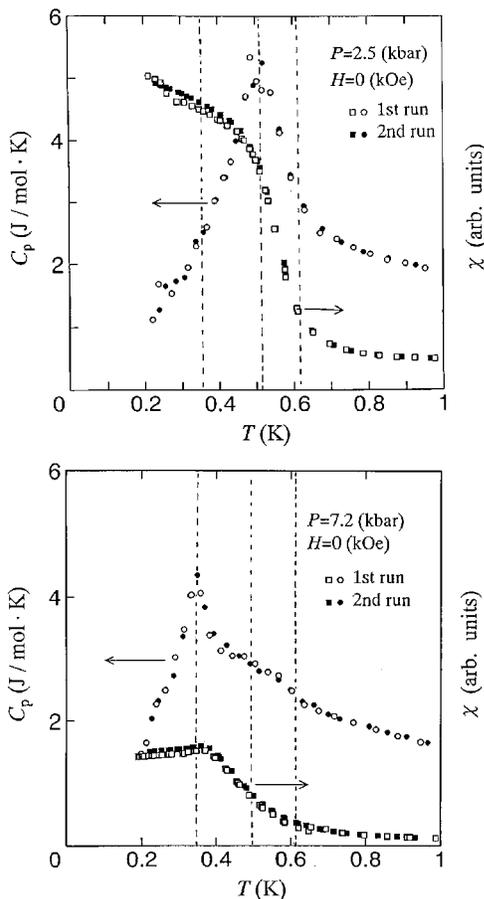
FIG. 6. Results of the simultaneous measurements of magnetic susceptibility and heat capacity of β-p-NPNN at $P=2.5$ and 7.2 kbar. The dotted line indicates the Curie temperatures for $P=P_o$, 2.5, and 7.2 kbar.
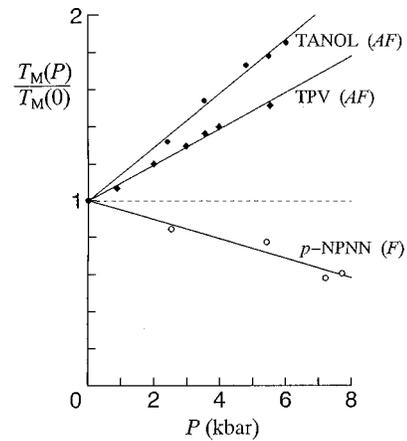
FIG. 7. Pressure dependence of the magnetic transition temperature $T_M(P)$ of the genuine organic ferromagnet, β-p-NPNN, and antiferromagnets, TANOL and TPV.

and the value of C_p becomes greater in the temperature range higher than $T_c(P)$. At $P=7.2$ kbar, a round shoulder appears clearly in the C_p curve for $T>T_c(P)$.

As in Fig. 6, the susceptibility for $P=7.2$ kbar exhibits a plateau below $T_c(P)$. Even under lower pressure this can be seen as a rather gradual change in χ against temperature, as in the results for $P=P_o$ and 2.5 kbar. Such a kind of plateau has also been observed in another organic ferromagnet with $T_c(P_o)=1.48$ K.[2] These properties of χ are related with the demagnetization effect and/or relaxation effect when measured by the ac method.

The pressure dependence of the Curie temperature is shown in Fig. 7, which can be expressed as

$$T_c(P)=T_c(P_o)(1-aP),\qquad(1)$$

with $a=0.05\pm0.01$ kbar^{-1}. This makes a noticeable contrast to the pressure-induced enhancement of the Néel temperature of the genuine organic antiferromagnets, 2, 2, 6, 6-tetramethyl-4-piperidinol-oxyl (TANOL) and 1, 3, 5-triphenylverdazyl (TPV) studied by some of the present authors.[9–11]

Prior to the discussion of the present results, it is useful to estimate here the temperature dependence of magnetic heat capacity $C_m(T)$ and that of entropy $S(T)$ under the pressure which are related by

$$S(T)=\int_0^T\{C_m(T)/T\}dT.\qquad(2)$$

The value of C_m in the lower temperature region $T\leq0.2$–0.3 K is extrapolated on the spin wave theory as

$$C_m(T)=AT^n+BT^{n+1}.\qquad(3)$$

In principle, n is $\frac{3}{2}$ for three-dimensional Heisenberg ferromagnet and $\frac{2}{2}$ for two dimensions.[20] Above 2 K, or $T>3T_c(P)$, $C_m(T)$ may be approximated, as in ordinary paramagnetic state, as $C_m=CT^{-2}$. Then the total heat capacity can be expressed as $CT^{-2}+DT^3$, the second term of which is the lattice contribution. Although the values of above parameters cannot be determined uniquely, we can smoothly extrapolate the observed C_m toward $T=0$ K and
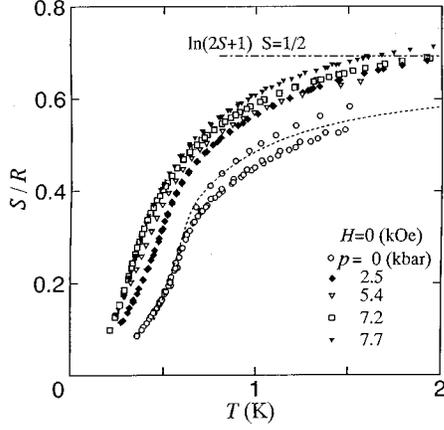
FIG. 8. Temperature dependence of the magnetic entropy of β-p-NPNN under the hydrostatic pressure. The scattering of the data for $P=0$ kbar mainly comes from the experimental error between first and second runs of measurements. The dotted curve is drawn in the reference of the previous report for $P=0$ kbar (Ref. 1).

$T \rightarrow \infty$ using these relations: anyhow the change of $C_m(T)$ or $S(T)$ is dominant in the temperature range where the experimental data are taken. Figure 8 shows the temperature dependence of the magnetic entropy. The experimental value of $S(\infty)$ at each pressure shows a little excess to the theoretical value of $S(\infty)=Nk_B\ln(2S+1)$ with $S=\frac{1}{2}$. The discrepancy may be due to the experimental error at higher temperatures where the signal ratio of the heat capacity becomes quite smaller in the present measurements with a small amount of the sample crystal.

The effects of applied magnetic field on χ and C_p are also examined at each pressure. Representative results are shown for χ at $P=7.7$ kbar in Fig. 9, and for C_p at $P=7.2$ kbar in Fig. 10. The anomalies of χ and C_p are easily affected by weak field even up to 1 kOe under pressure, just as those examined at $P=P_o$.[1] This implies that the ferromagnetism of β-p-NPNN does not change qualitatively under the present pressure range.

IV. DISCUSSION

The important feature of the experimental results of β-p-NPNN is twofold. One is the reduction of the Curie
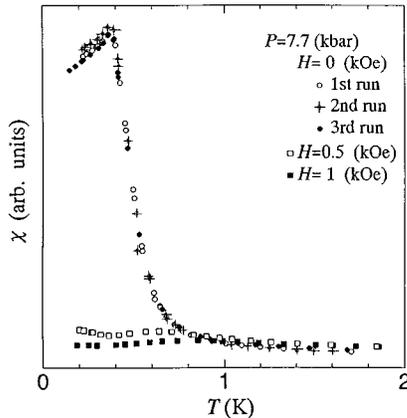
FIG. 9. Dependence of the magnetic susceptibility of β-p-NPNN on the applied field under the pressure $P=7.7$ kbar.
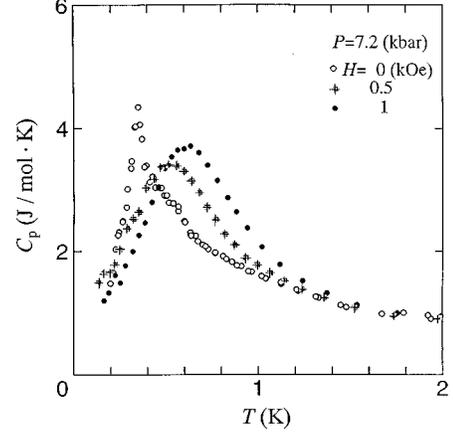
FIG. 10. Dependence of the heat capacity of β-p-NPNN on the applied field under the pressure of $P=7.2$ kbar.

temperature with increasing pressure, and the other is the lowering of the magnetic lattice dimensionality accompanying the short-range ordering appeared in the round shoulder of C_p in Fig. 6. Here we discuss these results taking the variation of exchange interactions in β-p-NPNN under pressure into consideration, after making some remarks on the pressure effects of dipole-dipole interactions.

A. Dipolar interactions in β-p-NPNN

Recently it has been suggested that the Curie temperature of β-p-NPNN is governed mainly by the dipole-dipole couplings.[16] If this is the case, the Curie temperature would increase with compression. The present results, decreasing $T_c(P)$ with pressurization, are in the opposite direction. In order to see the role of the dipolar couplings, we calculated the dipolar interactions, D, over a sphere of radius of 250 Å, assuming the ferromagnetic spin alignments along the a, b, and c axes, which are the principal directions in this case. In the calculation the spin density data obtained by neutron diffraction experiments are used with slight modification for normalization; $\rho_O=0.285$, $\rho_N=0.260$, and $\rho_C=-0.09$.[21] Our calculation yields the value of $D_a/k_B=-0.016$, $D_b/k_B=-0.029$, and $D_c/k_B=0.045$ K.[22] These values are too small by one order of magnitude to explain the observed $T_c(P_o)=0.6$ K. Therefore, we are of the opinion that the Curie temperature of β-p-NPNN is essentially determined by the exchange interactions. The results of the calculation also show that the ferromagnetic spin alignment along the b axis is most stable. This is consistent with the observations in ZF-μSR,[12] neutron diffraction,[13] and ferromagnetic resonance.[14] The dipole interaction seems to play a role in determining the direction of the magnetic easy axis, but only a minor role in the determination of the Curie temperature.

B. Exchange interactions in β-p-NPNN and their pressure dependence

We hereafter confine our attention to the intermolecular exchange interactions defined by the spin Hamiltonian

$$H=\sum H_{ij}=-2\sum J_{ij}S_iS_j, \qquad (4)$$

where S_i and S_j denote the $S = \frac{1}{2}$ Heisenberg spin operator for the molecules i and j, respectively, and the summation is taken over all adjacent molecular pairs in the crystal as illustrated in Fig. 2. In the above equation, only J_{ij} depends on pressure. It is suggested that there are two dominant exchange paths in this β-phase crystal. One is the interaction which links the molecules on the ac plane so as to afford a two-dimensional structure and the other is the interaction which links the molecules on the ac planes so as to build a diamondlike three-dimensional network (see Fig. 2). The molecular orbital calculation, based on the room temperature structure at $P = P_o$, gives the value of $2J_{12}/k_B = 0.48$ K for the intraplane interaction and $2J_{13}/k_B = 0.22$ K for the interplane interaction.[14] Interactions other than J_{12} and J_{13} are estimated to be much smaller, and these values result in the mean-field Curie temperature of 0.6 K in good agreement with the experimental result. On the other hand, the spontaneous magnetization of β-p-NPNN is shown to grow as the temperature decreases below $T_c(P_o)$, nearly in accordance with the isotropic three-dimensional Heisenberg model.[12]

The critical magnetic entropy of β-p-NPNN estimated here is $S(T_c) = 0.42S(\infty)$ as seen in Fig. 8, which is smaller than the theoretical value $0.62S(\infty)$ for the isotropic $S = \frac{1}{2}$ Heisenberg ferromagnet with fcc structure (the coordination number $z = 8$).[23] It is recalled here that $z = 8$ is also expected in β-p-NPNN (Fig. 2). The critical entropy becomes smaller with decreasing lattice dimensionality both in Ising and Heisenberg system.

Here we discuss the reduction of $T_c(P)$ and the lowering of the magnetic lattice dimensionality under pressure. The transition temperature of magnetic compounds with localized spin systems ordinarily increases with increasing pressure when their magnetic symmetry is unchanged. The reduction of $T_c(P)$ is rare and implies that the mechanism of charge transfer or symmetry of molecular orbitals is varied by the pressurization. First we consider pressure dependence of exchange interactions. We may estimate the effective value of the exchange interactions $\bar{z}\bar{J}$ from the ground state energy E in an isotropic Heisenberg magnetic system with the exchange interaction $\bar{J}$ by

$$E = -N\bar{z}\bar{J}S^2\{1 - r/zS\}. \qquad (5)$$

The value of r in Eq. (5) originates from the quantum effects which dominate in antiferromagnetic systems, and ranges in $0 \leq r \leq 1$.[24] In ferromagnetic systems as in the present crystal, we may set $r = 0$. The value of E is also related with the magnetic heat capacity as

$$E = -\int_0^\infty C_m dT. \qquad (6)$$

Following the same extrapolation process as employed in the estimation of the magnetic entropy in the previous section, we can get E experimentally at each pressure P by the integration of Eq. (6). The value of E for $P = P_o$ is 5.9 (J/mol), which give $\bar{z}\bar{J}/k_B = 2.9$ K, comparable order of magnitude with $(4J_{12} + 4J_{13})/k_B$ mentioned above. The discrepancy may be due the anisotropic structure of β-p-NPNN crystal. The pressure dependence of E, or $E(P)$, is roughly ex-
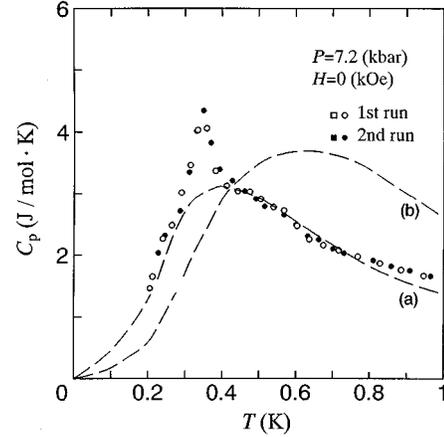
FIG. 11. Magnetic heat capacity of β-p-NPNN under the pressure $P = 7.2$ kbar. The curves correspond to the theoretical estimates of the heat capacity for the two-dimensional Heisenberg (a) ferromagnet and (b) antiferromagnet ($S = \frac{1}{2}$; $|J|/k_B = 0.4$ K) (Ref. 25).

pressed as $E(P) = E(P_o)(1 - 0.015P)$ in the present pressure range, suggesting effective reduction of magnetic interactions.

It is recalled here that the magnetic heat capacity at $P = 7.2$ kbar shows the characteristic shoulder above $T_c(P)$, which is compared with the theoretical results for a two-dimensional Heisenberg ferromagnet with $S = \frac{1}{2}$, rather than those for the antiferromagnet (Fig. 11).[25] This means that the lowering of the lattice dimension under the pressure. We expect from the crystal structure that only J_{12} is responsible to the two-dimensional short-range ordering under pressure. The transition temperature of two-dimensional layers weakly coupled through J_{13} is given, in the mean field approximation, by

$$T_c(P) \propto \{\xi_{2D}(J_{12})\}^2 J_{13}, \qquad (7)$$

where $\xi_{2D}(J_{12})$ is the spin correlation length within the isolated layer at $T = T_c(P)$.[26] The reduction of $T_c(P)$ indicates that compression results in the decrease of J_{13} and/or $\xi_{2D}(J_{12})$. Furthermore, the appearance of the short-range-ordering effect above $T_c(P)$ means that J_{13} changes more sensitively against pressure in β-p-NPNN.

C. Charge transfer under pressure

Now we consider the dependence of the exchange interaction on pressure based on the charge transfer mechanism reported in the study of galvinoxyl.[27] We write the exchange interaction in the form

$$J_{ij} = J_{ij}^K + J_{ij}^P, \qquad (8)$$

where J_{ij}^K and J_{ij}^P are the effective exchange coupling constants relevant to the kinetic and the potential exchange integrals, respectively. Both of them depend on the overlap of the molecular orbitals between the adjacent molecules in the real space. The kinetic term can be expressed as

$$J_{ij}^K = -t_{S-S}^2/U + t_{S-F}^2 J^{in}/U^2$$

$$+ \text{(terms related to other transfer paths)}, \qquad (9)$$

where the transfer integral t_{S-S} stands for the charge transfer between the SOMO's (singly occupied molecular orbitals) of molecules i and j, t_{S-F} does for that between SOMO and a fully occupied molecular orbital [e.g., NHOMO (next highest occupied molecular orbital)], U is the on-site Coulomb repulsion in SOMO, and J^{in} is the intramolecular exchange integrals between SOMO and the fully occupied molecular orbitals. The second term is an analog of the third-order effect in Anderson's theory,[28] the first term being the ordinary second-order perturbation. The essential factors for ferromagnetic coupling estimated from the study of the galvinoxyl are the large t_{S-F} and J^{in} and small t_{S-S}. In other words, the positive sign of the net exchange interactions, J_{ij}, results from the condition that the second term in Eq. (9) exceeds the other contributions such as the first term in Eq. (9) and J_{ij}^{P}. These conditions are well confirmed in galvinoxyl, and the origin of the feromagnetic interactions has been attributed to the contribution of the second term in Eq. (9).

The above conditions are also basically retained in β-p-NPNN and some other ferromagnetic radicals. In the present case, J_{ij}^{P} and t_{S-S} should be very small, because SOMO's are well separated from each other in the crystal. Therefore, J_{ij} is essentially determined by the second term in Eq. (9).

In the previous studies of organic antiferromagnetics,[9–11] on the other hand, the large enhancement of the Néel temperature under pressure has been attributed to the increase of t_{S-S} due to a small change transfer in the intermolecular distance or librational distortion under high pressure. The results for TANOL and TPV in Fig. 7 clearly exemplify the sensitiveness of the antiferromagnetic interactions to pressure. Another example of the strong dependence of the exchange interactions on structure is reported by Awaga *et al.*,[29] where the pressure is continuously controlled by a mixed crystal technique.[29] Thus the antiferromagnetic interaction, the first term in Eq. (9), seems to be readily affected by a small change in relative location of the molecules in the lattice.

In view of these experimental facts, the pressure effect on β-p-NPNN can be interpreted as follows. We first suppose that t_{S-S} is much more enhanced under pressure than t_{S-F}. With pressure insensitive U and J^{in}, the antiferromagnetic contribution increase more rapidly than the ferromagnetic one, though both increase with pressurization. Thus the balance shifts to the reudction to the net ferromagnetic interactions. This seems to be consistent with the fact that the pressure coefficient has similar values for the ferromagnetic and antiferromagnets as in Fig. 7. Next we infer that the fraction of the antiferromagnetic contribution in J_{12} is smaller than that in J_{13} at $P=P_o$. This means that the molecular pair, 1 and 2, has smaller value of t_{S-S}^{2}/t_{S-F}^{2} than

that of the pair, 1 and 3. This would explain the more sensitive reduction of J_{13} mentioned above, resulting in the reduction of the Curie temperature.

In Ref. 21, the lattice constants a, b, and c at room temperatures are reported to be shrunk by 1.4%, 1.7%, and 2.1% at 6 K, respectively, with the same crystal symmetry. By the compression of β-p-NPNN up to 7.7 kbar, they are expected to be shrunk by, at most, 2% from the reference of the compressibility of other organic compounds. The pressure-induced phase transition, as observed at low temperatures in the case of TMMC $[(CH_3)_4NMnCl_3]$,[30] is not the present case with a monotonic decrease in $T_c(P)$ as in Eq. (1). It should be remarked here for the fact that $T_c(P)$ of β-p-NPNN shows the reduction by about 40% against such a minute change of lattice deformation in this experiment.

The dependence of J_{ij} on the structural parameters such as distance or angle among radical molecules is theoretically estimated by the Hartree-Fock-based *ab initio* method.[31] In addition to these studies about β-p-NPNN, experimental information of the spin density or the spin delocalization in this crystal[21] is very important. In order to establish a more sophisticated physical picture, the structure and compressibility data under pressure at low temperatures are required. From the theoretical side, analyses of the contribution of the overlaps between SOMO's and between SOMO and the relevant occupied molecular orbital to the exchange interactions are also urged.

V. CONCLUSION

A drastic reduction of the Curie temperature of a genuine organic ferromagnet under the hydrostatic pressure has been observed with the β-phase p-NPNN crystal. This means that the ferromagnetic interactions mainly originate in the exchange interactions rather than the dipole couplings. The reduction of the effective exchange interaction is also verified by the consideration of the ground-state energy of this compound under pressures. The low dimensional magnetic behavior appearing under high pressure suggests that the ferromagnetism of this radical crystal is due to the cooperation of intra- and interlayer exchange interactions, the latter being more sensitively reduced by pressure. The strong pressure dependence of the critical temperature is explained by the charge transfer mechanism in which the net ferromagnetic coupling is determined by competition between ferromagnetic and antiferromagnetic interactions and that the latter is readily affected by pressurization.

*Present address: Department of Physics, Faculty of Science, Ehime University, Matsuyama 790, Japan.

†Present address: Department of Physics, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan.

‡Present address: Department of Materials Science, Faculty of Science and Engineering, Science University of Tokyo in Yamagu-

chi, Onoda, Yamaguchi 756, Japan.

[1] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, and M. Kinoshita, Chem. Phys. Lett. **186**, 401 (1991); Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, Phys. Rev. B **46**, 8906 (1992); M. Kinoshita, Mol. Cryst. Liq. Cryst.

232, 1 (1993); M. Kinoshita, Jpn. J. Appl. Phys. **33**, 5718 (1994) and references therein.

[2] R. Chiarelli, M. A. Novak, A. Rassat, and J. L. Tholence, Nature **363**, 147 (1993).

[3] T. Sugawara, M. Matushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, J. Chem. Soc. Chem. Commun., 1723 (1994).

[4] T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 29 (1994); J. Cirujeda, M. Mas, E. Molins, F. L. de Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, and J. Veciana, J. Chem. Soc. Chem. Commun., 709 (1995).

[5] K. Mukai, K. Nedachi, J. B.- Jamali, and N. Achiwa, Chem. Phys. Lett. **214**, 559 (1993); K. Mukai, K. Nedachi, K. Konishi, and K. Takeda, J. Magn. Magn. Mater. **140-144**, 1449 (1995); T. Ishida, H. Tsuboi, T. Nogami, M. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 919 (1994); T. Nogami, T. Ishida, H. Tsuboi, H. Yoshikawa, H. Yamamoto, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *ibid.*, 635 (1995).

[6] K. Awaga, T. Sugano, and M. Kinoshita, Chem. Phys. Lett. **141**, 540 (1987).

[7] K. Yamaguchi, M. Okuda, and M. Nakano, Chem. Phys. Lett. **191**, 237 (1992).

[8] See, for example, M. Tamura, D. Shiomi, Y. Hosokoshi, N. Iwamura, K. Nozawa, M. Kinoshita, H. Sawa, and R. Kato, Mol. Cryst. Liq. Cryst. **232**, 45 (1993).

[9] K. Takeda, N. Uryu, M. Inoue, and J. Yamauchi, J. Phys. Soc. Jpn. **56**, 736 (1987).

[10] J. Yamauchi, K. Takeda, and K. Konishi, Mol. Cryst. Liq. Cryst. **233**, 457 (1993).

[11] J. Yamauchi, K. Takeda, and M. Inoue, Chem. Lett., 1551 (1990).

[12] L. P. Le, A. Keren, W. D. Wu, Y. J. Uemura, M. Tamura, M. Ishikawa, and M. Kinoshita, Chem. Phys. Lett. **206**, 405 (1993); Y. J. Uemura, L. P. Le, and G. M. Luke, Synth. Met. **56**, 2845 (1993).

[13] A. Zheludev, E. Ressouche, J. Schweizer, P. Turek, M. Wan, and H. Wang, Solid State Commun. **90**, 233 (1993).

[14] K. Oshima, H. Kawanoue, Y. Haibara, H. Yamazaki, K. Awaga, M. Tamura, and M. Kinoshita, Synth. Met. **71**, 1821 (1995).

[15] M. Okumura, K. Yamaguchi, M. Nakano, and W. Mori, Chem. Phys. Lett. **207**, 1 (1993).

[16] J. S. Miller and A. J. Epstein, Ang. Chem. Int. Ed. Engl. **33**, 385 (1994).

[17] K. Takeda, K. Konishi, K. Nedachi, and K. Mukai, Phys. Rev. Lett. **74**, 1673 (1995); K. Takeda, K. Konishi, K. Nedachi, and K. Mukai, J. Magn. Magn. Mater. **140-144**, 1635 (1995).

[18] K. Awaga, T. Inabe, U. Nagashima, and Y. Maruyama, J. Chem. Soc. Chem. Commun., 1617 (1989); 520 (1990). Care should be given to the axis systems of the β-phase crystal in different references.

[19] K. Takeda, M. Wada, M. Inoue, and T. Haseda, Jpn. J. Appl. Phys. **26**, 947 (1987).

[20] K. Takeda, K. Amaya, and Y. Murakami, J. Phys. Soc. Jpn. **54**, 3091 (1985).

[21] A. Zheludev, M. Bonnet, E. Ressouche, J. Schweizer, M. Wan, and H. Wang, J. Magn. Magn. Mater. **135**, 147 (1994).

[22] M. Tamura and K. Kinoshita (unpublished).

[23] C. Domb and A. R. Miedema, *Progress in Low Temperature Physics* (North-Holland, Amsterdam, 1964), Vol. 4, Chap. 6.

[24] T. Nagamiya, K. Yoshida, and R. Kubo, Adv. Phys. **4**, 1 (1955).

[25] P. Bloembergen, Physica **85B**, 51 (1977).

[26] K. Takeda, H. Deguchi, T. Hoshiko, and K. Yamagata, J. Phys. Soc. Jpn. **58**, 3489 (1989).

[27] K. Awaga, T. Sugano, and M. Kinoshita, Chem. Phys. Lett. **141**, 540 (1987).

[28] P. W. Anderson, Phys. Rev. **115**, 2 (1959).

[29] K. A. Awaga, T. Okuno, A. Yamaguchi, M. Hasegawa, T. Inabe, Y. Maruyama, and W. Wada, Phys. Rev. B **49**, 3975 (1994).

[30] K. Takeda and T. Suzuki, Jpn. J. Appl. Phys. (Suppl.) **26**, 853 (1987).

[31] K. Yamaguchi, M. Okumura, J. Maki, T. Noro, H. Namimoto, M. Nakano, and T. Fueno, Chem. Phys. Lett. **190**, 353 (1992); K. Yamaguchi, M. Okumura, and M. Nakano, *ibid.* **191**, 237 (1992).