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Simultaneous observation of heat capacity and magnetic susceptibility of a genuine organic ferromagnet under high pressures [☆]

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Abstract

The magnetic interactions in β-phase p-NPNN (*p*-nitrophenyl nitronyl nitroxide), a prototype genuine organic ferromagnet, have been studied by simultaneous measurements of magnetic heat capacity and susceptibility under hydrostatic pressures. A drastic reduction of the Curie temperature from 0.6 K at 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. A lowering of the magnetic lattice dimensionality is also observed at temperatures slightly above the Curie temperature under pressure. These observations are interpreted in terms of the virtual charge transfer mechanism.

Keywords: Ferromagnet; Heat capacity; Magnetism

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1. Introduction

The realization of bulk ferromagnetism in a genuine organic substance has long been one of the major subjects in the field of molecular magnetism. The recent findings of organic ferromagnets consisting exclusively of light elements such as H, C, N, and O have attracted much attention [1–5]. So far about ten radical crystals have been found to be ferromagnetic. The essential condition for introducing ferromagnetic coupling between radical molecules is clear in some cases, where the intermolecular

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[☆] Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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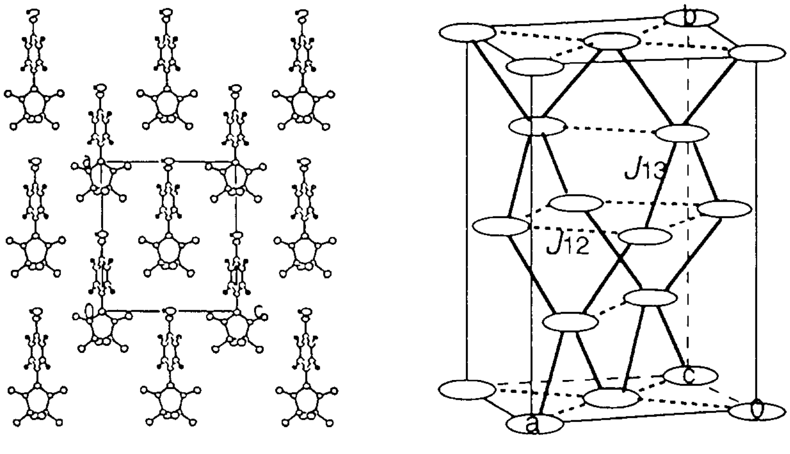
charge transfer between different orbitals, such as SOMO–NHOMO, plays an important role [6,7]; SOMO, singly occupied molecular orbital; NHOMO, next highest occupied molecular orbital. For experimental control of the charge transfer between these molecular orbitals, various derivatives of radicals have been prepared systematically, in which intermolecular exchange interactions are varied between -10 and 10 K in the temperature scale [8]. Another method to control the overlapping of molecular orbitals is to apply pressure to a radical crystal, so that we can check its magnetic parameters continuously as a function of molecular packing. However, the investigation of pressure effects on magnetic organic radical crystals has rarely been reported. In our previous studies on genuine organic antiferromagnets, we found that their Néel temperatures or exchange interactions increase more than 50% under a hydrostatic pressure p of 7 kbar [9–11].

In the present work, we will describe the pressure effect on the magnetic and thermal properties of β-phase p-nitrophenyl nitronyl nitroxide (p-NPNN, $C_{13}H_{16}N_3O_4$), a prototype organic ferromagnet. There are two important features of the results: one is the pressure-induced reduction of the critical temperature and the other is the lowering of the magnetic lattice dimensionality. We will discuss these results in terms of the charge transfer exchange mechanism.

2. Experimental

Crystals of β-phase p-NPNN were prepared by the method described previously [1]. The crystal belongs to the space group F2dd, taking $a = 12.374$, $b = 19.350$ and $c = 10.960$ Å [12]. The crystal structure is shown schematically in Fig. 1.



(a) (b)

Fig. 1. (a) The molecular arrangement on the ac-plane [12]. (b) Schematic drawing of the crystal structure of the β-phase p-NPNN. Each ellipsoid represents a radical molecule.

For the present study under hydrostatic pressure, we employed simultaneous measurements of a.c. magnetic susceptibility (200 Hz and 0.5 Oe peak-to-peak) and heat capacity using a CuBe pressure clamp cell [13]. The pressure calibration at low temperatures was performed by the pressure dependence of the superconducting transition temperature of metallic Sn [14]. In the CuBe cell, 0.389 g of polycrystalline β-phase p-NPNN and 0.334 g of the pressure transmission oil (Apieson-J oil) were set together with a small tip of Sn metal. The measurements were carried out at $p = 0.001\,(p_0)$, and 2.5, 5.4, 7.2 and 7.7 kbar. The susceptibility χ and heat capacity C_p were found to be reproducible for the pressure cycle $p_0 \leftrightarrow p$. In this paper, the Curie temperature $T_c(p)$ is defined as the temperature where the heat capacity gives a sharp peak of λ-type.

3. Results

The results at ambient pressure p_0 are shown in Fig. 2. The overall behavior of χ and C_p is essentially in agreement with that reported previously [1]. This proves that the crystals are stable enough even in the pressure transmission oil. A sharp heat capacity peak of λ-type appears at $T_c(p_0) = 0.61 \pm 0.02$ K, and exhibits an abrupt increase

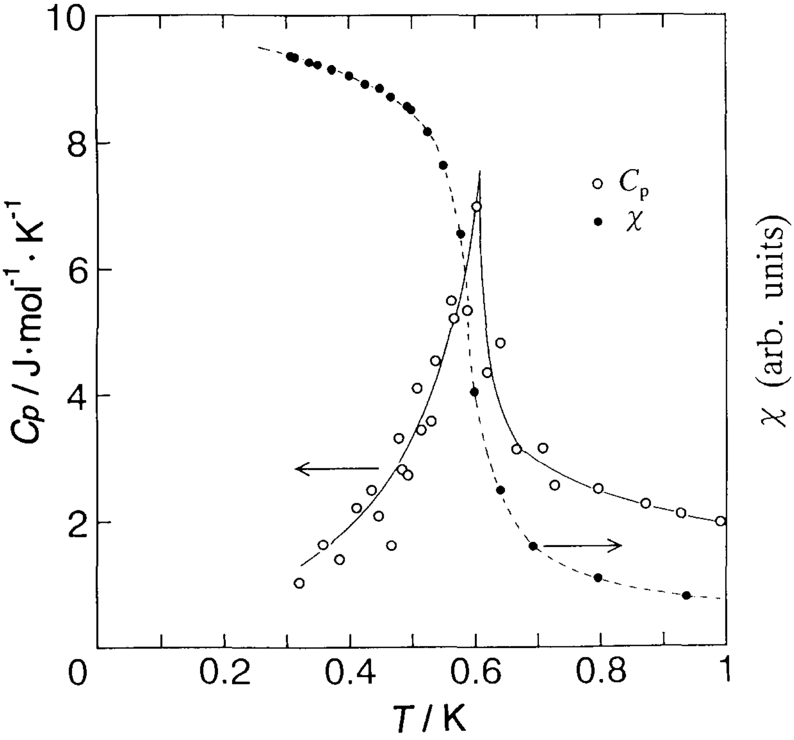


Fig. 2. The experimental results of the simultaneous measurements of heat capacity and magnetic susceptibility of the β-phase p-NPNN at $p = p_0 = 0.001$ kbar.

around $T_c(p_0)$, corresponding to the three-dimensional ferromagnetic ordering. The results of χ and C_p under pressure are shown in Figs. 3 and 4, respectively [14]. As the pressure increases, the anomalies in C_p and χ clearly shift to the lower temperature side. In Fig. 4, a round shoulder appears in the C_p curve at $T > T_c(p)$, which is due to the short-range ordering effect of the spin system with effectively lowered lattice dimension with pressure. The total magnetic entropy estimated from C_p is nearly equal to $R\ln(2S+1)$, independent of p, as shown in Fig. 5, where $S = 1/2$. This indicates that an $S = 1/2$ spin per molecule holds even under the pressures examined. The susceptibility

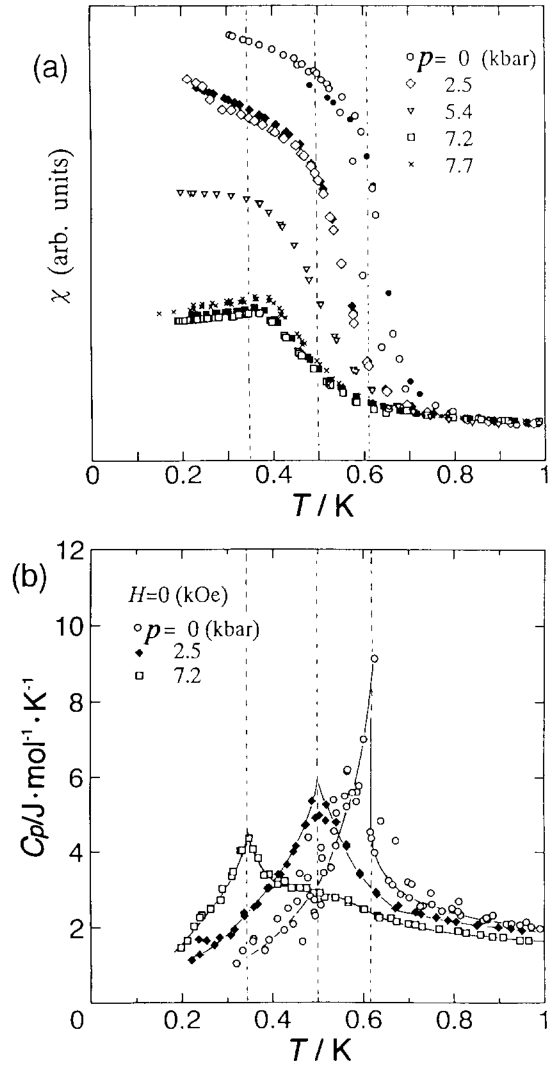


Fig. 3. Experimental results of β-phase p-NPNN under pressure: (a) magnetic susceptibility; (b) heat capacity [14].

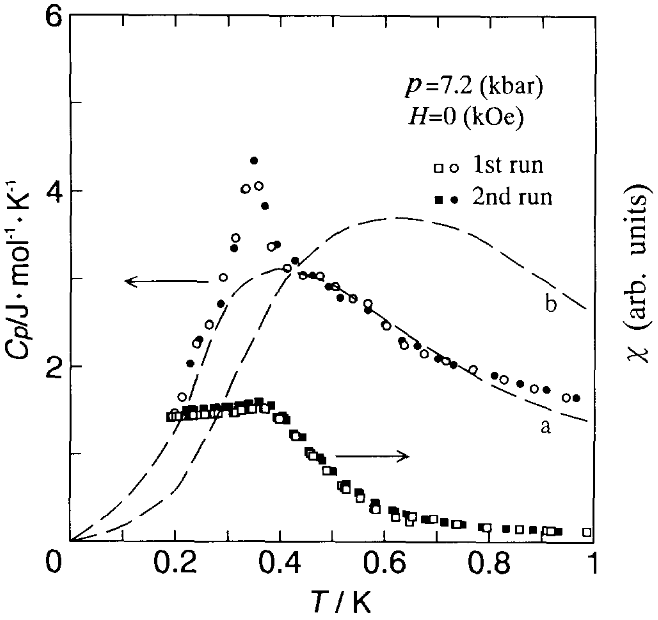


Fig. 4. Experimental results of the simultaneous measurements of heat capacity and magnetic susceptibility of β-phase p-NPNN at $p = 7.2$ kbar. The curves correspond to the theoretical estimates for the two-dimensional Heisenberg: curve a, ferromagnet; and curve b, antiferromagnet ($J/k_B = 0.4$ K) [18].

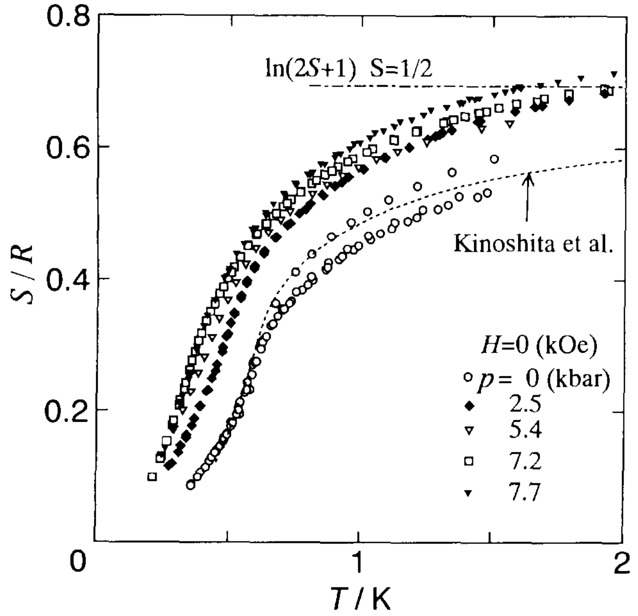


Fig. 5. Temperature dependence of the magnetic entropy of β-phase p-NPNN under pressure [14].

exhibits a plateau below $T_c(p)$ as in Figs. 3 and 4. Such a plateau has also been observed in another organic ferromagnet with $T_c(p_0) = 1.48$ K [2]. These properties of χ are related with the demagnetization effect and/or the relaxation effect when measured by the a.c. method.

The pressure dependence of the Curie temperature is shown in Fig. 6, and follows the equation

$$T_c(p) = T_c(p_0)(1 - ap) \tag{1}$$

where $a = 0.05 \pm 0.01\ \text{kbar}^{-1}$ for the β-phase p-NPNN. For comparison, the pressure dependences of the Néel temperature for the organic antiferromagnets studied previously [9] are also shown in Fig. 6.

The effects of the applied magnetic field on χ and C_p were also examined at each pressure. Representative results for χ at $p = 7.7$ kbar are shown in Fig. 7. The anomalies in χ and C_p are easily affected by a weak field even under pressure, just as those observed at $p = p_0$ [1]. This implies that the ferromagnetism of this crystal does not change qualitatively under the present pressure range.

4. Discussion

Here we will discuss the anomalous reduction of the Curie temperature and the lowering of the magnetic lattice dimensionality of the β-phase p-NPNN under pressure, considering intermolecular interactions.

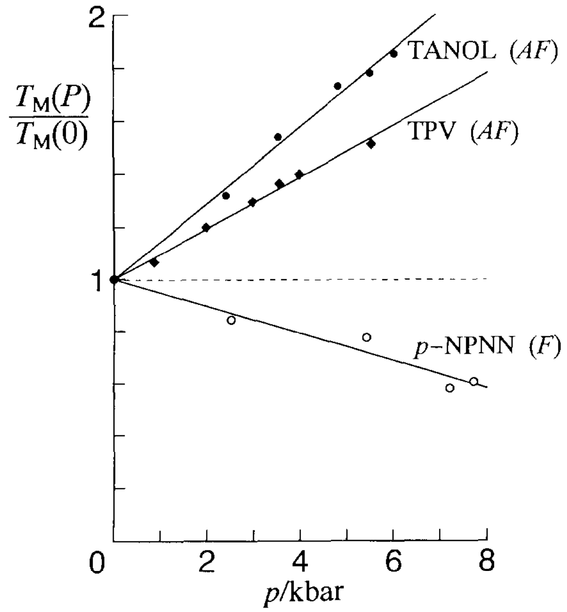


Fig. 6. Pressure dependence of the magnetic transition temperatures of genuine organic magnets; ferromagnetic β-phase p-NPNN, and antiferromagnetic TANOL and TPV.

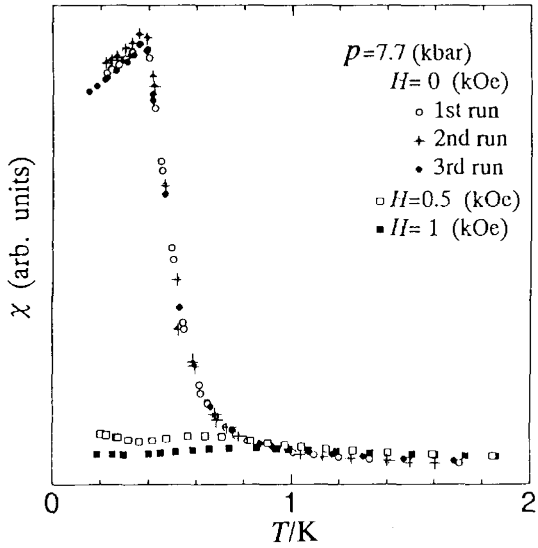


Fig. 7. The magnetic field dependence of the susceptibility of β-phase p-NPNN at $p = 7.7$ kbar [14].

4.1. Reduction of the Curie temperature under pressure

It has been suggested that the Curie temperature of this substance is governed by dipole–dipole coupling [15]. If this is the case, the Curie temperature would increase with compression. Furthermore, it is estimated that the distance between dipoles would not shrink more than 1%, at most, under the present pressure range. It is difficult to explain the observed reduction in the Curie temperature with this small fraction. Therefore, the dipolar interaction does not seem to play a role in determining the Curie temperature; it may act to determine the direction of the magnetic moments in the ordered state [16].

For most radical crystals with an unpaired electron per molecule, the intermolecular interactions are usually expressed by the Hamiltonian for the spin $S = 1/2$ system, as

$$H_{ij} = 2J_{ij}S_iS_j = -2(J^{\mathrm{K}}_{ij} - J^{\mathrm{P}}_{ij})S_iS_j \tag{2}$$

where J^{K}_{ij} ad J^{P}_{ij} are the effective exchange constants relevant to the kinetic and potential exchange integrals, respectively, both of which depend on overlapping of molecular orbitals. Prior to discussing the interactions under pressure, we will consider ferromagnetism in radical crystals at ambient pressure. From the study on galvinoxyl, the kinetic term can be expressed as

$$J^{\mathrm{K}}_{ij} = -t^2_{\mathrm{S\text{-}S}}/U + t^2_{\mathrm{S\text{-}F}}\,J^{\mathrm{in}}/U^2 + \text{terms related to other transfer paths} \tag{3}$$

where the transfer integral $t_{\mathrm{S\text{-}S}}$ indicates the charge transfer between the SOMOs of molecules i and j, $t_{\mathrm{S\text{-}F}}$ that between SOMO and a fully occupied MO, e.g. NHOMO, U the on-site Coulomb repulsion in SOMO, and J^{in} the molecular 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 [17], the first term being the ordinary second-order perturbation. The essential factors for ferromagnetic coupling established from the study on galvinoxyl are a large $t_{\mathrm{S-F}}$ and J^{in}, and a small $t_{\mathrm{S-S}}$. In other words, the positive sign of the net exchange interactions, J_{ij}, results from the condition that the second term in Eq. (3) exceeds the other contributions such as the first term in Eq. (3) and J_{ij}^{P}. These contributions are well confirmed in galvinoxyl, and the origin of the ferromagnetic interactions has been the attribution of the second term in Eq. (3). The above conditions are also basically retained in the β-phase p-NPNN [7] and some other ferromagnetic radical crystals. In the present case, J_{ij}^{P} and $t_{\mathrm{S-S}}$ should be very small, because SOMOs are very well separated from each other in the crystal. Therefore, J_{ij} is essentially determined by the second term in Eq. (5).

Now we consider the pressure dependence of the transition temperature. In the previous studies [9–11], the large enhancement of the Néel temperature of organic radical antiferromagnets under pressure has been attributed to the increase in $t_{\mathrm{S-F}}$ due to a small change in the intermolecular distance or librational distortion under high pressure. The results for TANOL and TPV in Fig. 6 clearly exemplify the sensitivity of the antiferromagnetic interactions to pressure. Another example of the strong dependence of the exchange interaction on structure is reported by Awaga and Maruyama [18]. Thus the antiferromagnetic interaction, the first term in Eq. (3), seems to be readily affected by a small change in the relative location of the molecules in the lattice.

In view of these experimental facts, the β-phase crystal can be interpreted as follows. We first assume that $t_{\mathrm{S\ F}}$ is much more enhanced under pressure than $t_{\mathrm{S-F}}$. With pressure-insensitive U and J^{in}, the antiferromagnetic contribution increases more rapidly than the ferromagnetic one, though both increase with pressurization. Thus the balance shifts to the reduction of the net ferromagnetic interactions. Next, we infer that the fraction of the antiferromagnetic contribution to J_{12} is smaller than that to J_{13} at $p = p_0$, where J_{ij} is shown schematically in Fig. 1. This means that the molecular pair, 1 and 2, has a smaller value of $t_{\mathrm{S\ S}}^2/t_{\mathrm{S-F}}^2$ than that of the pair 1 and 3. This would explain the more sensitive reduction in J_{13} mentioned above, resulting in the reduction of the Curie temperature.

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, analysis of the contribution of the overlaps between SOMOs and between SOMO and the relevant occupied MO to the exchange interactions is also recommended. It would be of great interest to see what happens at higher pressures, especially at $p \approx 20\,\mathrm{kbar}$ where $T_c(p)$ is expected to be zero.

4.2. The lowering of the magnetic lattice dimensionality

The effect of pressurization is not only the reduction of $T_c(p)$, but also the lowering of the magnetic lattice dimensionality, as seen in the round shoulder of the heat capacity in Fig. 4. From the crystal structure, we expect that only J_{12} is responsible for 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

$$T_c(p) \propto \{\xi_{2d}(J_{12})\}^2 J_{13} \tag{4}$$

where $\xi_{2d}(J_{12})$ is the spin correlation length within the layer at $T = T_c(p)$ and reflects the short-range ordering effect. The reduction in $T_c(p)$ indicates that compression results in a decrease in J_{13} and/or $\xi_{2d}(J_{12})$. Furthermore, the appearance of the short-range ordering effect $T_c(p)$ means that J_{13} changes more sensitively with pressure in the β-phase p-NPNN. In Fig. 4, the curves for the theoretical results for the two-dimensional Heisenberg magnets are given [19].

5. Conclusion

Under hydrostatic pressures, a drastic reduction in the Curie temperature of β-phase p-NPNN, a genuine organic ferromagnet, is observed; this means that the ferromagnetic interactions mainly originate in the exchange interactions rather than in the dipolar couplings. The low-dimensional behavior appearing under high pressures suggests that the ferromagnetism in this compound is due to the cooperation of intra- and inter-layer exchange interactions, the latter being more sensitively reduced with pressure. The strong pressure dependence of the critical temperature is explained by competition between ferro- and antiferro-magnetic interactions; the latter are readily affected by compression.

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