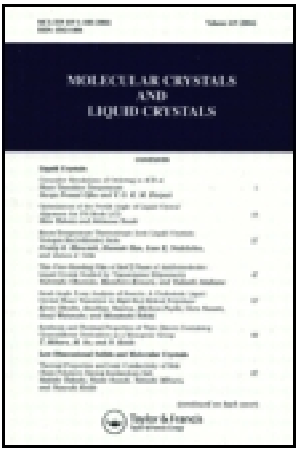

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Magnetism of the β-Phase p-Nitrophenyl Nitronyl Nitroxide Crystal

Kazuyoshi Takeda [a], Kensuke Konishi [a b], Masafumi Tamura [c] & Minoru Kinoshita [c]

[a] Department of Applied Science, Faculty of Engineering, Kushu University, Hakozaki, Higashi-ku, Fukuoka, 812, Japan

[b] Department of Physics, Faculty of Science, Ehime University, Matsuyama, 790, Japan

[c] Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, 106, Japan

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MAGNETISM OF THE β-PHASE *p*-NITROPHENYL NITRONYL NITROXIDE CRYSTAL

KAZUYOSHI TAKEDA*, KENSUKE KONISHI*,a), MASAFUMI TAMURA†, AND MINORU KINOSHITA†
* Department of Applied Science, Faculty of Engineering, Kushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan; † Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

Abstract The ferromagnetism of β-phase *p*-nitrophenyl nitronyl nitroxide has been established by various measurements at an ambient pressure. To get further insight into the magnetic interactions, the pressure effect on the magnetic and thermal properties has been examined in the pressure range of 0-7.7 kbar. Important feature of the results is twofold. One is a reduction of the Curie temperature with applied pressure. This suggests that the exchange interactions are mainly responsible for determination of the Curie temperature. Dipolar couplings are estimated to be too small to explain the observed Curie temperature. The other is the lowering of the lattice dimensionality. The heat capacity curve under the pressure of 7.2 kbar coincides with the theory for a two-dimensional Heisenberg ferromagnet above the Curie temperature. This suggests that the interactions between the neighboring *ac*-plane are more affected by compression of the crystal.

INTRODUCTION

The study of magnetic properties of organic radical crystals has attracted much attention in recent years. In particular, a movement to search out bulk ferromagnetism in organic materials consisting exclusively of light elements is quite active. Following the discovery of the first example of organic bulk ferromagnet,[1] several examples have been reported within a couple of years.[2-5]

Among them, the ferromagnetism of the β-phase crystal of *p*-nitrophenyl nitronyl nitroxide (β-*p*-NPNN, $C_{13}H_{16}N_3O_4$) has been well characterized by the measurements of susceptibility,[1] magnetization,[1] heat capacity,[1] zero-field muon spin rotation (ZF-μSR),[6] neutron diffraction[7] and ferromagnetic resonance[8] at an ambient pressure. Even so, detailed mode of action 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).[9] However, there remains a question experimentally which of the exchange or the dipolar couplings dominates in the *determination of the*

Curie temperature.

To elucidate this point, we have examined the effect of pressure on the magnetic and thermal properties of β-*p*-NPNN in the pressure range of 0-7.7 kbar. We also estimate the magnitude of the dipolar interactions. From the results, we conclude that the exchange interaction mainly governs the Curie temperature, whereas the dipolar interaction plays a role in determining the direction of the magnetic easy axis in the case of β-*p*-NPNN.

EXPERIMENTAL

The crystals of β-p-NPNN were prepared by the method described previously.[1] The crystal belongs to the space group of F2dd, and we use here the axis definition of a = 12.374, b = 19.350 and c = 10.960 Å. The crystal structure is schematically shown in Fig. 1.

The ac susceptibility and the heat capacity were measured simultaneously under hydrostatic pressure using a CuBe pressure clamp cell. The pressure was calibrated against the pressure dependence of the superconducting transition temperature of metallic tin (Sn).[11] 0.389 g of the polycrystalline β-*p*-NPNN and 0.344 g of the pressure transmission oil (Apieson-J) were placed in the CuBe cell together with a small tip of Sn metal. The susceptibility was measured at 200 Hz and peak-to-peak field of about 0.5 Oe. The measurements were carried out at P = 0.001 (=P_0), 2.5, 5.4, 7.2 and 7.7 kbar. The values of the susceptibility (χ) and heat capacity (C_p) were quite reproducible for pressure cycles of $P_0 \leftrightarrow P$. 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.

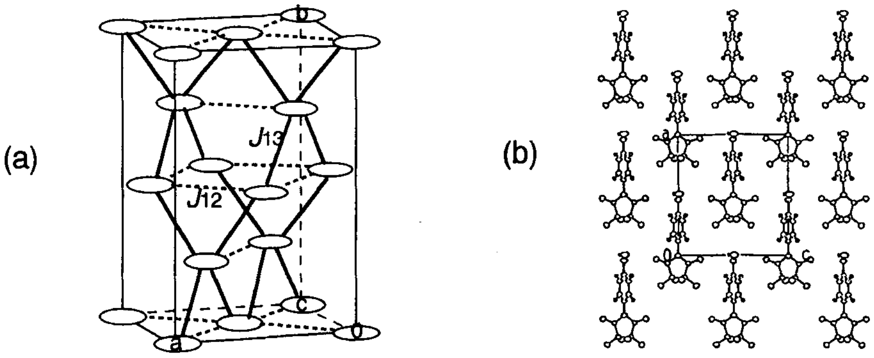

FIGURE 1 (a) Schematic drawing of the crystal structure of β-*p*-NPNN. Each ellipsoid represents the radical molecule. (b) The molecular arrangement on the *ac*-plane.

RESULTS

Behavior at an Ambient Pressure

Figure 2 shows the results of the magnetic susceptibility and heat capacity at an ambient pressure (P_0 = 0.001 kbar). The overall behavior is essentially in agreement with that reported previously.[1] This prooves that the crystals are stable enough even in the pressure transmission oil. The sharp heat capacity peak of λ-type appears at $T_C(P_0)$ = 0.61 ± 0.02 K and the susceptibility shows an abrupt increase around $T_C(P_0)$. This corresponds to the three-dimensional ferromagnetic ordering.

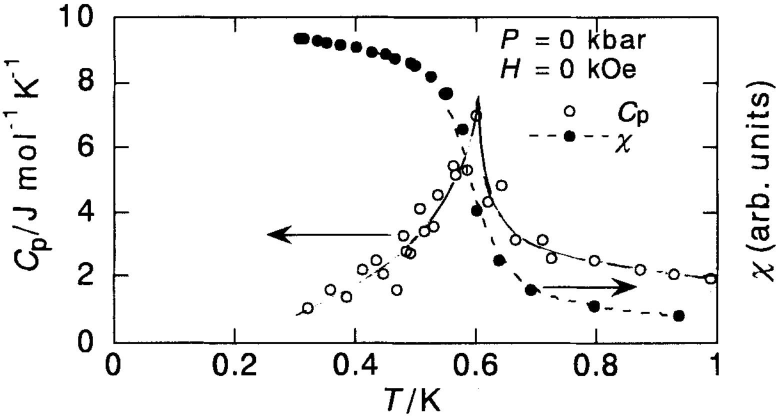

FIGURE 2 Magnetic susceptibility and heat capacity of β-*p*-NPNN at *P* = 1 bar.

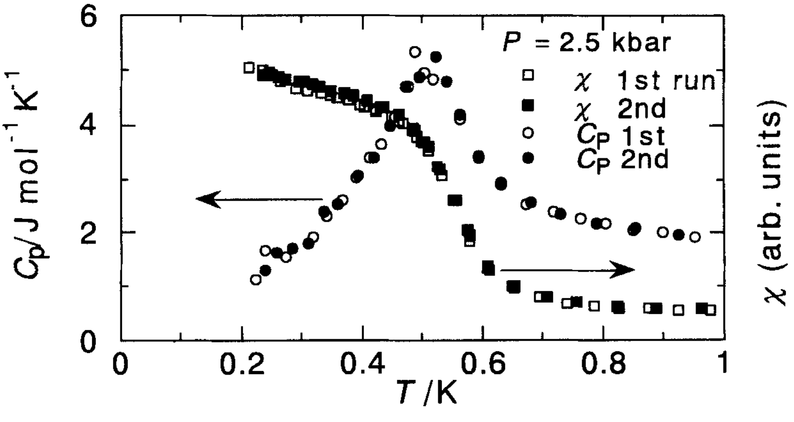

FIGURE 3 Magnetic susceptibility and heat capacity of β-*p*-NPNN at *P* = 2.5 kbar.

Behavior under High Pressure

As the pressure increases, these anomalies in C_p and χ clearly shift to the lower temperature side as seen in Figs. 3 and 4. In addition, the λ-type heat capacity peak becomes lower and the C_p value 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 at $T > T_C(P)$. The total magnetic entropy estimated from C_P up to 2 K is nearly equal to $R\ln(2S + 1)$, where S = 1/2, independent of pressure.

As in Fig. 4, the susceptibility exhibits a plateau below $T_C(P)$. Even under lower pressures this can be seen as a rather gradual change in χ against temperature, as in

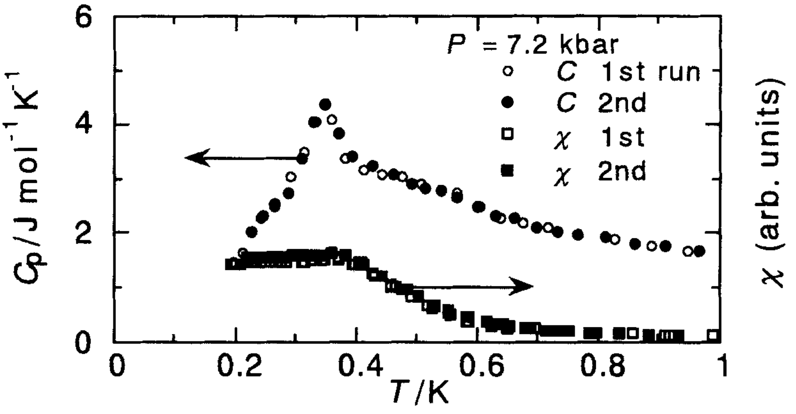

FIGURE 4 Magnetic susceptibility and heat capacity of β-p-NPNN at P = 7.2 kbar.

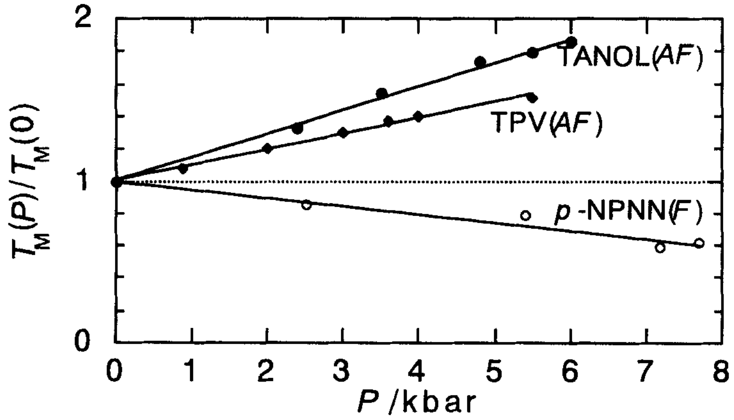

FIGURE 5 Pressure dependence of the magnetic transition temperature of the genuine organic ferromagnet (β-p-NPNN) and antiferromagnets (TANOL and TPV).

Figs. 2 and 3. Such kind of plateau has been also 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 relaxation effect when measured by the ac method.

Figure 5 shows the pressure dependence of the Curie temperature of β-*p*-NPNN. The Curie temperature follows the equation,

$$T_C(P) = T_C(P_0)(1 - aP), \tag{1}$$

where $a = 0.05 \pm 0.01\ \mathrm{kbar}^{-1}$ for β-*p*-NPNN. For comparison, the pressure dependence of the Néel temperatures is also shown in Fig 5 for the organic antiferromagnets studied previously.[11]

Effect of External Field

The effects of applied magnetic field on χ and C_P are also examined at each pressure. Representative results at P = 7.7 kbar are shown in Fig. 6 for χ. The anomalies of χ and C_P are easily affected by weak field even under pressure, just as those shown at $P = P_0$.[1] This implies that the ferromagnetism of this crystal does not change qualitatively under the present pressure range.

DISCUSSION

Ferromagnetism of β-*p*-NPNN

The β-phase crystal of *p*-NPNN shows a typical bulk ferromagnetism below the Curie temperature T_C = 0.6 K. The detailed magnetic properties are well investigated both in

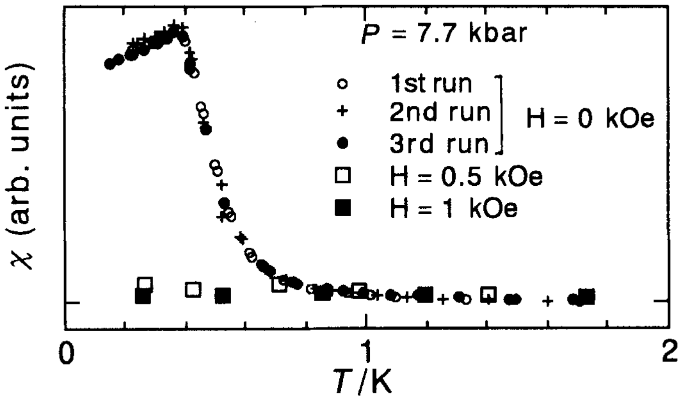

FIGURE 6 Field dependence of the magnetic susceptibility of β-*p*-NPNN at P = 7.7 kbar.

the paramagnetic and ferromagnetic region.[1] Pressure effect in the paramagnetic region has also been reported.[13]

The ZF-μSR experiments have shown that the spontaneous magnetization grows, as the temperature decreases below T_C, nearly in accordance with the isotropic three-dimensional Heisenberg model, and that the magnetic easy axis is along the *b*-axis.[6] The ferromagnetic resonance experiments by Oshima also shows that the *b*-axis is the easy axis.[8]

It is suggested that there are two types of exchange interaction paths in the β-phase crystal. One is the interaction which links the molecules on the *ac*-plane so as to afford a two-dimensional structure[10] and the other is the interaction which connects the molecules on the neighboring *ac*-planes so as to build a diamond-like three dimensional network (see Fig. 1).[1,14] The molecular orbital calculation, based on the room temperature structure at $P = P_0$, gives the values of $2J_{12}/k_B = 0.48$ K for the former and $2J_{13}/k_B = 0.22$ K for the latter.[8] Other interactions are estimated to be much smaller, and these values result in the mean-field Curie temperature of 0.60 K in good agreement with the experimental result.

Role of Dipolar Interaction 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.[15] 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; $\rho_O = 0.285$, $\rho_N = 0.260$ and $\rho_C = -0.09$.[16] Our calculation yields the values of $D_a/k_B = -0.016$, $D_b/k_B = -0.029$ and $D_c/k_B = 0.045$ K.[17] These values are too small by one order of magnitude to explain the observed $T_C(P_0) = 0.6$ 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,[6] neutron diffraction[7] and ferromagnetic resonance,[8] where the magnetic easy axis of β-*p*-NPNN is shown to be the *b* axis. Therefore, in the present case of β-*p*-NPNN, the dipolar 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.

Lower Dimensionality under Pressure

From the discussion above, we hereafter confine our attention to the intermolecular exchange interactions defined by the spin Hamiltonian,

$$\mathcal{H} = \Sigma\, \mathcal{H}_{ij} = -2\Sigma\, J_{ij}\, S_i{\cdot}S_j\,, \tag{2}$$

where S_i and S_j denotes the $S = 1/2$ Heisenberg spin operator for the molecules i and j, respectively, and the summation is taken over all the adjacent molecular pairs in the crystal. In eq. (2), only J_{ij} depends on pressure.

As mentioned above, the effect of pressure is not only the reduction of $T_C(P)$ but also the lowering of the lattice dimensionality. 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

$$T_C(P) \propto \{\, \xi_{2d}(J_{12})\,\}^2\, J_{13}, \tag{3}$$

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 of $T_C(P)$ indicates that compression results in the decrease in 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.

Charge Transfer Exchange Mechanism

The dependence of the exchange interaction on pressure can be explained by the charge transfer mechanism reported in the study on galvinoxyl.[18] We write the net exchange interaction in the form,

$$J_{ij} = J_{ij}{}^{\mathrm{K}} + J_{ij}{}^{\mathrm{P}}, \tag{4}$$

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

In the light of the study on galvinoxyl, the kinetic term can be expressed as,

$$J_{ij}{}^{\mathrm{K}} = -t_{\mathrm{S\text{-}S}}{}^2/U\ + t_{\mathrm{S\text{-}F}}{}^2\, J^{\mathrm{in}}\,/U^2 + \text{(terms related to other transfer paths)}, \tag{5}$$

where the transfer integral $t_{\mathrm{S\text{-}S}}$ stands for the charge transfer between the SOMO's of molecules i and j, $t_{\mathrm{S\text{-}F}}$ stands for that between SOMO and a fully occupied MO (*e.g.*, NHOMO), U is the on-site Coulomb repulsion in SOMO, and J^{in} is the intramolecular exchange integrals between SOMO and the fully occupied MO's. The second term is an analog of the third-order effect in Anderson's theory [19], the first term being the ordinary second-order perturbation. The essential factors for ferromagnetic coupling established from the study on galvinoxyl are the large $t_{S\text{-}F}$ and J^{in} and small $t_{S\text{-}S}$. In other words, the positive sign of the net exchange interactions, J_{ij}, results from the condition that the second term in eq. (5) exceeds the other contributions such as the first term in eq. (5) and $J_{ij}{}^{P}$. These conditions are well confirmed in galvinoxyl, and the origin of the ferromagnetic interactions has been attributed to the contribution of the second term in eq. (5).

Reduction of the Curie Temperature under Pressure

The above conditions are also basically retained in β-phase *p*-NPNN [20] and some other ferromagnetic radical crystals. In the present case, $J_{ij}{}^{P}$ and $t_{S\text{-}S}$ 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. (5).

In the previous studies [12], on the other hand, the large enhancement of the Néel temperatures of organic antiferromagnet under pressure has been attributed to the increase of $t_{S\text{-}S}$ due to a small change in the intermolecular distance or librational distortion under high pressure. The results for TANOL and TPV in Fig. 4 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.,[21] where the structure is continuously controlled by a mixed crystal technique. Thus the antiferromagnetic interaction, the first term in eq. (5), 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 the β-phase crystal can be interpreted as follows. We first suppose that $t_{S\text{-}S}$ is much more enhanced under pressure than $t_{S\text{-}F}$. 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. This seems to be consistent with the fact that the pressure coefficient has similar values for both the ferromagnet and antiferromagnets. Next, we infer that the fraction of the antiferromagnetic contribution in J_{12} is smaller than that in J_{13} at $P = P_0$. This means that the molecular pair, 1 and 2, has smaller value of $t_{S\text{-}S}{}^2/t_{S\text{-}F}{}^2$ 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 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 SOMO's and between SOMO and the relevant occupied MO to the exchange interactions are also urged. It would be of great interest to see what happens at higher pressures, especially $P \approx 20$ kbar where $T_C(P)$ is expected to be zero.

Conclusion

The reduction of the Curie temperature is observed in β-phase *p*-NPNN under high pressure: this means that the ferromagnetic interactions mainly originate in the exchange interactions rather than the dipolar couplings. The low-dimensional behavior appearing under high pressure suggests that the ferromagnetism in β-phase *p*-NPNN is due to the cooperation of intra- and inter-layer exchange interactions, the latter being more sensitively reduced by pressure. The strong pressure dependence of the critical temperature is explained by assuming that the net ferromagnetic coupling is determined by competition between ferromagnetic and antiferromagnetic interactions and that the latter is readily affected upon pressurization.

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