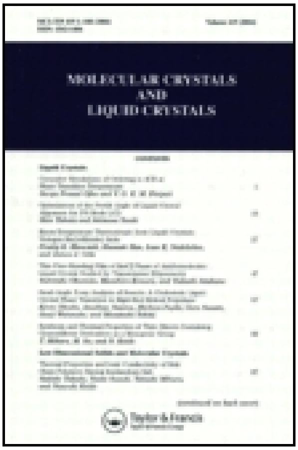

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Ferromagnetic to Antiferromagnetic Transition of p-Nitrophenyl Nitronyl Nitroxide

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Ferromagnetic to Antiferromagnetic Transition of *p*-Nitrophenyl Nitronyl Nitroxide

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A pressure-induced ferromagnetic to antiferromagnetic transition has been found in the polycrystalline sample of the β-phase crystal of *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN). As the pressure increases, the ferromagnetic transition temperature decreases with simultaneous decrease of the ac-susceptibility in the ordered state. Further increase of pressure above about 6.5 kbar results in antiferromagnetic behavior of χ_{ac}-T and M-H curves. The observed ferromagnetic to antiferromagnetic transition suggests that one of the exchange paths has changed the sign of the interaction. This is discussed in relation to the structural change under high pressure.

Keywords: *p*-nitrophenyl nitronyl nitroxide; magnetism; bulk organic ferromagnet; pressure effect; ferromagnetic to antiferromagnetic transition

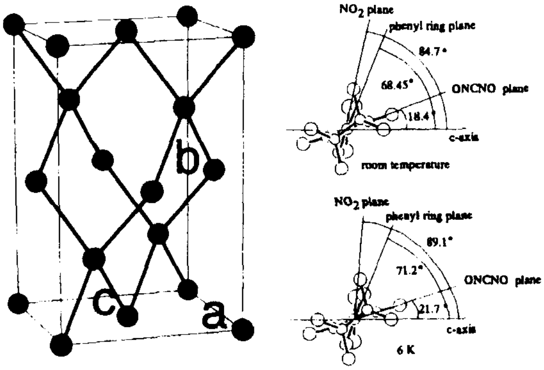
INTRODUCTION

The ferromagnetism of purely organic radical crystals has been one of the major topics in recent years. The first example of organic ferromagnets was realized in 1991 in the orthorhombic β-phase crystal of *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN) with the transition temperature of 0.6 K[1-3]. Since then, several organic crystals have been shown to undergo a ferromagnetic transition at temperature below 1.5 K[4]. Among them, the ferromagnetism of the β-phase crystal of *p*-NPNN has been well characterized by various measurements, such as susceptibility, magnetization heat capacity, zero-field muon spin rotation, neutron diffraction and ferromagnetic resonance, at an ambient pressure[3]. Recently, we have been studying the pressure effect on this magnetic material in order to obtain further insight into the exchange mechanisms.

In the previous studies[5,6], we have shown from the measurements of ac-susceptibility and heat capacity under pressures up to about 7 kbar that the ferromagnetic Curie temperature decreases as the pressure increases and the reduction of ferromagnetic interactions from the three to two dimensional occurs. The present study has been undertaken to see what will happen when the pressure is further increased.

CRYSTAL STRUCTURE

Figure 1(a) shows a bird's-eye view of the crystal structure of the β-phase



(a) (b)

FIGURE 1 (a) A schematic draw of the crystal structure of the β-phase of *p*-nitrophenyl nitronyl nitroxide, where each circle represents the molecule and (b) the tilt angles of the ONCNO fragments, the phenyl ring and the nitro group with respect to the ac-plane at room temperature and at 6 K.

crystal, where each sphere stands for the *p*-NPNN molecule. The crystal belongs to the space group of *F2dd* (a = 12.374, b = 19.350, and c = 10.960 Å) and the lattice is similar to that of diamond, but elongated along the *b*-axis. All the molecules are arranged in a parallel manner with the long molecular axis along the *a*-axis. The best fit planes of the ONCNO fragments are tilted by ±18.40° from the *ac*-plane, those of the phenyl groups by ±68.45°, and those of the nitro groups by ±84.70°.

The crystal structure at 6 K is also known from the neutron diffraction measurements[7]. The crystal thermally shrinks with keeping the symmetry, and the lattice constants of a= 12.16, b = 19.01 and c = 10.71 Å are reported. The contraction is the largest along the *c*-axis (2.24%). As a result, the molecules are tilted with respect to the *ac*-plane more than those at room temperature. The tilt angles are ±21.7°, ±71.2°, and ±89.1°, respectively. These tilt angles are summarized in Figure 1(b). These results indicate that the molecules, when the crystal is cooled, suffer librational rotation of ±3.3° about the *a*-axis with keeping the molecular shape, only the nitro groups being further rotated internally by ±1°.

It is to be noted that the density of the β-phase crystal (ρ_o = 1.42, ρ_c = 1.416 g/cm^3) is the largest among the four polymorphic phases (ρ_o = 1.37 or

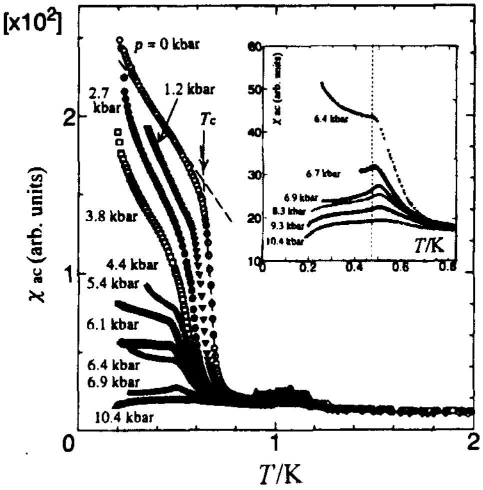


FIGURE 2 The pressure dependence of ac-susceptibility of β-*p*-NPNN under various pressures.

$\rho_c = 1.354$ g/cm^3 for α-phase, $\rho_c = 1.348$ for γ-, and $\rho_c = 1.333$ g/cm^3 for δ-phase). The density increases to $\rho_c = 1.498$ g/cm^3 at 6 K.

PRESSURE DEPENDENCE OF AC-SUSCEPTIBILITY

Figure 2 shows the temperature dependence of ac-susceptibility measured under various pressures up to 10.4 kbar. The critical temperature, T_c, decreases with the increase of pressure up to 6 ~ 7 kbar. The critical temperature is defined here by the crossing point of the extrapolated lines as shown in Figure 2, which nearly agrees with that determined from the heat capacity measurements in the previous studies[5,6].

The critical temperature, T_c, changes as

$$T_c(p) = T_c(p_0)(1 + ap)$$

with $a = -0.048$ kbar^{-1} at $p < 6$ kbar, flinches at $p_c = 6.5 \pm 0.5$ kbar and begins to increase with a small but positive value of $a = +0.004$ kbar^{-1} at $p > 7$ kbar. Figure 3 summarizes the temperature dependence of T_c.

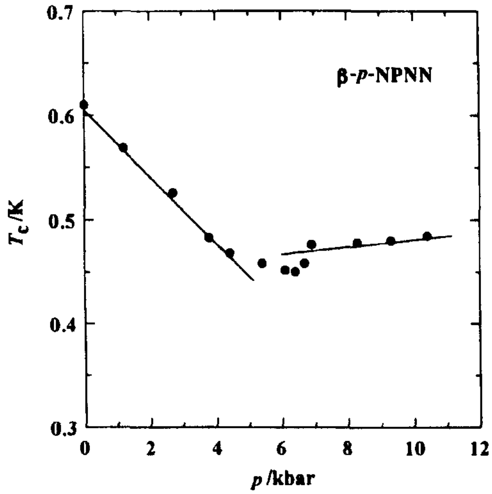


FIGURE 3 The pressure dependence of the critical temperature.

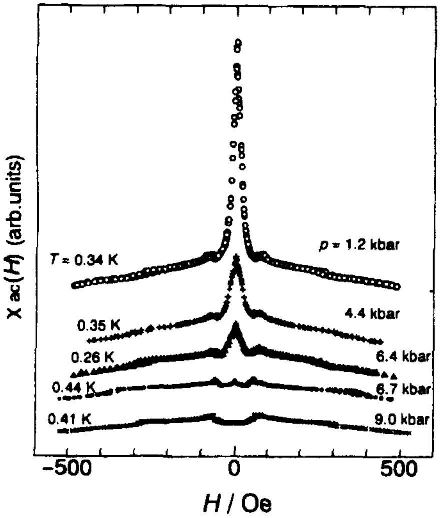


FIGURE 4 External field dependence of ac-susceptibility under pressure in the ordered state of β-*p*-NPNN.

A more remarkable change is observed in the magnitude of the susceptibility in the ordered state below T_c. It decreases very sensitively with the increase of pressure, giving only a trace at p = 10.4 kbar, where the susceptibility is slightly larger than that in the paramagnetic region. At the same time, the shoulder-like curves at around T_c change into cusps at $p > 6.5$ kbar. This is shown in the inset of Figure 2.

PRESSURE DEPENDENCE OF MAGNETIZATION

The magnetization, M, of an ordinary ferromagnet draws a characteristic hysteresis loop in a single step around $H = 0$ against sweep of external field $+H \leftrightarrow -H$, while an antiferromagnet, including a metamagnet or a canted weak ferromagnet, gives an M-H curve in at least a double step having a spin-flopping field, H_{sf}. In order to see how the above change in the magnetism of the β-phase crystal appears in the magnetization, we determined the relative values of M by integrating $\chi_{ac}(H)$.

Figure 4 shows the field dependence of $\chi_{ac}(H)$ at several fixed pressures and at several constant temperature below $T_c(p)$. The center peak at $H = 0$ Oe is distinct in the ferromagnetic region of $p < p_c$, and the peak becomes so small as to disappear in the region of $p > p_c$, indicating that the ferromagnetism has almost disappeared. The small cusps are always observed at $H \approx \pm 50$ Oe.

Figure 5 illustrates the results of the corresponding integration of $\chi_{ac}(H)$ against H. Since $\chi_{ac}(H)$ does not show any significant relaxation effect for the ac field $H_{ac}(\nu) < 1$ Oe with $\nu = 15.9$ Hz, $\chi_{ac}(H)$ is practically regarded as the differential susceptibility, dM/dH. Thus integration of the curves in Figure 4 yields the magnetization isotherms. The magnetization curves thus obtained are shown in Figure 5 only in the low field range. The growth of M is rapid at 1.2 kbar. However, it becomes gradual at higher pressure and finally, at $p = 9.0$ kbar, the magnetization becomes to draw a curve qualitatively different from that in the ferromagnetic state. It looks like a curve for an antiferromagnet with a spin-flopping field of $H_{sf} \approx \pm 50$ Oe. A small hysteresis is observed even at $p = 9.0$ kbar. This may be due to canted

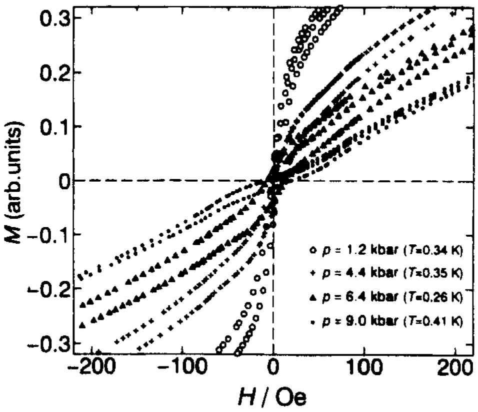


FIGURE 5 Magnetization curves under pressure below the critical temperature.

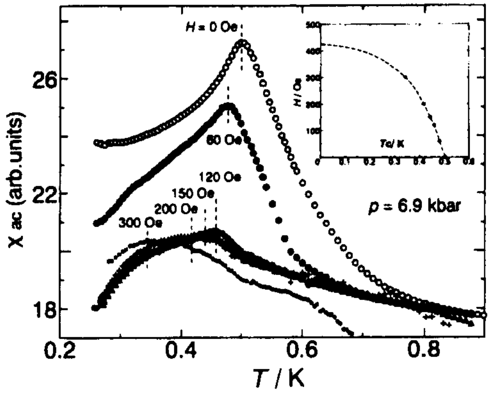


FIGURE 6 Temperature dependence of ac-susceptibility of *p*-NPNN as a function of external field strength under 6.9 kbar. The inset shows the field dependence of the critical temperature.

weak ferromagnetic moments or surface effect. Canted ferromagnetic moments have been observed even in the Heisenberg organic ferromagnets with small anisotropy in *g*-factor ($\Delta g/g = 0.3\%$)[8].

FIELD DEPENDENCE OF SUSCEPTIBILITY AT p = 6.9 KBAR

Another experimental fact for the transition to an antiferromagnet is demonstrated in Figure 6 by the temperature dependence of $\chi_{ac}(H)$ measured at various applied field strengths and at constant pressure of $p = 6.9$ kbar. The cusp or the critical temperature of $\chi_{ac}(H)$ clearly shifts down to the lower temperature side with the increase of field strength. This is again a characteristic feature of antiferromagnets. A similar behavior has been observed in the case of the antiferromagnetic γ-phase crystal of *p*-NPNN[2]. The inset of the figure shows the relation between the applied field and the critical temperature.

LATTICE CONSTANTS UNDER HIGH PRESSURE

The lattice constants of the β-phase *p*-NPNN crystal have been determined by the Riedvelt analysis of the x-ray powder patterns under various pressures up to 12.6 kbar and at room temperature using an imaging plate. The powder patterns observed at various pressures are similar to one another, indicating that the crystal symmetry is not affected by pressurization up to 12.6 kbar. The peaks, of course, shift toward the direction of wider angles or lattice contraction as the pressure increases. The lattice constants obtained by the Rietveld analysis are plotted against pressure in Figure 7. The crystal shrinks in two steps. The linear and volume compressibilities are summarized in Table I. The biggest shrinkage (~4.5%) is found again along the *c*-axis as in the case of thermal shrinkage. The crystal density increases up to as large as 1.58 g/cm^3 at 12.6 kbar.

The thermal and compressive contraction may or may not be the same, but the thermal contraction at 6 K nearly corresponds to the compressive contraction at about 4 kbar. From these, we could expect that the molecules are librationally rotated about the *a*-axis to some more extent under pressures up to about 5.5 kbar. However, the plane of the nitro group has already been at the nearly upright orientation at 6 K (or at about 4 kbar) against the

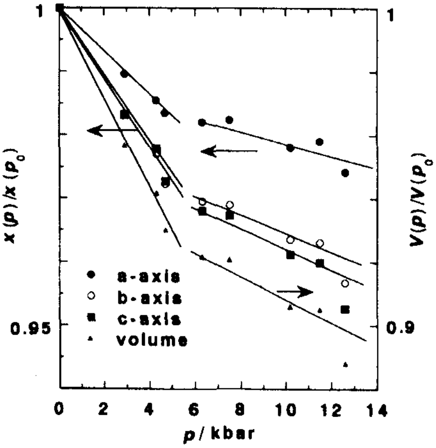


FIGURE 7 Pressure dependence of the lattice parameters and the unit cell volume of β-*p*-NPNN.

TABLE I Compressibility of the β-phase *p*-NPNN crystal in the units of μbar^{-1}.

	$\kappa_a = -\frac{1}{a}\frac{\partial a}{\partial p}$	$\kappa_b = -\frac{1}{b}\frac{\partial b}{\partial p}$	$\kappa_c = -\frac{1}{c}\frac{\partial c}{\partial p}$	$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p}$
$p < 5.5$ kbar	3.44	5.66	5.51	14.3
$p > 5.5$ kbar	1.15	1.84	2.23	4.90

ac-plane, and further pressurization beyond 5.5 kbar would not increase the tilt angle for the nitro groups. Then, the molecules themselves would suffer an internal rotation under higher pressures. The two-step contraction observed can be understood in this way. An internal rotation of the five-membered ring consisting of the ONCNO fragment and the bulky tetramethyl ethylene group would be the most probable candidate to take place in order for the molecule to become more and more planar and for the crystal to become more compact.

Such a molecular deformation would cause a change in the electronic structure of the molecule and in the intermolecular magnetic interactions. At this moment, we cannot conclude definitely, because the data of the real crystal structure of the β-phase at low temperature and under high pressure are not available. However, it is natural to expect that the molecules take a more planar form and a more parallel arrangement in the crystal. Then the intermolecular charge transfer interaction between the SOMO's on adjacent molecules would become more efficient, resulting in an interchange of the importance of the ferromagnetic and antiferromagnetic interactions.

SUMMARY

We have studied the pressure effect on the magnetic properties of the polycrystalline sample of the β-phase *p*-nitrophenyl nitronyl nitroxide and observed the ferromagnetic to antiferromagnetic transition at $p_c = 6.5 \pm 0.5$ kbar. The transition has been established by the measurements of the pressure dependence of ac-susceptibility as functions of temperature and magnetic field under various conditions. The critical temperature decreases as $T_c(p) = T_c(p_0)[1 - 0.048\,p]$ in the ferromagnetic region, where $T_c(p_0) = 0.61$ K and p is in the units of kbar, whereas that in the antiferromagnetic region

increases with the small positive coefficient as $T_c(p) \propto [1 + 0.004\,p]$.

We have also examined the contraction of the crystal under various pressures and at room temperature and found that the lattice parameters change in a two-step manner with keeping the crystal symmetry. From analogy to the thermal contraction, the first step contraction by compression is ascribed to a change due to librational molecular rotation about the *a*-axis. On the other hand, the second step contraction is supposed to be due to internal rotation of the five-membered ring of the molecule. The ferro- to antiferromagnetic transition is briefly discussed in relation to these structural deformation. To obtain further insight into the transition and the magnetic interactions, the structural studies at low temperature and under high pressure are indispensable.

Acknowledgments

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