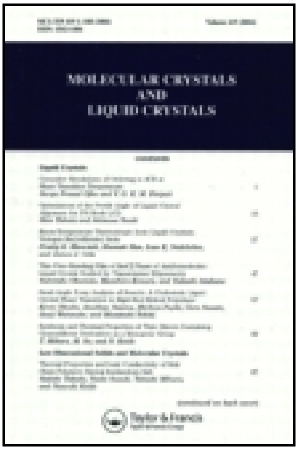

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Pressure Induced Enhancement of Tc in Weak-Ferromagnetic Radical Crystal 1,3,5-Triphenyl-6-Oxoverdazyl

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Pressure Induced Enhancement of *Tc* in Weak-Ferromagnetic Radical Crystal 1,3,5-Triphenyl-6-Oxoverdazyl

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Study of pressure effect of organic weak-ferromagnet 1,3,5-triphenyl-6-oxoverdazyl (TOV) with the transition temperature $T_c(P_0) = 5.0$ K (P_0; ambient pressure) has been motivated by the experimental finding that slight dilution of TOV with the non-magnetic derivative changed the Weiss temperature (Θ) from negative to positive, i.e. from antiferromagnetic (AF) to ferromagnetic (F). We understood that above change of Θ would originate from the slight change of the crystal structure by an internal stress. Expecting the pressurization would bring about the same result as the dilution effect, we measured the ac magnetic susceptibility of pure TOV under the pressure up to $P = 10.9$ kbar. The pressure effect of pure TOV, however, revealed no transition from AF to F, but did the enhancement of $T_c(P)$. The pressure dependence of $T_c(P)$ is characterized with $T_c(P) = T_c(P_0)\ (1 + 0.086\ P)$, and $T_c(P)$ exceeds 10.0 K at P= 10.9 kbar.

Keywords: pressure effect; organic weak-ferromagnet

INTRODUCTION

Genuine organic radical crystals, consisting of only light elements such as C, H, N, O, etc., usually have antiferromagnetic (AF) intermolecular interactions. Recently some ferromagnetic (F) radical crystals, which lead to the bulk-ferromagnetic ordering, have been synthesized[1–4]. The ordering temperature (T_c), however, is generally very low such as $T_c = 0.61$ K in β-phase p-nitrophenyl nitronyl nitroxide (abbreviated as β-phase p-NPNN)[1], $T_c = 1.48$ K in 1,3,5,7-tetramethyl-2,6-diazaadamantane-N,N'-dioxyl [2], and $T_c = 0.28$ K in 4-(p- chlorobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl (p-Cl-C_6H_4CH=N-TEMPO)[3]. It is very difficult to make T_c of organic bulk-ferromagnet much larger. But there remains another possibility to realize the ferromagnetic moment at high temperature, by making use of an organic weak-ferromagnet (WF), which has a slight antisymmetric interaction (D) as well as fairly large AF intermolecular interaction (J). Generally the Hamiltonian of WF with the Dzyaloshinsky-Moriya (D-M) type of interaction is expressed as

$$\mathcal{H} = -\sum_{i,j}\{2JS_i \cdot S_j + D_{i,j} \cdot (S_i \times S_j)\} \quad . \tag{1}$$

Realizing large AF intermolecular interaction is relatively easy in organic radical crystals, and hence the higher transition temperature (T_c) can be expected in the WF radical crystals. In the TCNQ-salt series, which include the charge transfer complex, the weak-ferromagnetic behavior at room temperature has been reported[4]. Among the genuine organic radical crystals, however, the largest T_c is $T_c = 36$ K of a sulfur-nitrogen radical (β-phase p-NCC_6F_4CNSSN)[5], and the second is probably $T_c = 5.0$ K of 1,3,5-triphenyl-6-oxoverdazyl (TOV)[6].

Organic weak-ferromagnet TOV is magnetically approximated as an $S = 1/2$ two-dimensional (2D) Heisenberg AF system with the effective AF exchange interaction $J/k_B = -4.2$ K[7]. In spite of the AF background, the magnetic susceptibility (χ) increases rapidly below $T_c = 5.0$ K, and turns to decrease around 2.0 K. The measurement of heat capacity found no anomaly except for the broad maximum of 2D Heisenberg AF short range order around 5.0 K. The magnetic anisotropy is about 1 kOe, and assumed to be the D-M type from the result of ESR[7]. The crystal structure of

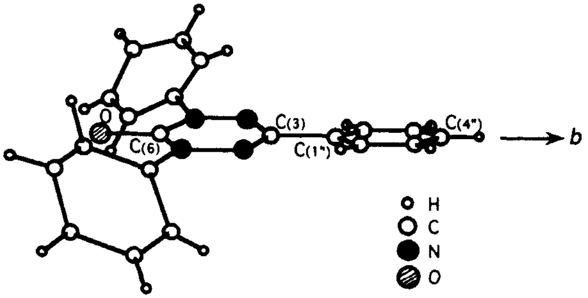

FIGURE 1: Molecular structure of TOV. The *b*-axis is the two-fold axis.

TOV consists of two kinds of sublattice, leading to the existence of two D-M vectors with opposite sign[7]. The hump of χ' around 2.0 K is assumed to be originated from the canceling of the net moments with two D-M vectors by the development of 2D correlation length. Furthermore the behavior of χ' around T_c = 5.0 K is characterized as the spin crossover from the Heisenberg to the Ising spin in 2D system[7].

On the other hand, the slight dilution of TOV by a non-magnetic derivative TOV-H (amine precursor of TOV) changes Weiss temperature (Θ) from negative (Θ = -12 ± 2 K for x = 0) to positive (*e.g.* Θ = 2.6 ± 0.5 for x = 0.03)[8]. We interpreted this experimental fact as follows: The internal stress by doping TOV-H in TOV would cause the slight change of the crystal structure, and induced the change of dominant intermolecular interaction from AF to F. We expected that the pressurization of pure TOV might bring about the same result as the dilution effect, and hence measured the ac magnetic susceptibility of pure TOV under the pressure.

EXPERIMENTAL

The crystal of TOV was synthesized according to the procedure reported[9]. Figure 1 shows the molecular structure of TOV. There is a two-fold symmetry within a molecule. This crystal was a needle along the c-axis. The crystal structure of TOV belongs to the space group $C2/c$ with the lattice parameters a=19.213Å, b=11.392Å, c=7.304Å and β=90.72°[9].

The ac magnetic susceptibility (χ) of pure polycrystalline TOV was measured by the ac-bridge (H_{ac} = 1.0 Oe peak-to-peak and f = 15.9 Hz) under the hydrostatic pressure up to 10.9 kbar. The hydrostatic pressure was attained with the Cu-Be pressure clamp cell, in which the polycrystalline sample of TOV (54.2 mg) mixed with the pressure transmission oil (Apiezon-K grease; 29.6 mg) and some tips of Al (7.6 mg) was enclosed in the teflon sample cell. The absolute value of real pressure at low temperatures was estimated by the pressure dependence of superconducting transition temperature $T_s(P)$ of Al with $T_s(P_0)$ = 1.17 K[10]. The susceptibility of the blank cell (i.e. the clamp cell, Al etc.) was subtracted from the total susceptibility.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the pressure dependence of χ' of TOV. It looks easier to determine the transition temperature $T_c(P)$ from the point of intersection of two straight lines extrapolated from above and below around $T_c(P)$. Figure 3 shows the experimental result of χ', in which the temperature of the X-axis is normalized with each $T_c(P)$. We can see a distinct critical point around $T/T_c(P) = 1$, below which χ' increases rapidly. The transiton temperature ($T_c(P)$) is clearly enhanced toward high temperature by the pressurization; $T_c(P_0)$ is about 5.0 K and $T_c(P = 10.9$ kbar) exceeds 10.0 K. Furthermore this enhancement of $T_c(P)$ can be more clearly seen in the experimental result of χ'' shown in Fig. 4. Figure 5 shows the pressure dependence of $T_c(P)$, which is estimated from the experimental results of χ' and χ''. $T_c(P)$ of TOV is characterized with the following pressure dependence,

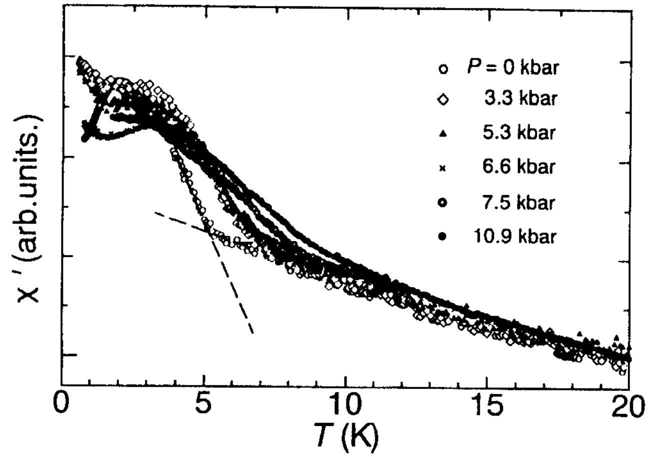

FIGURE 2: Pressure dependence of χ' of pure TOV in the pressure region up to 10.9 kbar. The temperature at the intersection of two broken lines stands for T_c at $P = P_0$.

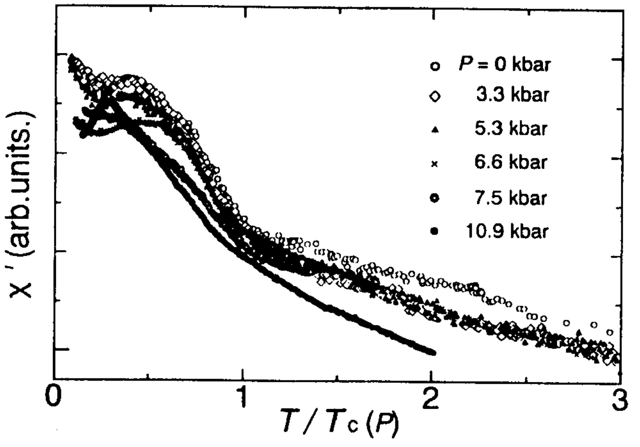

FIGURE 3: Pressure dependence of χ' of pure TOV in the pressure region up to 10.9 kbar. The temperature of the X-axis is normalized with each $T_c(P)$.

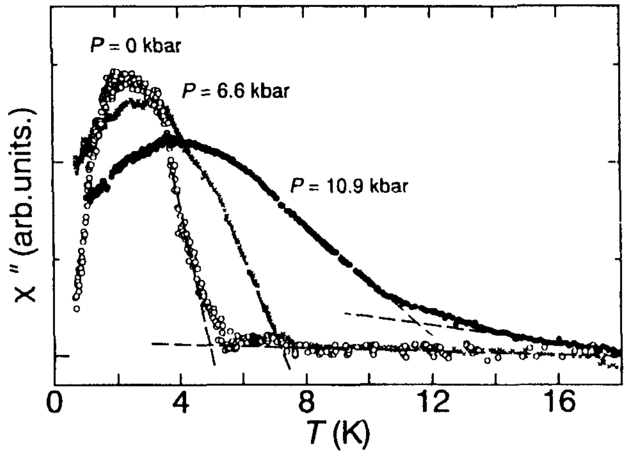

FIGURE 4: Pressure dependence of χ'' of pure TOV in the pressure region up to 10.9 kbar. The temperature at the intersection of two broken lines stands for T_c at each pressure.

$$\begin{aligned} T_c(P) &= T_c(P_0)\,(1 + aP) \quad , \\ a &= 0.086\ [\mathrm{kbar}^{-1}] \quad . \end{aligned} \tag{2}$$

The enhancement of $T_c(P)$ is as much as those of bulk-antiferromagnets such as 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (TANOL: $T_c(P_0) = 0.49$ K, $a = +0.150$ kbar^{-1})[11,12], 1,3,5-triphenylverdazyl (TPV: $T_c(P_0) = 1.70$ K, $a = +0.093$ kbar^{-1})[12], and 1,3-bisdiphenylene-2-p-chlorophenyl allyl (p-Cl-BDPA: $T_c(P_0) = 3.25$ K, $a = +0.086$ kbar^{-1})[12]. This enhancement of $T_c(P)$ of TOV gives us the great possibility to increase $T_c(P)$ more and more by higher pressure. When the pressure higher than 20 GPa can be applied without changing the crystal symmetry, $T_c(P)$ of TOV will exceed 100 K. We are preparing the experiment under higher pressure ($P \gg 10$ kbar) with the diamond anvil cell.

Here we consider the relation among the net moment M_0, D and J in the weak-ferromagnet of D-M type. M_0 is expressed with the saturation

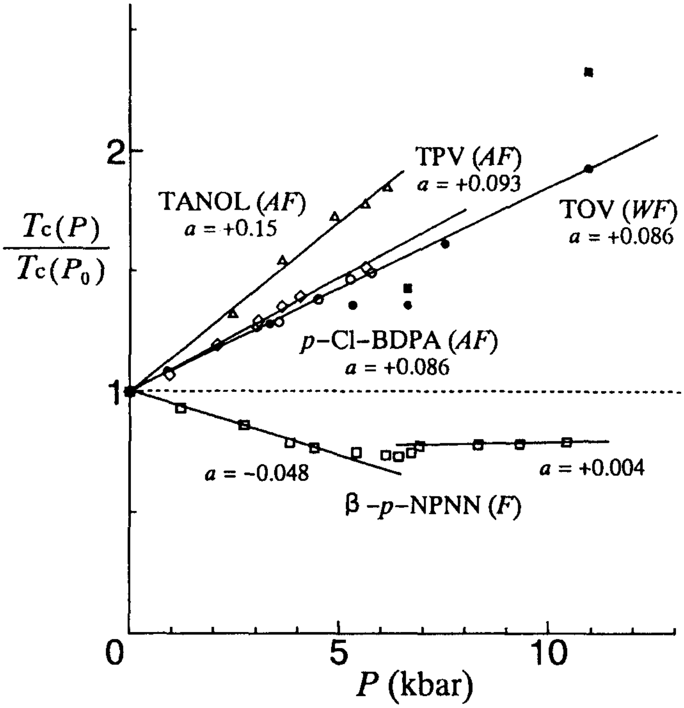

FIGURE 5: Pressure dependence of $T_c(P)$ of pure TOV in the pressure region up to 10.9 kbar. Here each $T_c(P)$ is normalized with $T_c(P_0)$. ● and □ stand for $T_c(P)$ estimated from χ' and χ'', respectively. The results of TANOL (△), TPV (◇), *p*-Cl-BDPA (○) and *β*-*p*-NPNN (□) were referred to refs. 11,12, ref. 12, ref. 12 and ref. 13, respectively.

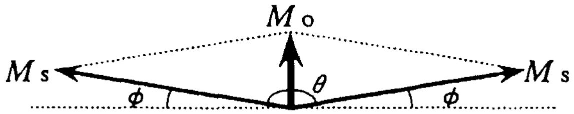

FIGURE 6: Net moment (M_0) of weak-ferromagnet. M_s stands for the saturation moment ($Ng\mu_B S$).

moment M_s ($=Ng\mu_B S$) and the canting angle ϕ as follows:

$$M_0 = 2M_s \sin\phi \quad , \tag{3}$$

where ϕ is assumed as in Fig. 6. On the other hand, the stable condition for ϕ, given by $\partial\langle\mathcal{H}\rangle/\partial\theta = 0$, yields the following relation.

$$\tan\theta = \left|\frac{D}{2J}\right| \quad . \tag{4}$$

Consequently M_0 for a small ϕ can be expressed with D and J as follows:

$$M_0 \simeq 2M_s \cdot |D/2J| = M_s|D/J| \quad . \tag{5}$$

While T_c is assumed to be proportional to J, and the following equation can be derived.

$$M_0 T_c = M_s|D| \quad . \tag{6}$$

When the magnitude of $|D|$ is given, the right-hand side of Eq.(6) becomes a constant, giving a limitation for magnitudes of T_c and M_0. If we want to have the higher T_c, the smaller moment we would have in this canting mechanism. Otherwise we have to make $|D|$ itself larger, although it seems to be difficult to introduce large $|D|$ in genuine organic compounds. The magnitude of $|D|$ is derived from the second order of perturbation including the spin-orbital interaction $\lambda\boldsymbol{L}\cdot\boldsymbol{S}$, where $\boldsymbol{L}$ and $\boldsymbol{S}$ stand for the orbital and the spin angular momentums, respectively. We may suggest to introduce some metallic elements with larger $\lambda\boldsymbol{L}\cdot\boldsymbol{S}$ interaction in organic compounds for realizing effective canted moments. Recently a few weakferromagnets with higher ordering temperatures have been reported[4,5], and it is interesting to check the limitation given here in these compounds.

Finally we compare the pressure effect of TOV with the dilution effect of TOV. On the other hand, the pressurization of TOV enhances $T_c(P)$, below which χ increases rapidly, toward high temperature, maintaining the The magnetic susceptibilities of $(TOV)_{1-x}(TOV\text{-}H)_x$ at $x \neq 0$ increase monotonously below much lower temperature than 5.0 K[8]. On the other hand, χ increases rapidly, toward high temperature, maintaining the shape of χ at ambient pressure. This experimental result of pressure effect is considered to be brought about by the enhancement of the AF intermolecular interaction within the D-M mechanism, without accompanying the transition from AF to F. Furthermore the hump of χ', which can be clearly seen around 2.0 K at ambient pressure, seems to shift toward higher temperature by the pressurization, making the shape of the hump vaguer. This may be due to the suppression of the net moments in the pressurized system with higher T_c as expected from Eq.(6).

CONCLUSION

The weak-ferromagnetism (WF) of TOV has been maintained under the pressure, in spite of our expectation that WF (or AF) turns into F as seen in the dilution effect. However, we have found that the transition temperature increases up to 10 K at $P = 10.9$ kbar. This fact is mainly brought about by the pressure induced enhancement of the antiferromagnetic interaction. These experimental result gives us great hope for realization of the spontaneous magnetization at higher temperature. We are preparing the measurement of magnetic susceptibility of TOV under higher pressure ($P \gg 10$ kbar) with the diamond anvil cell. Finally, considering the fact that the pressure effect gives entirely opposite results to the dilution effect, we speculate that some drastic change in the electronic state is caused in the diluted system even at the limit of the slightest dilution. Recently J.B.Jamali *et al.* have reported the following experimental result[14]. The crystal structure of diluted TOV is quite different from that of pure TOV, and the nearest neighboring distance elongates by the dilution. This experimental result suggests that the dilution effect for TOV can be characterized as the negative pressure.

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