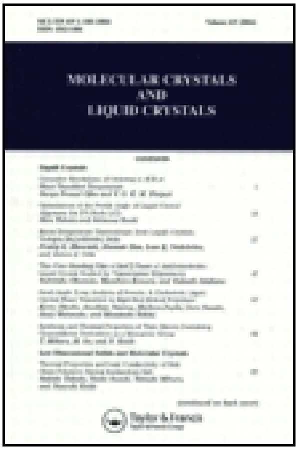

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Alloying Effects on Intermolecular Magnetic Interactions in Verdazyl Radical Alloy Crystal, (TOV)$_{1-x}$(TOV-H)$_x$, x=0.0 ~; 0.09 (TOV: 1,3,5-Triphenyl-6-Oxoverdazyl)

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Alloying Effects on Intermolecular Magnetic Interactions in Verdazyl Radical Alloy Crystal, $(TOV)_{1-x}(TOV\text{-}H)_x$, x=0.0 ~ 0.09 (TOV : 1,3,5-Triphenyl-6-Oxoverdazyl)

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To study the alloying induced drastic antiferro/ferro change of intermolecular magnetic interaction in 1,3,5-triphenyl-6-oxoverdazyl (TOV) radical alloy crystal, $(TOV)_{1-x}(TOV\text{-}H)_x$, measurements of high-field magnetization, magnetic susceptibility, and powder X-ray diffraction pattern on this radical alloy have been carried out, where TOV-H is an amine precursor of TOV. The antiferromagnetic (AFM) exchange interaction in pure TOV crystal has changed drastically to ferromagnetic (FM) type by slight alloying (x = 0.03), due to intermolecular distance expansion. The observed magnetization , $M(x, H)$, for the TOV radical alloy at 1.7 K has shown deviation from a simple Brillouin function, and thus the $M(x, H)$ was analyzed approximately by two terms. The composition rate dependence of the lattice parameters of the TOV radical alloy crystals showed an abnormal elongation of the distance of about 15% between radicals along the *c*-axis at x = 0.03. Based on the experimental facts, we will discuss the effects of elongation of inter-molecular distance on the mechanism of magnetic interaction between the delocalized radical spins.

Keywords: organic radical magnetism; antiferro/ferro change; alloying effect

INTRODUCTION

Mechanism of intermolecular ferromagnetic interaction in organic free radical crystals is the subject of great interest in molecular magnetism[1]. We have already reported a variety of intermolecular magnetic exchange interactions among verdazyl series of pure organic radicals[2], in which the unpaired electron, $S=1/2$ spin, is delocalized mainly on central four nitrogen atoms with a polarization over the entire molecules. As one of the experimental techniques to control the mechanism of magnetic exchange interaction among the radical spins, we look for the spatial dependence of the intermolecular interaction due to alloying effects in the titled sample. To explain the experimental facts on the magnetism of organic radicals, however, there is no satisfied and unique theoretical model at this stage. Yamaguchi *et al.*[3] suggest that when too large an intermolecular separation there is, the spin-polarization (SP) term often plays an important role in remote ferromagnetic intermolecular interaction[4], in comparing to the molecular direct overlap terms.

1, 3, 5-Triphenyl-6-oxoverdazyl (TOV) is one of the stable verdazyl radicals with a known crystal structure at room temperature, and recently has been reported to be a typical pure organic antiferromagnet, which can be characterized by a most highest transition Néel temperature of $T_N = 5.5 \pm 0.2$ K [5]. The experimental evidences of the weak ferromagnetism, as well as the anisotropic magnetization, below Néel temperature for pure TOV radical have been already reported at ambient pressure for powder and single crystal form[5]. To study the effect of pressure on this verdazyl, the measurement of the *ac* magnetic susceptibility of pure TOV under hydrostatic pressure up to 10.9 kbar has been carried out by Mito *et al.*[6].

In the present work, measurements of the *dc* magnetic susceptibility, the high-field magnetization, and the powder X-ray diffraction patterns of the TOV radical alloy systems, $(TOV)_{1-x}(TOV\text{-}H)_x$ (x = 0.0 ~ 0.09), were performed to study the alloying induced drastic antiferro/ferro change of magnetic exchange interactions in the TOV radical crystals. These experimental findings are discussed in the recent theoretical background of the intermolecular magnetic interactions[3]. The present article provides the first study of the effect of elongation of intermolecular distance on the mechanism of magnetic exchange interaction in organic radical crystals.

EXPERIMENTAL

The TOV and TOV-H were prepared according to the method of Neugebauer *et* *al.*[7] (Fig. 1). The powder samples of the TOV radical alloy crystals, $(TOV)_{1-x}$ $(TOV\text{-}H)_x$ (x = 0.0 ~ 0.09), were obtained by the following procedures : the TOV and TOV-H were dissolved into CH_2Cl_2 in the round-bottomed flask in the ratio of 1-x to x at 20°C. The solvent was slowly evaporated using rotary evaporator. This flask was connected to a vacuum line (5×10^{-3} Torr) for two hours to remove the solvent completely.

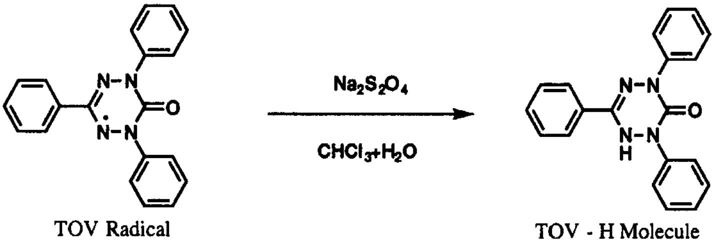

FIGURE 1 : Molecular structure of TOV and TOV-H.

The *dc* magnetic susceptibilities of the TOV radical alloys, $(TOV)_{1-x}(TOV\text{-}H)_x$ (x = 0.0 ~ 0.09), were measured in the temperature range of 2.0 - 300.0 K, by SQUID magnetometer under steady magnetic fields of 200 Oe. Ultra high-field magnetization measurement was carried out on the TOV radical alloy crystals at 1.7 and 4.2 K, by using a pulsed-field magnetometer up to 24 T, at Institute for Solid State Physics, University of Tokyo. The experimental data have been corrected for the Pascal's diamagnetic part, that is, -0.181×10^{-3} emu/mol, and the sample holder magnetization in each case. In order to obtain the information on the lattice parameters of the radical alloy systems, the powder X-ray diffraction patterns of the TOV radical alloys, $(TOV)_{1-x}(TOV\text{-}H)_x$ with x = 0.0, 0.03, 0.05, 0.09 and 1.0, were measured at 300 K by using a convergent monochromatic Cu K_α beam of STOE transmission X - ray diffractometer with a curved germanium monochromator.

RESULTS AND DISCUSSION

Observation of Alloying-Induced Antiferro/Ferro Change of Magnetism in TOV Radical Alloy System

To study the effect of inter-molecular spacing alteration on magnetic exchange interaction in the TOV radical crystal due to radical alloying, amine precursor of TOV (TOV-H) was chosen as the best dopant. The *dc* magnetic susceptibilities of the TOV radical alloy, $(\mathrm{TOV})_{1-x}(\mathrm{TOV\text{-}H})_x$, were measured to study the alloying induced drastic antiferro/ferro change of intermolecular magnetic exchange interaction. The temperature dependence of the inverse magnetic susceptibilities per one-mole TOV radical, $1/\chi_M$, of $(\mathrm{TOV})_{1-x}(\mathrm{TOV\text{-}H})_x$ (x = 0.0~ 0.09) are shown in Fig. 2. The susceptibility follows the Curie-Weiss law above 50 K, where the magnetic exchange interaction among the TOV molecules is antiferromagnetic (AFM) type for the pure radical (x = 0.0) with a negative Weiss constant ($\Theta = -12.0 \pm 1.0$ K) at paramagnetic regions (Fig. 2). A remarkable effect of the slight alloying has been observed for the TOV radical alloy crystals, where the negative AFM Weiss constant for pure sample (x = 0.0) has changed to the positive FM one in radical alloys; $\Theta = +2.6 \pm 0.5$ K at the doping of 3%, for example. The radical alloys with x= 0.05 and 0.09 also show positive Weiss constants of $\Theta = +1.6$ and 0.9 K, respectively.

The ultra high field magnetization measurements were performed for TOV radical alloy, $(\mathrm{TOV})_{1-x}(\mathrm{TOV\text{-}H})_x$, at 1.7 K and 4.2 K in pulsed magnetic fields up to 24 T, using an induction method. The magnetization $M(x, H)$ curve at 1.7 K drastically changes with slight alloying, as shown in Fig. 3. For the nominally pure TOV crystal (x = 0.0), the magnetization process follows that of the Heisenberg antiferromagnet. The most noticeable point is that the alloying effect is drastic on this antiferromagnet system. The magnetization curves for the TOV radical alloys with x = 0.03, 0.05 and 0.09 show a FM intermolecular exchange interaction. By increasing the applied field, for example at x = 0.03, the magnetization increases faster than that of the usual paramagnetic Brillouin

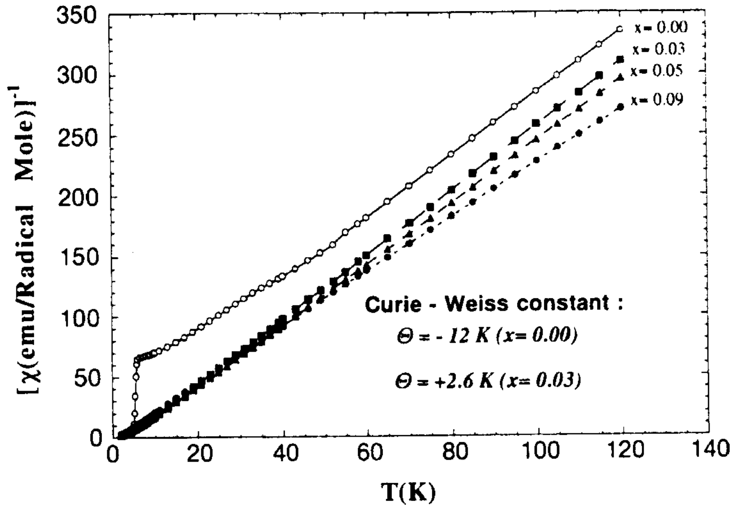

FIGURE 2: Inverse magnetic susceptibilities of the TOV radical alloy crystals, $(TOV)_{1-x}(TOV\text{-}H)_x$, x = 0.0, 0.03, 0.05, 0.09, (2 - 120 K).

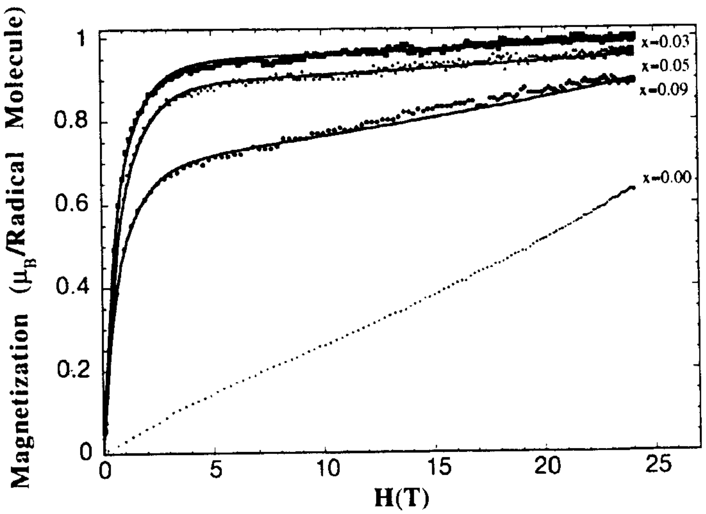

FIGURE 3: Magnetization vs. ultra high magnetic field for the TOV radical alloys, $(TOV)_{1-x}(TOV\text{-}H)_x$, up to 24 T at 1.7 K.

function with $S=1/2$, up to 5 T. For more higher applied fields, however, the deviation from the Brillouin curve appears and the magnetization increases almost linearly up to $H = 24$ T, but still levels off to the saturation value of $M_S = 1.0\ \mu_B$ per radical molecule, for $x = 0.03$.

To discuss about the mechanism of intermolecular magnetic exchange interaction in the TOV radical alloy crystals, we look for the molecular packing changes by alloying in X-ray powder diffractometry patterns. Figure 4 shows the powder X - ray diffraction patterns of the TOV radical alloy crystals, $(TOV)_{1-x}(TOV\text{-}H)_x$ ($x = 0.0, 0.03, 0.05, 0.09$, and 1.0), in the range of $2\theta = 5.0° - 45.0°$ at room temperature. The X-ray diffraction pattern of the pure TOV radical crystal ($x = 0.0$) is quite different from that of the TOV-H crystal ($x = 1.0$). However, the diffraction patterns of the radical alloys ($x = 0.03, 0.05, 0.09$) are similar to that of TOV-H crystal ($x = 1.0$), as described later. This means : (1) the TOV radical alloy crystals ($x = 0.03 \sim 0.09$) belong to the same crystal structure system with that of the TOV-H crystal, and (2) the TOV-H molecule homogeneously distributes in the AFM matrix of the TOV in each sample, and a single phase solid solution is produced in the TOV radical alloy crystals. This kind of remarkable effects of radical alloying in X-ray diffraction pattern is consistent with the drastic change of magnetism from the pure TOV crystal to the radical alloy system, which has been shown in Figs. 2 and 3.

Antiferro/Ferro Change of Magnetic Exchange Interaction due to Intermolecular Space Expansion in TOV Radical Alloy Crystals

The ultra high field magnetization curve of the TOV radical alloy crystals has shown the deviation from a simple Brillouin function with a positive exchange interaction, above 5 T region, simulated by molecular field theory, as shown in Fig. 3. In this regards, the magnetization curves observed for the radical alloy, $(TOV)_{1-x}(TOV\text{-}H)_x$, were analyzed approximately by the following two terms:

$$M(x, H) = f_1(x) M_{\text{ferro}}(H) + f_2(x) M_{\text{antiferro}}(H) \qquad (1),$$

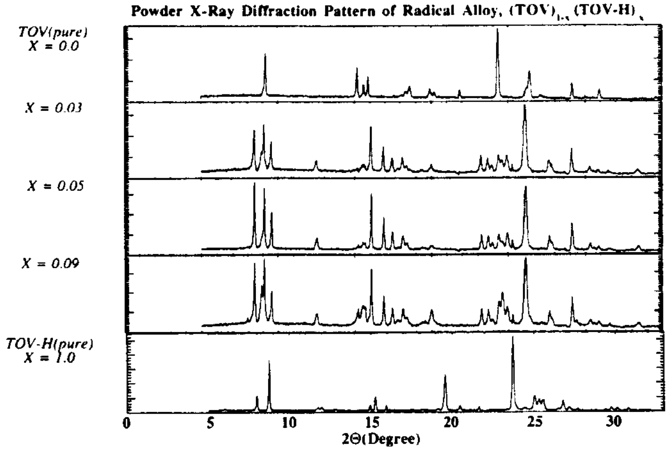

FIGURE 4 : Powder X-ray diffraction pattern of $(TOV)_{1-x}(TOV\text{-}H)_x$ radical alloy, x= 0.0 ~ 1.0, at room temperature.

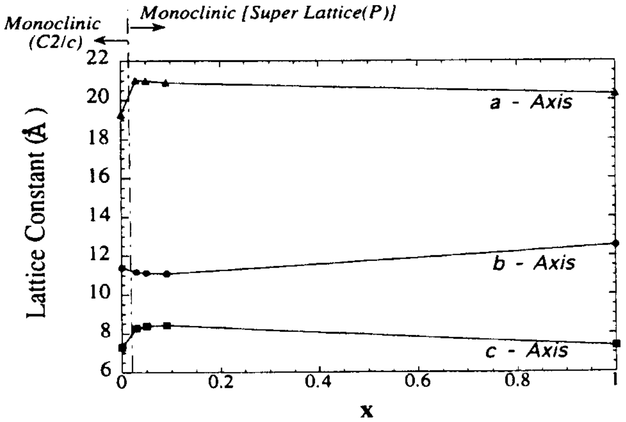

FIGURE 5 : Lattice constants as a function of alloying rate for TOV radical alloy crystals.

where the first and second terms represent the contributions from the ferromagnetic exchange interaction and antiferromagnetic one, respectively, whose fractions are given by $f_1(\mathrm{x})$ and $f_2(\mathrm{x})$. $M_{\mathrm{ferro}}(H)$ is given by $M_{\mathrm{ferro}}(H) = Ng\mu_B S\,\mathrm{B}(y)$, with S=1/2 and g = 2.0023, where B(y) is :

$$\mathrm{B}(y) = \tanh(y), \quad y = \frac{g\mu_B S}{kT}(H + N_W M) \qquad (2),$$

where N_W is the molecular field constant and k is the Boltzman constant. The magnetization curve, $M_{\mathrm{x}=0.0}(H)$, of pure TOV radical crystal (x = 0.0) has shown saturation value around H_c = 32 T, and the extrapolated magnetization curves, $M(\mathrm{x}, H)$, of the radical alloys above 24 T reach to the saturated value of 1.0 μ_B around the same field as the pure TOV. Therefore, the $M_{\mathrm{antiferro}}(H)$ was estimated from experimental magnetization data of the pure TOV radical, $M_{\mathrm{antiferro}}(H) = M_{\mathrm{x}=0.0}(H)$. The results calculated by using Eq. (1) reproduce well the general features of the experimental data for x = 0.03, 0.05 and 0.09, as shown by the solid curves in Fig. 3. The AFM exchange interaction in pure TOV crystal (x = 0.0) with a negative value for exchange integral estimated from high field magnetization (zJ/k_B = -21.6 ± 2 K) has changed drastically to FM exchange interaction in the TOV radical alloy crystals, by small amount of dopant (x = 0.03), with a positive value for FM exchange integral estimated from high field magnetization, (zJ/k_B = +3.5 ± 0.5 K). The estimated FM exchange integral for the radical alloys with x = 0.05 and 0.09 are +3.4 K and +3.5 K, respectively. Based on the proposed two terms model, the matrix part of the radical alloy shows FM exchange interaction and the terminal radical spins close to the TOV-H molecules add a small amount of AFM exchange term. By increasing the alloying rate, x, the FM term has been decreased from 92% to 65%, and the AFM part has been increased from 8% to 37%, non-linearly, for x = 0.03 and 0.09, respectively. This non-linear changing of the FM and AFM parts by increasing alloying rate indicates that the AFM type exchange in the TOV radical alloy crystals operates between terminal spins, and it is also proportional to the number of nearest terminal spin pairs on the edge of the ferromagnetic matrix, which is estimated to be non-linear function.

In order to study the effect of inter-molecular space expansion on the mechanism of organic radical magnetism the measurements of the powder X-ray diffraction pattern, as well as the magnetization, have been carried out in powder samples of the TOV radical alloys, $(TOV)_{1-x}(TOV\text{-}H)_x$ (x = 0.0, 0.03, 0.05, 0.09 and 1.0). Lattice cell parameters and Miller Indices for all peak lists of the TOV radical alloys have been simulated by applying the STOE program, which includes Werner's trial-and-error indexing algorithm[8] for all crystal systems except for triclinic. All samples with x > 0 are successfully indexed in the superlattice monoclinic crystal system, and Fig. 5 shows that by the small amount alloying of TOV-H a drastic change of intermolecular spacing happens. In fact, the X-ray diffraction patterns of the radical alloys with x = 0.03 ~ 0.09 show that the intermolecular distance along the *c* - axis, in which the nearest neighbor distance is shorter than that in other directions, elongates about 15% and the lattice constants are almost independent of x in this concentration range. This remarkable change of molecular packing of the TOV radical alloy is considered to induce the drastic antiferro/ferro change of magnetic interaction in the TOV radical alloy system.

To explain the positive FM interaction for TOV radical alloy system, we note that, first, the intermolecular distance expansion in TOV radical alloy, due to alloying with TOV-H molecule, decreases the SOMO- SOMO direct overlap. Second, as a result of the X-ray diffraction patterns, the molecular packing and electronic state of the TOV radical in radical alloy crystals are different from pure sample. On the other hand, the McLachlan molecular orbital calculation[9] for pure TOV crystal gives the distribution of the spin density as the $S=1/2$ spin mainly delocalized among four nitrogen atoms, but also yields nonvanishing spin densities with alternative positive and negative signs on the C(3)-phenyl ring of the radical. Then, it is expected that the spin density product term, or so called McConnell[10] term, operates as a dominant part for effective magnetic exchange interaction in TOV radical alloy, and brings about the positive FM interaction due to products of spins with different signs. In fact, the McConnell's model says that the effective exchange interaction between two radicals can be ferromagnetic type, if the spin destiny product be negative. Besides, it is worthy to recall that the crystal shrink effects in the pressurized

TOV radical crystal (x = 0.0) has been studied by Mito *et al.*[6], at the pressure around 10 kbar, and the interlayer AFM interaction became more stronger by increasing the pressure, and this result indicates that the molecular orbital direct overlap terms is dominant for the AFM of pure TOV radical crystal. In summary, we measured magnetic susceptibilities, high field magnetizations and powder X-ray patterns of the TOV radical alloys to investigate the drastic antiferro/ferro change of magnetic exchange interactions in radical alloy systems due to intermolecular distance expansion.

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References

[1] M. Kinoshita, *Jpn. J. Appl. Phys.*, **33,** 5718 (1994).
[2] See, for example, K. Mukai, M. Nuwa, K. Suzuki, S. Nagaoka, N. Achiwa, and J.B. Jamali, *J. Phys. Chem. B* **102,** 782 (1998).
[3] K. Yamaguchi and T. Fueno, *Chem. Phys. Letters* **159,** 465 (1989).
[4] M. Okumura, K. Yamaguchi, M. Nakano, and W. Mori, *Chem. Phys.Lett* **207,** 1 (1993).
[5] (a) R.K. Kremer *et al., Chem. Phys. Letters* **230,** 255 (1994). (b) M. Mito *et al., J. Phys. Soc. Jpn.* **66,**2147 (1997). (c) J.B. Jamali *et al., J. Mag. Mag. Mater.,* **177–181,** 789 (1998).
[6] M. Mito, M. Hitaka, T. Kawae, K. Takeda, K. Suzuki, and K. Mukai, this proceeding in press.
[7] F.A. Neugebauer, H. Fischer, and C. Krieger, *J. Chem. Soc. Perkin Trans* **2,** 535 (1993).
[8] P.E. Werner, L. Eriksson, and M. Westdahl, ***J. Appl.Cryst*** **18,** 367 (1985).
[9] A.D. McLachlan, *Mol. Phys.* **3,** 233 (1960).
[10] H.M. McConnell, *J. Chem. Phys.* **39,** 1910 (1963).