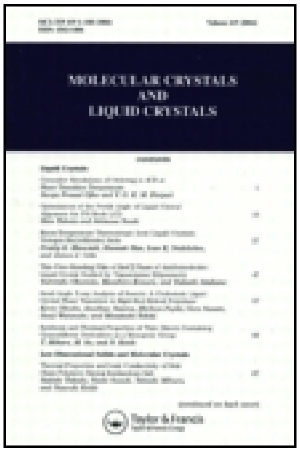

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# MAGNETISM OF AN ORGANIC RADICAL CRYSTAL WITH WEAK FERROMAGNETIC MOMENT BELOW 5.4 K

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Abstract From the measurements of magnetic susceptibility, heat capacity, magnetization and EPR, the magnetism of the organic radical crystal of 1,3,5-triphenyl-6-oxoverdazyl is revealed to be descrived by a two-dimensional quantum Heisenberg antiferromagnet with the effective intra-plane exchange interaction $J/k_{\mathrm{B}}=-4.3$ K. The appearance of weak ferromagnetic moment is observed below 5.4 K. The magnetic susceptibility, however, shows its broad maximum around 2 K and decrease toward the low temperatures. These results are shown to be described by a four-sublattice model with two Dzyaloshinsky-Moriya vectors of opposite sign on the ac-plane. A proposal is made for crystal symmetry in which weak ferromagnetic moment is stabilized without direct ferromagnetic interactions.

## INTRODUCTION

Genuine organic radical crystals are interested not only in the field of material science, but in physics of quantum statistics. Their crystal structures often offer magnetically ideal low-dimensional lattices, and unpaired electrons on the molecular orbitals contribute to bring about intermolecular interactions expected in the isotropic

Heisenberg spin system with $S=1/2$. Experimental check of quantum statistics has been quantitatively studied for various model systems, such as one-dimensional Heisenberg organic ferromagnets in magnetic fields, for example.[1] On the other hand, the discovery of high $T_c$ superconductors of $La_2CuO_4$ series has revived interest in the study of quantum spin correlations on two-dimensional (2-d) lattices. Ground state properties and thermodynamic quantities such as spin correlation length for the 2-d antiferromagnet with $S=1/2$ have been investigated theoretically.[2-8] The corresponding experimental study for the correlation length is limited to the paramagnetic state of $La_2CuO_4$ series with the high ordering temperature.[9,10]

In this paper, we report magnetism of another 2-d quantum antiferromagnet of genuine organic radical crystal, 1,3,5-triphenyl-6-oxoverdazyl (TOV), in which the development of spin correlations is examined from thermal and magnetic properties at low temperatures, as well as from the temperature dependence of weak ferromagnetic moments of this system. The appearance of the weak-ferromagnetic moment around the temperature nearly equal to the dominant "antiferromagnetic" interactions is explained from the structural symmetry and the Dzyaloshinsky-Moriya (D-M) interactions. A new strategy is proposed to realize weak ferromagnetic moment without direct ferromagnetic interactions.

## EXPERIMENTALS

The crystal of TOV was synthesized according to the procedure reported.[11] The outer shape of the crystal was slender like a needle along the c-axis. With the limited amount of available sample (0.4483 gr), the experimental ambiguity of the intrinsic heat capacity (adiabatic method) became relatively large above 10 K when compared to that of addenda. However, below 5 K, where the characteristic broad maximum of the heat capacity appeared, the magnetic heat capacity was reasonably obtained down to 0.6 K. The ac magnetic susceptibility was measured with two types of Hartshorn bridge depending on the temperature ranges 2.1 K-150 K and 0.7 K-10 K. In the later temperature range, the heat capacity measurement mentioned above was simultaneousely performed with the ac susceptibility measurement in external fields. A SQUID magnetometer was employed for the magnetization measurement at 2.0 K and 3.0 K. At the present stage of synthesis, only a small single crystal was available for the experiment of EPR at X-band.

## RESULTS AND DISCUSSION

### Crystal structure and possible magnetic interactions

Prior to the discussion of the present results, it is helpful to give details of the crystal structure determined by Neugebauer et al..[11]The crystal structure of TOV belongs to the space group $C_{2/c}$ with the lattice parameters a=19.213Å, b=11.392Å, c=7.304Å and $\beta$=90.72°. The molecular structure of TOV and its molecular packing are shown when viewed down on the bc-plane in Figure 1. There exists inversion center between adjacent molecules on A- and B- sublattices along the c-axis, and translation symmetry on A- and/or B- sublattices along the a-axis. The McLachlan molecular orbital calculation gives larger spin density on centered verdazyl nitrogens and small but significant value on two phenyls connected to the nitrogens. The overlapping of molecular orbitals of $\pi$-electrons along the b-axis is expected to be much weaker than in the ac-plane, giving negligible magnetic interactions along this direction.

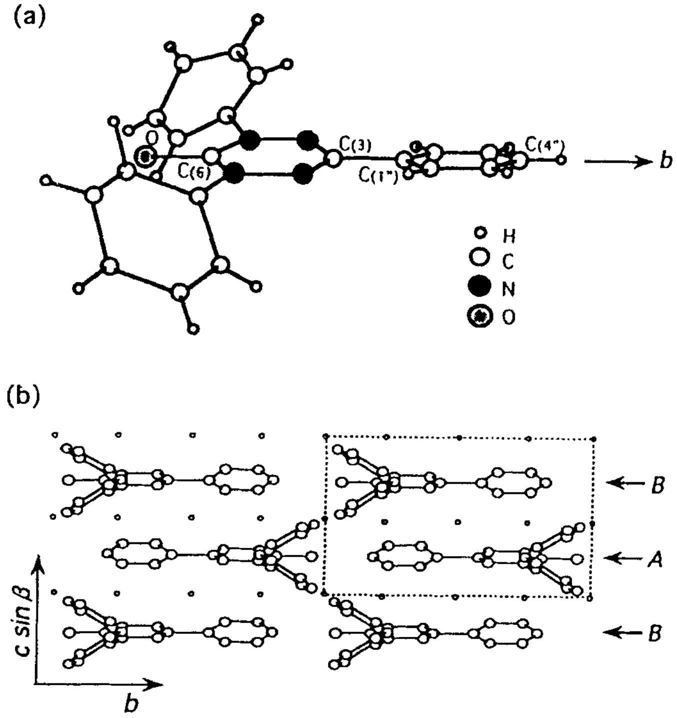

FIGURE 1 Molecular structure of TOV(a) and molecular packing projected on the bc-plane (by F. A. Neugebauer et al.[11]).

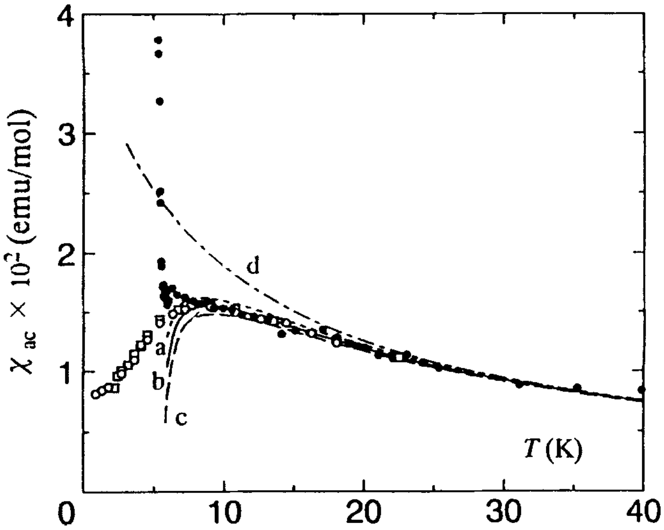

FIGURE 2 Experimental results(black points) of the ac susceptibility of TOV. Solid curves represent the theoretical results of HTSE for $|J|/k_B$ = 4.5±0.5 K. The results by the Quantum Monte Carlo[4] and the mean field theory are given by open marks and the broken curve(d), respectively.

## Characteristic properties of 2-d Heisenberg model with $S$=1/2

The present experimental results on TOV crystal are summerized as folows:

(1) The inverse susceptibility at higher temperature above 30 K obeys the Curie-Weiss law with the negative Weiss temperature $\Theta$=−9.9 K, and the Curie constant C=0.375 emu·K/mol for $S$=1/2 and $g$=2.00. In the framework of molecular field theory, $\Theta$ is geven by

$$\Theta = 2z|J|S(S+1)/3k_B. \qquad (1)$$

Assuming that the magnetic correlations are dominant on the ac-plane with the coordination number z=4, we may estimate an effective exchange constant $|J|/k_B$ = 4.5 K. Below 30 K, the susceptibility $\chi$ deviates from the Curie-Weiss law and is reproduced by the theory for the high temperature series expansion for the $S$=1/2 2-d antiferromagnetic Heisenberg system with $|J|/k_B$=4.5 K down to 9 K(Fig.2), where the theory shows the broad maximum.[12] The susceptibility for the lower temperatures gradually increases as shown in Figure 3 giving a very high and round maximum around 2 K.

(2) The magnetic heat capacity of TOV crystal is shown also in Figure 3. The characteristic broad maximum of the 2-d Heisenberg system appears around 5 K which is reproduced by the high temperature series expansion[12] with $|J|/k_B$=4.3

K for $T \geq 5$ K. The quadratic temperature dependence of low temperature heat capacity is also explained by the spin wave theory for 2-d antiferromagnet with $|J|/k_B = -4.3$ K.[13] The quantum spin wave theory for $S=1/2$ gives $|J|/k_B = -3.7$ K.[14] The overall behavior of the results are also in agreement with the quantum Monte Carlo simulation for 2-d antiferromagnet.[4]

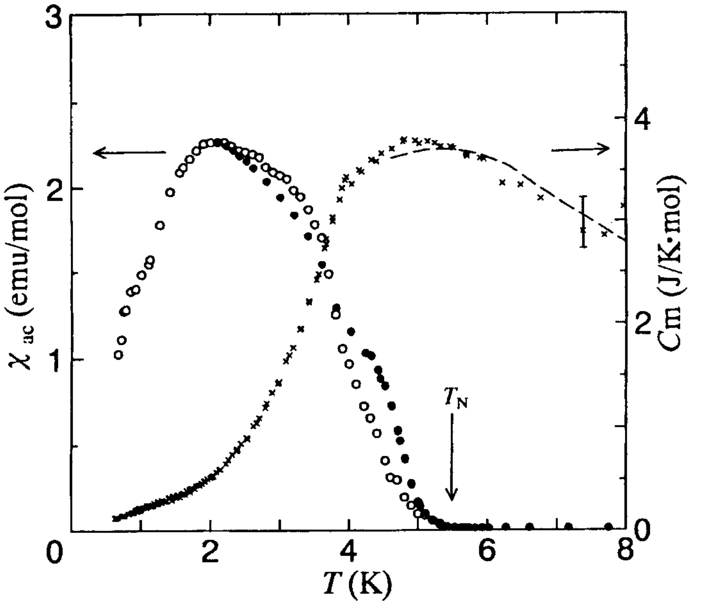

FIGURE 3 Magnetic susceptibility (open and closed circle) and magnetic heat capacity (cross) of TOV crystal.

(3) The peak-to-peak linewidth of the EPR at 4.2 K shows the characteristic angular dependence of $(3\cos^2\theta - 1)^2$ for the 2-d Heisenberg antiferromagnet, as well as the Lorentzian line shape of the EPR just around the magnetic angle of $\theta = 54°$.[15] The temperature dependence of $g$-shift for the three crystal axes is observed, which is also expected in the 2-d Heisenberg antiferromagnet as in $K_2MnF_2$.[16]

## A model for weak ferromagnetism of TOV crystal

The appearance of weak ferromagnetic moment in the present compound is reported by R. K. Kremer et al. and J. B. Jamali et al..[17] We have also observed spontaneous magnetization at 2 K and 3 K, which is given by $M(H,T)=M(0,T)+\chi H$ with a spontaneous magnetization $M(0,T)$. These results show the spontaneous magnetic moment increases below 5.5 K, as the enhancement of magnetic susceptibility as shown in Figure 3.

Here we discuss the anomalous temperature dependence of susceptibility of TOV based on the interplay of the Dzyaloshinsky-Moriya interaction and the development of spin correlation length on the ac-plane, since the other effects are expected minute. Taking the crystal symmetry and experimental results into consideration, we may consider a four-sublattice model as in Figure 4. A- and B-sublattices alternatively locate along the c-axis (See Figures 1 and 2). The middle point of $\boldsymbol{S}_i^{\mathrm{A}}$ and $\boldsymbol{S}_i^{\mathrm{B}}$ is the inversion center, and then the D-M interaction is prohibited between them. While, we assume the D-M vector $\boldsymbol{D}_{ij}^{\mathrm{A}}$ and $\boldsymbol{D}_{ij}^{\mathrm{B}}$ between adjacent two spins on the same sublattices. First, we suppose $\boldsymbol{D}_{ij}^{\mathrm{A}} = \boldsymbol{D}_{ij}^{\mathrm{B}}$, though this is not the present case, then the spin arrangement(b) is stabilized under the condition

$$\boldsymbol{D}_{ij} \cdot (\boldsymbol{S}_i \times \boldsymbol{S}_j) = \boldsymbol{D}_{ji} \cdot (\boldsymbol{S}_j \times \boldsymbol{S}_i). \tag{2}$$

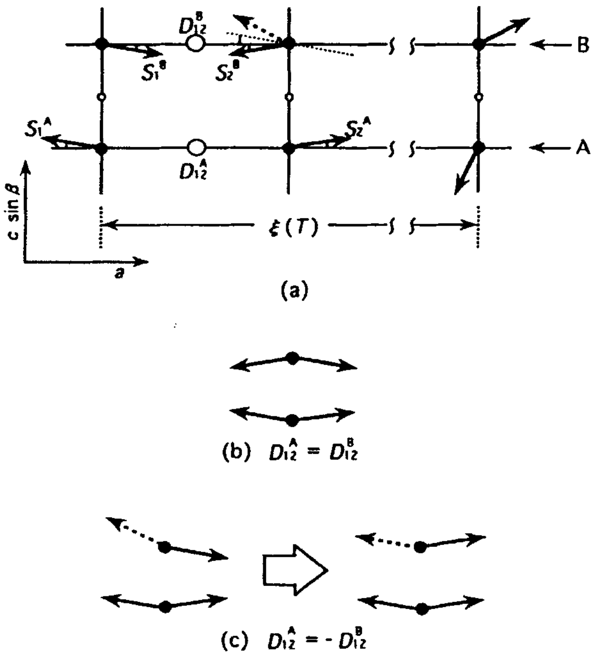

FIGURE 4 Four sublattice model with inversion center and the Dzyaloshinsky -Moriya vectors along the c- and a- axces, respectively (a). $\xi(T)$ is a measure of the system size or spin correlation length on the ac-plane. The net magnetic moment cancels for the D-M vectors $\boldsymbol{D}_{12}^{\mathrm{A}} = \boldsymbol{D}_{12}^{\mathrm{B}}$ (b), whereas it does not for the opposit sign (c).

In this case the net magnetic moment does not appear. In the case $\boldsymbol{D}_{\rm ij}^{\rm A} = -\boldsymbol{D}_{\rm ij}^{\rm B}$(c), which is possible in the TOV crystal, there remains canting moment. However, when we extend the system size $\xi(T)$ along the a-axis under the condition mentioned above the net moment for each sublattice rotates depending on the canting angle, and the bulk magnetization may disappear in the limit of $\xi(0) \rightarrow \infty$ for $T \rightarrow 0$, vanishing magnetic susceptibility, as well.

The canting angle $\phi$ of TOV is estimated much smaller than one degree from the magnetization curve measured at 2 K and 3 K, and also from ref.17. With such a small $\phi$, however, the large system size $\xi(T)$ is necessary for $\chi$ and/or the total moment to vanish. That is, $\chi$ and/or magnetic moment reflect the development of $\xi(T)$ in the region $\xi(T) \ll \pi/\phi$. The system size or spin correlation length is evaluated theoretically, for the 2-d quantum antiferromagnet, which gives $\xi(T) \simeq 20 \sim 30(5)$ lattice sites at $k_{\rm B}T/|2J| \simeq 0.23$ (1.0), which corresponding to $T \simeq 2$ K for $|J| \simeq 4.3$ K.[5,8,10]

The present analysis gives a possibility to realize weak ferromagnet by introducing inversion center and two D-M vectors of opposite sign between adjacent radical molecules as in Figure 4, without introducing direct ferromagnetic interactions. The weak ferromagnetic moment becomes dominant if we can synthesize the system with $\xi = 2$,or a ladder model,of the same crystal symmetry mentioned above. It will appear around the temperature corresponding to the dominant antiferromagnetic interaction along the ladder, althogh heuristic properties are expected at the lowest temperatures for quantum ladder systems.[18]

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