Magnetic Two-dimensionality and Antiferromagnetism in the DANO Crystal

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An organic free radical crystal, the di-*p*-anisyl nitric oxide (DANO) crystal, was found to exhibit the characteristics of the two-dimensional Heisenberg spin system in its magnetic susceptibility at low temperatures and in its angular dependence of the ESR line width at room temperature. A distinct minimum of magnetic susceptibility due to a phase transition to antiferromagnetic spin ordering was observed at 1.67 K; this is consistent with the results of the NMR measurements, while another unexplainable anomaly was found near 2.7 K. The magnetic anisotropy field, H_A, along the a-axis, perpendicular to the magnetic easy-plane, was determined to be $(3\pm1)\times10^2$ Oe at 0 K from the analysis of the antiferromagnetic resonance; it was attributed to the magnetic field originating from the spin magnetic dipoles distributed over the radical molecules. The ratio of the anisotropy field to the exchange field within the magnetic two-dimensional plane, H_A/H_E, and that of the Néel temperature to the Weiss temperature, T_N/θ, were found to be 5×10^{-3} and 0.34 respectively. The ratio of the inter-plane exchange interaction to the intra-plane one, J'/J, was estimated therefrom to be of the order of 10^{-3}.

Recently, a number of magnetic studies of organic free radical crystals have been performed in spite of difficulties in the purification of the samples and the complexity of the structure; these studies have revealed the magnetic-ordering phenomena at low temperatures in some typical crystals.[1-4] Above the magnetic-ordering temperatures they generally exhibit the characteristics of low-dimensional magnetic systems.[5-8] The low-dimensional characteristics of these organic radical crystals are a consequence of the crystal structures with a pile of plane radical molecules. The magnetic moment originates from an unpaired electron spin in a 2pπ-orbital stretched perpendicularly to the molecular plane. When each molecule is stacked plane-to-plane in the crystal, an unpaired electron spin interacts magnetically with those of only a few neighboring molecules through an overlapping of the 2pπ-orbitals; this causes the low-dimensional magnetic characters of these organic radical crystals.

The magnetically one-dimensional systems[5-8] have been extensively studied in organic radical crystals. Radical crystals with a two-dimensional character can be formed only under favorable conditions with regard to the crystal structure. These crystals, if ideal, can be expected to show interesting magnetic behavior; that is, as is well known, the ideal two-dimensional Heisenberg spin system cannot exhibit a long-range ordered state. In the real systems, a small deviation from the ideal system, such as the existence of a weak anisotropy and/or of interlayer interaction, gives rise to three-dimensional ordering at a finite temperature.[9]

The crystal of the di-*p*-anisyl nitric oxide radical, $(CH_3OC_6H_4)_1NO$ (hereafter abbreviated to DANO), may be possibly regarded as a two-dimensional magnetic system, judging from its crystal structure[10] and from thermal and magnetic properties of the powdered sample studied by Duffy *et al.*[11] However, they found a weak anomaly around 2.7 K and ascribed it to the three-dimensional magnetic ordering. Recently, we also found that the DANO crystal undergoes the antiferromagnetic transition at 1.67 K from the results of NMR measurements of its single crystal.[12] The cause of the magnetic phase transition in this crystal was not clarified in the previous study.

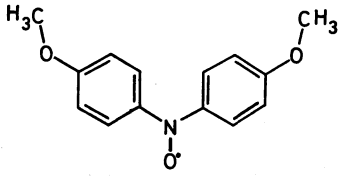

Fig. 1. DANO.

This paper will deal with the results of magnetic susceptibility and ESR measurements of powdered and single crystal of DANO. The measurements were undertaken in order to examine the magnetic two-dimensionality and to study the magnetic ordering of this crystal.

Structural Consideration

The DANO radical shown in Fig. 1 is a nitroxide radical. The ESR[13] and ENDOR[14] spectra of the DANO in solution revealed that the unpaired electron is distributed mainly on a 2pπ-orbital of the N–O group and partially on 2pπ-orbitals of the two phenyl rings. The 2pπ-orbital of the N–O group is stretched perpendicularly to the plane made of the –C–NO–C– group.

An X-ray analysis of the DANO crystal by Hanson[10] showed that the crystal structure belongs to the orthorhombic space group Aba2 and that a unit cell with four molecules has dimensions of $a=7.33$ Å, $b=26.8$ Å, and $c=6.25$ Å. Ignoring the twist of the two phenyl rings, it can be said that all the molecules in the unit cell occupy crystallographically equivalent sites and make the plane formed by the –C–NO–C– group parallel to the bc-plane and the axis of the N–O bond to the c-axis, resulting in the 2pπ-orbital of the N–O group being stretched along the a-axis. The distances from an N-atom to the first, second, and third nearest neighboring molecules in the ac-plane are 4.8 Å, and 6.2 Å, and 7.3 Å respectively. The layer of the molecules parallel to the ac-plane is separated from the adjacent one by 13.4 Å. Figure 2 is a schematic drawing of the crystal structure, which is simply assumed to be face-

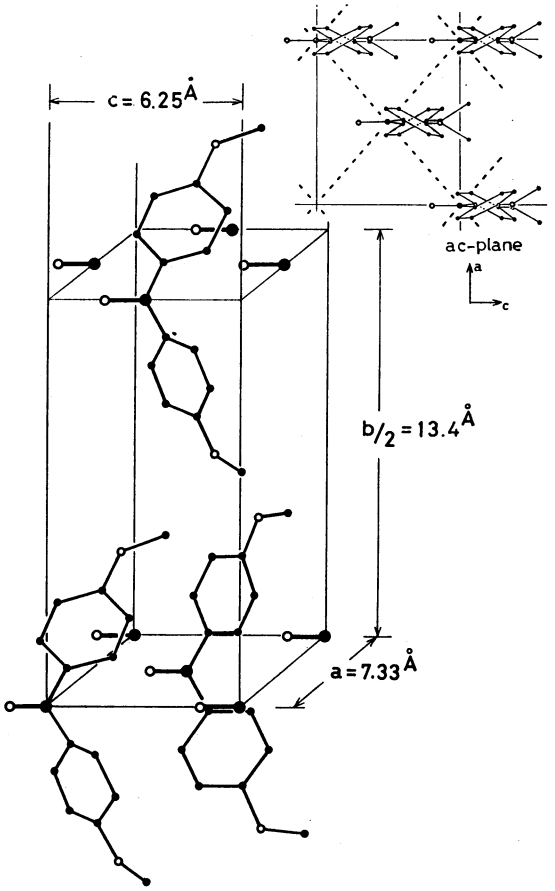

Fig. 2. Crystal structure of DANO crystal. The inset shows the projection to (010) plane.

centered orthorhombic.

Generally, the overlapping of the orbitals of magnetic electrons gives a measure of the magnitude of the exchange interaction. One can assume from the above-mentioned directional configuration of the 2pπ-orbital of the N–O group that the magnitude of the exchange interaction with nearest neighbors much exceed those with the second and the third nearest neighbors in the ac-plane, while the exchange interaction between the ac-planes is much weaker than those in the ac-plane. As a consequence, the DANO crystal may be regarded as forming a two-dimensional magnetic lattice with a nearly quadratic network.

Experimental

Fine copper-colored powder of the DANO crystal was synthesized by the method of Meyer *et al.*[15] After it has been recrystallized several times from ethanol, dark brown platelets with (010) crystal faces were obtained. Elementary analysis gave these values: C, 68.92; H, 5.79; N, 5.75% (calcd: C, 68.84; H, 5.79; N, 5.73%). Its crystallographic axes were determined with a polarized microscope.

The magnetic susceptibility was measured from 1.55 K to 300 K by means of a magnetic torsion balance[16] under magnetic fields of 8 kOe to 11 kOe, calibrated with that of Mn–Tutton salt. The ESR absorptions were observed by means of a conventional spectrometer with operating frequencies of 9.5 GHz and 35.5 GHz. The magnetic field was calibrated using Mn^{2+} doped in MgO (1/2000) after correction by DPPH recrystallized from ether (g=2.0036).

Results

Magnetic Susceptibility. At high temperatures, the magnetic susceptibility of a powdered sample obeys the Curie–Weiss law $\chi=C/(T-\theta)$, with $\theta=-4.9\pm0.3$ K and $C=0.377$,* determined in the temperature range between 300 and 63 K; from these results the radical concentration was evaluated to be more than 97%. The diamagnetic correction, -1.35×10^{-4} emu/mol, estimated from Pascal's law[17] was used in this evaluation.

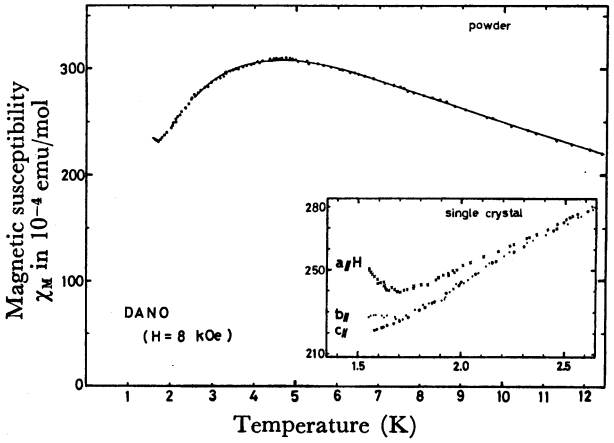

Fig. 3. Temperature dependence of the magnetic susceptibility of DANO crystal. Solid line indicates the results of the HTS calculation for $J/k=-2.45$ K.

With a lowering of the temperature, a broad maximum of the magnetic susceptibility, $\chi_{max}=304\times10^{-4}$ emu/mol, appears at 4.6 ± 0.2 K, as is shown in Fig. 3. Besides a vague anomaly near 2.7 K, reported by Duffy *et al.*,[11] a distinct minimum of the magnetic susceptibility was observed at 1.67 ± 0.02 K.

The inserted figure in Fig. 3 shows the magnetic susceptibility of a single crystal along three crystallographic axes. On account of inaccuracy in the sample weight, the observed values were scaled to that of the powdered sample at 4.2 K; the correction for the diamagnetic anisotropy, less than -1.1×10^{-4} emu/mol, was neglected. The susceptibility is clearly anisotropic below about 2.5 K, and only the susceptibility along the a-axis exhibits a distinct minimum at 1.67 K. This minimum in susceptibility of the single crystal can not be attributed to the origin in impurity but is attributable to the existence of the magnetic ordering of spins.

ESR Absorption. The ESR absorption of a single crystal was measured in order to study variations in the g-value and in the linewidth between 1.3 K and 300 K. Only a single absorption line was observed in the field from 0.5 kOe to 13.0 kOe at all temperatures. At room temperature the g-tensor coincides with that of the isolated radical,[18] and its principal

* The small disagreement between the θ, C, and χ_{max} values in the present work and those in Ref. 11 is probably due to the existence of an impurity, judging from the fact that, in the latter, the authors used a fitting parameter of magnetic susceptibility; p=0.93 or 0.95.

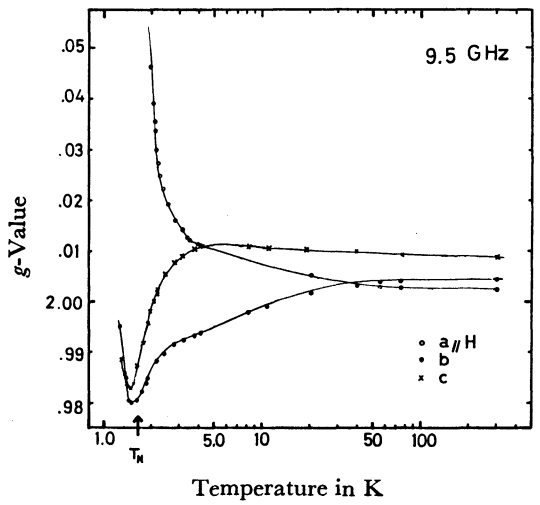

Fig. 4. Temperature dependence of g-values.

axes are parallel to the crystal ones. The g-value shown in Fig. 4 is strongly dependent on the temperature but not on the sample size. Above 2 K, the g-values observed at 9.5 GHz and 34.4 GHz are in agreement with each other within an error of ± 0.0002, and they shift monotonically with the temperature. Below 2 K, but above T_N, a marked shift of the g-value was observed; this is attributable to the shortr-ange magnetic ordering, as has been demonstrated for typical one-dimensional antiferromagnets.[19]

At room temperature the line width shows its maximum when the external field, H_0, is applied parallel to the b-axis and shows its second extremum when H_0 is applied parallel to the a- or c-axes, while it has its minimum value when H_0 and the b-axis make an angle of about 55°, as is indicated in Fig. 5.

Figure 6 shows the temperature dependence of the line width. The line width observed at 9.5 GHz is anomalously broadened up to more than 500 Oe at 1.3 K as compared with the width of less than 20 Oe

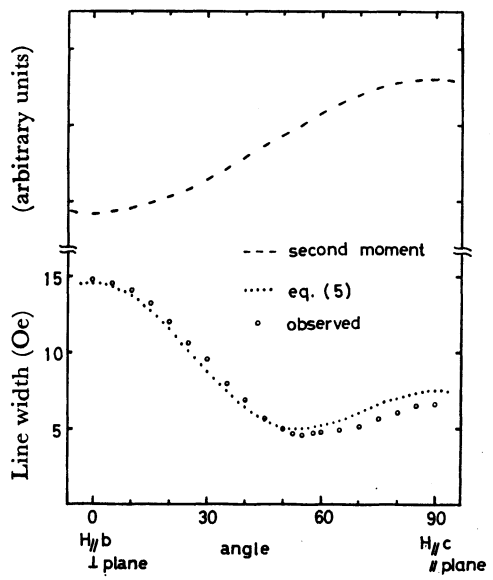

Fig. 5. Angular dependence of ESR line width at room temperature in the bc-plane.

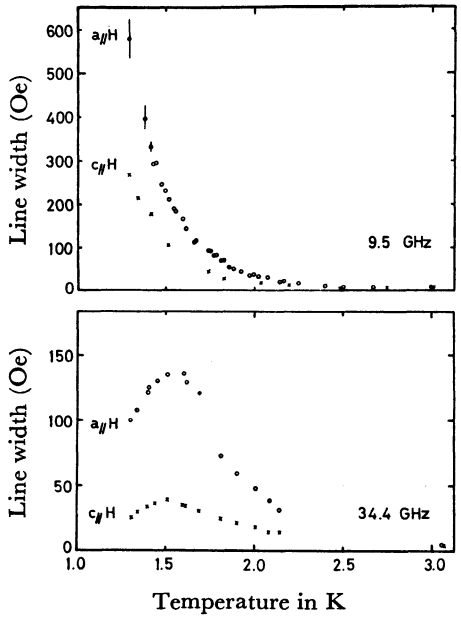

Fig. 6. Temperature dependence of ESR line width at low temperatures measured at a) 9.5 GHz and b) 34.4 GHz.

at 3 K. On the other hand, the linewidth observed at 34.4 GHz shows its maximum at about 1.6 K. With a lowering of the temperature, the absorption line can be observed continuously across the transition temperature, accompanied by a gradual shift of the resonance field although the paramagnetic resonance switches over to the antiferromagnetic resonance (AFMR) at T_N; below this temperature, the resonance position is determined by the AFMR condition.

Discussion

Magnetic Two-dimensionality. The DANO crystal can be expected to be an isotropic two-dimensional antiferromagnetic spin system, with $S=1/2$, coupled with four nearest neighboring spins, on the following grounds: 1) The unpaired electron distributed in the $2p\pi$-orbital has a spin with $S=1/2$. 2) As the observed g-tensor is almost isotropic and is nearly equal to that of the free electron, the magnetic exchange interaction is considered to be approximately isotropic, that is, of the Heisenberg type. 3) From structural considerations, the radical spins may be supposed to interact predominantly with those in the two-dimensional plane. 4) The dominant exchange interaction, J, within the two-dimensional plane is considered to be negative, judging from the negative Weiss temperature.

According to the high-temperature-series expansion (HTS) method applied to the two-dimensional Heisenberg spin system, the magnetic susceptibility is expanded as a function of $x=kT/2JS(S+1)$ as;

$$Ng^2\mu_B^2/\chi\cdot|J| = 3x + \sum_n C_n/x^{n-1} \quad (n=1, 2, \cdots) \qquad (1)$$

where C_n are the HTS coefficients.[20,21] By utilizing the first ten terms for the $S=1/2$ system, the broad maximum in the curve of the magnetic susceptibility *versus* the temperature can be reproduced. The

temperature of the susceptibility maximum, T_{max}, and the maximum value of the susceptibility, χ_{max}, are, respectively, given as;[22]

$$\left.\begin{aligned} kT_{max}/|J|\cdot S(S+1) &= 2.53\pm 00.5 \text{ for } S=1/2 \\ \chi_{max}\cdot|J|/Ng^2\mu_B{}^2 &= 0.0469\pm 0.0001. \end{aligned}\right\} \quad (2)$$

The combination of these two equations gives a parameter independent of J;

$$\chi_{max}\cdot T_{max}/C = 0.356. \quad (3)$$

The observed values, $\chi_{max}=304\times 10^{-4}$ emu/mol and $T_{max}=4.6\pm 0.2$ K, yield $\chi_{max}\cdot T_{max}/C=0.36\pm 0.01$, which is consistent with the two-dimensional character of the DANO crystal. The solid line in method for Fig. 3 shows the susceptibility calculated by the HTS $J/k=-2.45$ K. In the temperature range of $T>0.9\cdot S(S+1)\cdot|J|/k$, where the HTS method is valid, the present model explains satisfactorily the magnetic susceptibility of the DANO crystal. In the molecular-field theory, the Weiss temperature is given by;

$$\theta = (2/3)\cdot z\cdot S(S+1)\cdot J/k, \quad (4)$$

which yields $J/k=-2.45\pm 0.1$ K, in excellent agreement with the value obtained by the HTS method.

In the recent ESR studies, the effects of magnetic low-dimensionality on the line width have been the topics of great interest.[23] Experimental studies have revealed that, in the two-dimensional system, the angular dependence of the ESR line width, ΔH, at high temperatures cannot be explained by either the three-dimensional-exchange narrowing theory or the dipolar width obtained by the second moment, but is roughly of the form:[24]

$$\Delta H = A(3\cos^2\varphi - 1)^2 + B. \quad (5)$$

Here φ is the angle of the external magnetic field with respect to the normal direction of the two-dimensional plane. The angular dependence of this form was interpreted successfully by the theory taking into account the spin diffusion in the plane.[25] The theory predicts that the angular dependence observed in the two-dimensional system is different from both that in the one-dimensional system and that in the three-dimensional system. In Fig. 5 the angular dependence calculated from Eq. (5) and the dipolar width obtained by the second moment are compared with the line width in the ab-plane observed at 9.5 GHz. Hence, the angular dependence of the line width observed here indicates the two-dimensional characteristics of the magnetic system.

Antiferromagnetism and Magnetic Anisotropy. To investigate the ordered state of the DANO crystal, the results of ESR measurements in 34.4 GHz at 1.39 K ($T/T_N=0.83$) are discussed in terms of the antiferromagnetic resonance (AFMR).[26] The AFMR in an organic free radical crystal was recently reported with regard to the *p*-Cl-BDPA crystal,[27] in which the AFMR was observed in the vicinity of the paramagnetic resonance field because of the very small magnetic anisotropy in contrast with the cases of the antiferromagnets of ionic crystals.[26] In the case of the DANO crystal, the resonance field begins to shift remarkably around 2 K and finally shifts to almost 1 kOe at 1.3 K,

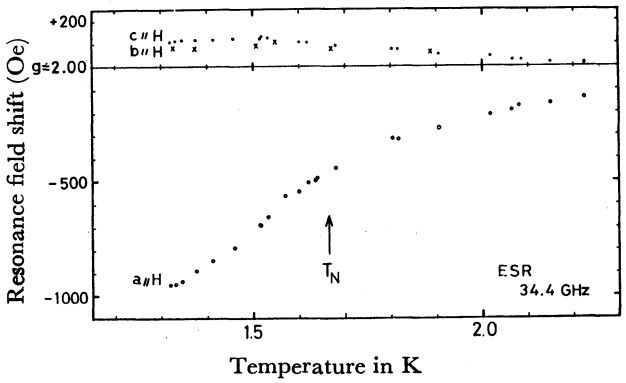

Fig. 7. Temperature dependence of the resonance field at 1.39 K measured at 34.4 GHz.

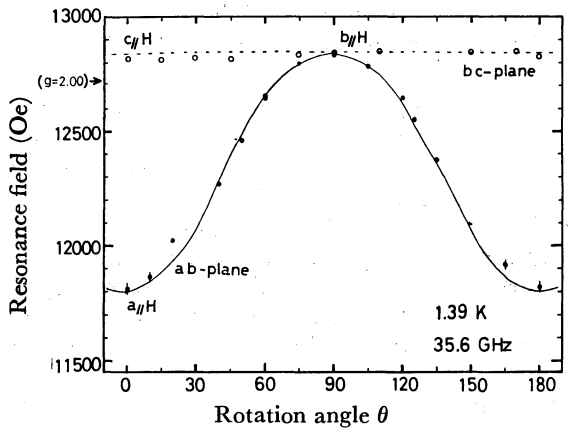

Fig. 8. Angular dependence of AFMR line field at 1.39 K measured at 34.4 GHz.

but no indication of anomaly appears at $T_N=1.67$ K, as is shown in Fig. 7. Fig. 8 shows that the resonance field at 1.39 K has predominantly a uniaxial symmetry around the a-axis and takes the minimum field along the a-axis. The downward shift of the resonance field in the a-axis suggests that this axis is perpendicular to the spin-easy axis.[26] The most remarkable feature of the DANO crystal is the following; its AFMR is observed continuously on the rotation of the external field from the spin-easy axis to the spin-hard axis, indicating the absence of spin flipping; this is confirmed by magnetic torque measurements.[28] These results can be understood reasonably by the model that the DANO crystal is a collinear antiferromagnet with a spin-easy plane perpendicular to the a-axis.[29] It must be noted here that the spin-easy plane (bc-plane) is prependicular to the two-dimensional plane (ac-plane). When the external field, H_0, is applied along the a-axis nearly perpendicular to the sublattice magnetization, the resonance condition is given by:[29]

$$H_0{}^2 = (\omega/\gamma)^2 - C, \quad C = 2H_AH_E, \quad (6)$$

where H_A and H_E are the anisotropy field along the hard axis and the effective exchange field respectively, ω and γ are calculated from the resonance frequency, 34.4 GHz, and $g=2.0055$ as usual.

According to the molecular field theory, $\sqrt{C}$ is in proportion to the sublattice magnetization, M, which is given by the Brillouin function as a function of the

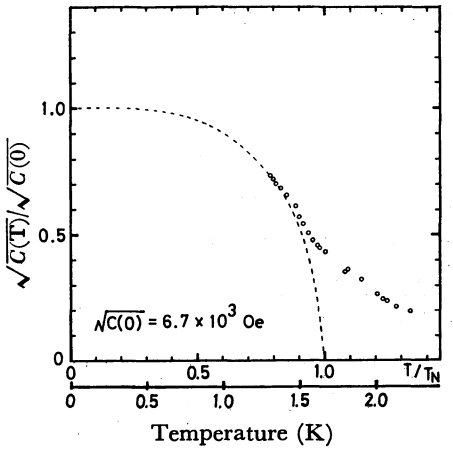

Fig. 9. Temperature dependence of $\sqrt{C}$.

temperature. Figure 9 shows the observed temperature dependence of $\sqrt{C}$ fitted to the Brillouin function for $S=1/2$ at 1.3 K. By the extrapolation of $\sqrt{C}$ along the Brillouin function to $T=0$ K, $\sqrt{C}(0)=(6.7\pm1.0)\times 10^3$ Oe is obtained. In the molecular-field theory, the exchange field is expressed by

$$H_E = 2z|J|\cdot S_z/g\mu_B. \quad (7)$$

Numerical calculations for $z=4$ and $J/k=-2.45$ K yield $H_E=7\times10^4$ Oe at 0 K. From this value, together with $\sqrt{C}(0)$, $H_A=(3\pm1)\times10^2$ Oe at 0 K is obtained.

In the orthorhombic crystals, the magnetic anisotropy energy, F_A, can be generally expressed by the following formula:

$$F_A = (1/2)(K_a\cos\theta_a + K_c\cos\theta_c) \quad (8)$$

where K_a and K_c are the anisotropy constants in the direction of the a-axis and the c-axis respectively with reference to the b-axis. θ_a and θ_c are the angles which the sublattice magnetization makes with the a-axis and the c-axis respectively. Then the effective anisotropy field in each direction, H_A^i, is derived by means of the following equation:

$$H_A^i = K_i/M \quad (i=a, c).$$

In an $S=1/2$ spin system with isotropic-g such as the DANO crystal, the magnetic anisotropy is mainly caused by the magnetic dipolar interaction. The magnitude of the classical magnetic dipolar anisotropy energy was calculated by the direct sum method, taking into account the magnetic dipoles within a diameter of 60 Å. For the examination of the effect of the spin delocalization in the molecule, numerical calculations were performed for the following two cases: 1) the case where the whole magnetic moment ($1\,\mu_B$) is localized at the center of the N–O bond, and 2) the case where the magnetic moment is delocalized over the molecular frame according to the spin density distribution, as calculated by a simple Hückel molecular orbital theory, as is shown in Table 1. In the course of the calculation of the magnetic dipole field, a collinear two-sublattice antiferromagnetic ordering was assumed. The contribution from the spins in the neighboring two-dimensional plane was found to be negligibly small for any spin configuration.

Table 1 summarizes the numerical values of H_A^i.

Table 1. Observed and calculated anisotropy fields with reference to the b-axis in the antiferromagnetic state

	Anisotropy observed from AFMR (Oe)	Dipolar field anisotropy (Oe) Case 1	Case 2
H_A^a	300	216	195
H_A^c	0	106	10

Case 1: spin localized at the center of the N–O bond, Case 2: spin density 0.42 at N, 0.22 at O, 0.06 at *ortho*-C and 0.06 at *para*-C.

In the case 1, the anisotropy field, H_A^c, which should be equal to H_A^a in the case of an ideal quadratic lattice, becomes about 1/2 of H_A^a in the actual lattice shown in Fig. 2. When the delocalization of the spin over the entire molecule is taken into consideration, H_A^a becomes about 1/20 of H_A^a, and the a-axis becomes a unique spin-hard axis (case 2). This corresponds to the experimental result that the system is almost isotropic around the a-axis; *i.e.*, $H_A^c=0$. The observed anisotropies, $H_A=H_A^a=300$ Oe and $H_A^c=0$ Oe, can be approximately explained by the contribution from the magnetic dipoles delocalized over the DANO molecule.

Magnetic Phase Transition. The temperature of the magnetic phase transition of the DANO crystal was determined to be $T_N=1.67$ K from the magnetic susceptibilities of the single crystal and the powdered samples; this value is compatible with the results of the NMR experiments. The resonance-field shift of the ESR spectra, however, shows no anomaly at the transition temperature; thus, no clear distinction was found between the paramagnetic and the antiferromagnetic resonances. This unusual result may be attributed to the well-developed short-range magnetic ordering near T_N. No anomaly was observed either at T_N in the specific heat measurements reported by Duffy *et al.*[11] Bloembergen *et al.* showed that, in the two-dimensional system, the specific heat anomaly is expected to be vanishingly small even if a magnetic ordering occurs as a result of a deviation from the ideal system.[30] The absence of any anomaly at the magnetic-phase-transition temperature in the specific heat and the ESR spectra suggests that the two-dimensionality of the DANO crystal is nearly ideal.

The phase-transition temperature of the two-dimensional system is greatly raised by the interplane exchange interaction, J', and the magnetic anisotropy field, H_A.[9] As a result, J'/J can be evaluated from T_N/θ and H_A/H_E. Table 2 lists the H_A/H_E, T_N/θ, and J'/J

Table 2. Magnetic properties in some two-dimensional magnetic systems with $S=1/2$.

Sample	T_N/θ	H_A/H_E	J'/J
DANO	0.34	5×10^{-3}	10^{-3} a)
Rb_2CuCl_4	0.37	10^{-4}	8×10^{-3}
$Rb_2CuBrCl_3$	0.43	10^{-4}	1.6×10^{-2}

a) Estimated from the data T_N/θ and H_A/H_E of DANO in comparison with those of other samples in this table.

values of some typical two-dimensional magnets with $S=1/2$ listed in a review paper by De Jongh *et al.*,[9] together with those of the DANO crystal. From a comparison of these data, a plausible J'/J value for the DANO crystal is less than 10^{-3}. The three-dimensional magnetic ordering at 1.67 K of the DANO crystal is, therefore, caused by deviations from the ideal two-dimensionality, the existence of J' or H_A, even though these are very small.

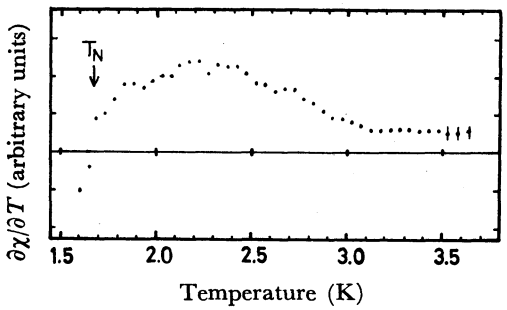

Fig. 10. Temperature derivative of magnetic susceptibility of powdered sample.

Duffy *et al.*[11] assigned weak anomalies in both the magnetic susceptibility and the specific heat near 2.7 K to a three-dimensional magnetic phase transition. In the present experiment, a slight anomaly in the $\partial\chi/\partial T$ spread in the temperature range between 2.4 and 2.9 K was found, as is shown in Fig. 10, while, by the measurements of single crystals, we could hardly detect the anomaly since the accuracy of the measurements is poor for the small single-crystal. In the ESR absorption, nothing anomalous—only a gradual change—was observed at 2.7 K. The shift of the proton-NMR lines also changes gradually and loses its proportionality to the magnetic susceptibility below about 2.7 K. These results do not support the model of the three-dimensional magnetic phase transition at 2.7 K, but they indicate the occurrence of some change, in the short-range magnetic ordering. Further study is necessary to clarify this phenomenon around 2.7 K.

In conclusion, 1) the DANO crystal is an isotropic, nearly two-dimensional spin system with a 10^{-3} ratio of the interplane exchange interaction to the intraplane interaction, 2) the absence of the anomaly in the ESR spectra at T_N is the direct consequence of the short-range magnetic ordering, and 3) the magnetic dipoles distributed over the molecule mainly yield the anisotropy in the ordered state, which orientates the magnetic moment perpendicularly to the a-axis.

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