
Ko-ichi Hiraki*, Yoshiaki Kobayashi**, Toshikazu Nakamura, Toshihiro Takahashi, Shuji Aonuma1, Hiroshi Sawa1, Reizo Kato1 and Hayao Kobayashi2

Department of Physics, Gakushuin University, Mejiro 1-5-1, Toshima-ku, Tokyo 171
1Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo 106
2Department of Chemistry, Toho University, Miyama 2-2-1, Funabashi 274

(Received December 15, 1994)

The antiferromagnetic state of the title compound has been investigated by the measurements of 1H-NMR lineshape and nuclear spin-lattice relaxation rate, T1, on a single crystal sample. Below the Néel temperature, TN = 6.7 K, the resonance line was observed to split into three pairs of peaks. The angular dependence of the lineshape has revealed the magnetic structure of this compound; i) the antiferromagnetic moments are localized at Cu2+ sites and are regularly ordered with a three-fold periodicity along the stacking c-axis; ii) the easy axis is in the ab-plane and the c-axis is the hard axis; iii) a model of the three dimensional arrangement of the magnetic moments well explaining the experimental results is proposed.

\[
\text{(DMe-DCNQI)}_2\text{Cu, antiferromagnetic state, } 1H\text{-NMR, nuclear relaxation rate, lineshape analysis}
\]

§1. Introduction

The Cu salts of DCNQI, (R1,R2-DCNQI)2Cu, (R1,R2-DCNQI=2,5-disubstituted R1,R2-N,N'-dicynanoquinonediimine) are new type of organic conductors, in which 3d-electrons of Cu ions are strongly coupled with \(\pi\)-electrons of DCNQI molecules.1-5) This system has a tetragonal unit cell composed of one-dimensional (1D) columns of DCNQI's along the c-axis.2-5) The average valence of Cu ions, which are coordinated tetrahedrally by the CN-groups of DCNQI molecule, has been found to be close to +4 / 3.5,6) (DCNQI)2Cu are separated into two groups from the aspect of their conductive behaviors at ambient pressure;3,4)

Group I salts behave metallic down to low temperatures, while Group II salts exhibit a metal-insulator (M-I) transition at 70–200 K. Magnetic susceptibility, \(\chi\), in the metallic state is Pauli-like (almost temperature independent).7) Below the M-I transition temperature, \(T_{MI}\), of the Group II salts, \(\chi\) follows a Curie-Weiss law;7,8) the value of the Curie constant suggests that one third of Cu ions behaves as magnetic Cu2+ ions. The Group II salts show antiferromagnetic (AF) orders at lower temperatures.8,9) (DMe-DCNQI)2Cu (where DMe-DCNQI is 2,5-dimethyl-DCNQI: abbreviated to DMe-salt, hereafter) belongs to the Group I salt, but under pressure (\(\geq 300\) bar), it shows an M-I transition and an AF order just as the Group II salts do.

The magnetic properties of the AF state were studied by analyzing 1H-NMR for a Group II salt, (DBr-DCNQI)2Cu (DBr-salt, where DBr-DCNQI is 2,5-dibromo-DCNQI) and the DMe-salt at 4.5 kbar.10) A peak anom-
aly of the relaxation rate, $T_1^{-1}$, at the Néel temperature, $T_N$, and a remarkable broadening of resonance line below $T_N$ were clearly observed for both salts. Since polycrystalline samples were used in these measurements, however, detailed information on the AF features was not obtained.

Recently, it has been found that the substitution of $^1$H sites of DMe-DCNQI molecule with $^2$H (D) (deuteration) gives the same effect as applying pressure.\textsuperscript{11-13} It is considered that the deuteration induces an effective pressure (the so-called chemical pressure) in the crystal. Selectively deuterated (DMe-DCNQI [3,3;1]d$_7$)$_2$Cu (DMe-d$_7$ salt), where seven $^1$H sites (2 × 3 of the methyl groups and 1 of the 2 sites on the six-membered ring) of the DCNQI molecule are substituted with deuterons, exhibits an M-I transition even at ambient pressure as a Group II salt. This salt has a unique crystallographic $^1$H site as shown in Fig. 1. This is advantageous for $^1$H-NMR measurements in two respects; i) the nuclear dipolar width of $^1$H-NMR line is much smaller than that of the undeuterated sample, and ii) the lineshape analysis becomes much simpler, as shown later.

The purpose of the present work was to determine the magnetic structure of the antiferromagnetic states of the DMe-d$_7$ salt from microscopic point of view by means of $^1$H-NMR measurements on a single crystal sample. Firstly, we measured the temperature dependence of $^1$H spin-lattice relaxation rate, $T_1^{-1}$, to confirm the M-I transition and the AF transition. We estimated the effective exchange interaction from the characteristic frequency of fluctuating local fields at the $^1$H sites. Then we measured the precise angular dependence of the NMR lineshape in the AF state. From the observed lineshape, the local fields at the $^1$H sites were analyzed to derive the ordered magnetic moments at the Cu$^{2+}$ sites.

§2. Experimental

DMe-DCNQI-d$_7$ molecule was synthesized by applying a $^1$H/$^2$D exchange reaction described elsewhere.\textsuperscript{14} Single crystal samples were prepared by the usual diffusion method in an acetonitrile (CH$_3$CN) solution containing neutral DMe-DCNQI-d$_7$ and CuI.

A needle-like crystal with the size of $0.5 \times 0.5 \times 1.2$ mm$^3$ was used for the measurements. The alternating field (48.2 MHz) for NMR measurements was applied parallel to the needle-axis (the crystallographic c-axis) and the external field was rotated in the ab-plane (perpendicular to the c-axis).

$T_1^{-1}$ was measured with a conventional home-made pulsed-NMR spectrometer, in the temperature range between 1.4 K and 100 K. The width of $\pi/2$-pulse was 1.1 $\mu$sec corresponding to the radio-frequency amplitude, $H_r$, of 53 Oe. $T_1^{-1}$ was determined from the recovery of free induction decay (FID) signal following a comb of saturating pulses.

$^1$H-NMR resonance lines were measured by a home-made cw (continuous wave) NMR spectrometer with a hybrid-junction. $^1$H resonance line derivatives were obtained by the usual field-modulation and field-sweep method and were accumulated on a signal averager, IWATSU SM2100A. The modulation field amplitude was selected small (<1.4 Oe) enough to observe the detailed structure of resonance line. In order to avoid the effect of saturation due to the inhomogeneously long $T_1$, we detected the dispersion component of the resonance signals, instead of the absorption. Since the field-derivative of the dispersion lines was obtained, the peak position of each line was regarded as the resonance center. The angular dependence of the lineshape was examined at different field directions with the steps

---

**Fig. 1.** Molecular structure of DMe-DCNQI [3,3;1]d$_7$. 
of 5 degrees.

The external field is 11.3 kOe ± 400 Oe, which is larger than the spin-flop field, $H_f$ (a broad spin-flop transition was observed in the field range, $2 \sim 7$ kOe). At this field, the electron magnetic moments in the AF state should be almost perpendicular to the external field. This fact is important to analyze the lineshape, as discussed later.

§3. Results

3.1 $^1H$ spin-lattice relaxation rate, $T_{1}^{-1}$

Figure 2 shows the temperature dependence of $^1H$ spin-lattice relaxation rate, $T_{1}^{-1}$. At 78.5 K, the relaxation rate exhibits a step-like enhancement. This is an indication of the M-I transition and reflects the appearance of localized Cu$^{2+}$ spins in the insulating state. At lower temperatures, $T_{1}^{-1}$ decreases gradually and forms a peak at 7 K. The relaxation curves were well described by single exponential functions above 7 K, as shown in Fig. 3(a).

Below this temperature, we observed several drastic changes in the NMR characteristics; i) the line width abruptly increased so that the intensity of the FID signal decreased; ii) the relaxation curves became non-single exponential (Fig. 3(b)) suggesting the appearance of an inhomogeneity of $T_1$. We determined the initial slope and the long-time tail of the recovery

---

Fig. 2. Temperature dependence of the $^1H$ spin-lattice relaxation rate, $T_{1}^{-1}$. Below $T_{N}$, the initial slope and the slope of long-time tail of recovery curve are shown with a line connecting them.

Fig. 3. Typical nuclear relaxation curve above $T_{N}$ (a) 8.5 K and below $T_{N}$ (b) 4.2 K.
curve in this temperature range, as measures of the distribution of $T_i$. iii) The relaxation rate, $T_i^{-1}$, decreased rapidly at lower temperatures. These facts are clear evidence that the system is in an antiferromagnetically ordered state. The line broadening is caused by the onset of static local fields, and the inhomogeneity of $T_i^{-1}$ should be induced by the so-called $^1$H spin decoupling.\(^{10}\) This temperature, 7 K, agrees well with the Néel temperature, $T_N$, determined by the static susceptibility measurement.\(^{8}\)

The temperature dependence of $^1$H-$T_i^{-1}$ in the paramagnetic insulating state ($T_N < T < T_{MI}$) shows a general behavior observed in a standard antiferromagnet. The relaxation rate for nuclei at a nonmagnetic site is expressed as\(^{15}\)

$$T_i^{-1} = \sqrt{2\pi (A/h)^2 [S(S+1)/3]}/\omega_{ex},$$

where $A$ and $S$ are the electron-nuclear coupling constant and the spin number of the magnetic moment, respectively, and $\omega_{ex} = (J/h)\sqrt{S(S+1)}$ with the exchange interaction $J$ and the number of the nearest neighbors $z$. Since the relaxation is caused by the dipolar coupling between the $^1$H nuclei and the magnetic moments, we can take $A/h = \gamma_1 g \mu_B \sqrt{S(S+1)}/r^3$, where $\gamma_1$, $g$, $\mu_B$ and $r$ are nuclear gyromagnetic ratio, $g$-value of the ordered electron moment, the Bohr magneton and the distance between the magnetic moment and the nucleus, respectively. Using the relation, $k_B T_N = 2JzS(S+1)/3$, in the molecular field approximation, with $z=4$, $S=1/2$, and $T_N=6.7$ K for this salt, the relaxation rate is estimated as 30 s$^{-1}$, as an average for the different proton sites. This agrees quite well with the observed values of $T_i^{-1}$.

### 3.2 $^1$H-NMR Lineshape

The $^1$H-NMR line observed by the cw NMR method above $T_C$ was a single line with a narrow width of 2 Oe, as expected from the crystal structure. In the AF state, on the contrary, the resonance line was observed to split into six lines spread in a wide filed range of about ±200 Oe (Fig. 4).

This is clearly due to the onset of large local fields at the $^1$H sites associated with the AF ordering. The appearance of six separated lines are easily explained as follows. Since the one-third of Cu ions are magnetic Cu$^{2+}$,\(^{7,8}\) as mentioned before, and there exists a lattice modulation with a three-fold periodicity\(^2\) along the c-axis in the insulating state, it is natural to assume that the Cu$^{2+}$ and Cu$^{1+}$ ions form a regular array along the c-axis as $-Cu^{2+}-Cu^{1+}-Cu^{1+}-$, as shown in Fig. 5. Because of this three-fold periodicity, $^1$H-sites are divided into three inequivalent sites. Each site should be further divided into two, corresponding to two sublattices in the ordered AF state. The lineshape reasonably reflects this situation. We defined each $^1$H site as A-, B- or C-site as depicted in Fig. 5. The outermost, the middle and the innermost pairs of the lines in Fig. 4 are the contributions of the A-site (the 1st nearest neighbor), the B-site (the 2nd nearest neighbor) and the C-site, respectively. Thus this model explains the profile of the observed lineshape. This is consistent with the result on powdered sample of the DMe-salt under pressure and the DBr-salt.\(^{10}\) The existence of well-separated six resonance lines is microscopic direct evidence of a regular arrangement of magnetic sites with a three-fold periodicity.

The lineshape is quite sensitive to the field direction as shown in Fig. 6. The separation of each pair of lines is plotted as a function of the field direction in Fig. 7, when the external field is rotated in the ab-plane. The origin of the angle is arbitrary, since the crystal orientation perpendicular to the needle axis was difficult.
Fig. 5. Schematic view of the molecular stack and the periodic array of Cu$^{2+}$ and Cu$^{+}$ ions along the $c$-axis. Three magnetically inequivalent $^1$H-sites, A-, B- and C-sites, are defined.

Fig. 6. Field orientation dependence of the $^1$H-NMR lineshape in the AF state.

Fig. 7. Field orientation dependence of the pair separations measured at 4.2 K for the three $^1$H-sites. Solid lines show the calculated results with several assumptions given in the text.

Fig. 8. $^1$H-NMR lineshape at various temperatures. Field orientation was fixed at the angle where the pair separations are maximum.

to determine. According to the analysis given later, the $a$-axis should correspond to $\Phi = 20^\circ$. We find the pair separations ($H_A$, $H_B$ and $H_C$) change with a 90$^\circ$ period. The angular dependence is found proportional to $|\sin 2(\Phi - \Phi_0)|$.

Figure 8 shows the temperature dependence
of the $^1$H-NMR lineshape, in the field direction giving the largest line separation. We can reconfirm that the appearance of broadening at 6–7 K is followed by the line splitting at lower temperatures. The temperature dependence of the pair separations $H_A$, $H_B$ and $H_C$ is shown in Fig. 9. The solid lines are the well-known Brillouin function for $S=1/2$ with the molecular-field approximation. The agreement is sufficient. From the least square fitting to the Brillouin function, we determined the the Néel temperature, $T_N$, as 6.7 K.

§4. Analysis of the Magnetic Structure

The excess local field at a $^1$H-site is essentially the dipole field, $H_d$, made by the localized magnetic moments. Since the dominant contribution comes from the nearest neighbor site, we first consider the local field made by a single moment, $\mu$. It is given by

$$H_d = -\frac{\mu}{r^3} + \frac{3}{r^5} r(\mathbf{r} \cdot \mathbf{\mu}),$$

where $r$ is the positional vector from $\mu$ to the $^1$H-site. When the external field is large enough compared with $H_d$, only the component of $H_d$ parallel to the external field appears as the shift of the resonance position. Thus the contribution of $\mu$ to the pair separation is expressed as

$$H_{\delta \phi} = H_d \cdot \hat{H}_0$$

$$= -\frac{\mu \cdot \hat{H}_0}{r^3} + \frac{3}{r^5} (r \cdot \mu)(r \cdot \hat{H}_0),$$

(3)

where $\hat{H}_0$ is the unit vector parallel to the external field.

In a field larger than the spin-flop field, $H_{sf}$, the local moment, $\mu$, is no more parallel to the easy axis but changes the direction to gain magnetic energy. In the present situation, where $H_0$ is about twice as large as $H_{sf}$, we can assume that $\mu \perp \hat{H}_0$. The actual direction of $\mu$ depends on the principal axes of the anisotropy field. Since the crystal symmetry around the magnetic Cu$^{2+}$ site is rather high, we considered the following cases; i) the c-axis is parallel to the easy axis, ii) to the intermediate axis and iii) to the hard axis. The angular dependence of $H_{\delta \phi}$ for the field rotating in the ab-plane is now easily calculated. Suppose that a magnetic moment, $\mu$, is located at the origin and the rectangular coordinates, $x$, $y$, $z$ are defined as parallel to the crystallographic a, b and c-axis, respectively. The polar coordinates of the vector $r$ are given by $r$, $\theta$ and $\phi$, as shown in Fig. 10.

In the case i), $\mu$ stays parallel (or antiparallel) to the c-axis independent of the field direction, so that we obtain

$$H_{\delta \phi}(\Phi) = \pm \frac{3}{r^3} \mu \cos \theta \sin \theta \cos (\Phi - \phi),$$

(4)
where $\Phi$ is the angle between $\hat{H}_0$ and the $a(x)$-axis and $\mu = |\mu|$. While the lineshape should be mainly determined by the contribution from the nearest neighbor site, this $\Phi$-dependence does not explain the experimental results.

In the case ii), $\mu$ is expected to undertake a spin-flop transition, when the field is rotated in the easy-hard plane; $\mu$ suddenly flips up from the $ab$-plane to the direction perpendicular to the plane at a certain angle determined by the anisotropy parameters. The NMR lineshape should exhibit a sharp change at this angle. This again contradicts the observed results.

The observed angular dependence shown in Fig. 7 is well explained by assuming the case iii), where $\mu$-vector stays in the $ab$-plane and almost perpendicular to $\hat{H}_0$:

$$H_{d\theta}(\Phi) = \pm \frac{3\mu}{r^3} \sin \theta \sin(\Phi - \phi) \sin \theta \cos(\Phi - \phi) = \pm \frac{3\mu}{2r^3} \sin^2 \theta \sin(2(\Phi - \phi)).$$  \quad (5)$$

The $90^\circ$-periodicity of $H_A$, $H_B$ and $H_C$ against $\Phi$ is thus a clear evidence that the hard axis is the $c$-axis (the easy axis is in the $ab$-plane). This result is consistent with the observed anisotropy of the static susceptibility.\(^8\)

More precisely, the separation of the resonance line is given as the vector sum of all neighboring magnetic sites, $i$, as

$$H_{A}, H_{B}, H_{C}(\Phi) = 2 \left| \sum_{i} H_{d\theta}^{(i)}(\Phi) \right| = 2 \left| \sum_{i} (\pm^{(i)}) \frac{3\mu_i}{2r_i^3} \sin^2 \theta_i \sin(2(\Phi - \phi_i)) \right|.  \quad (6)$$

Here the sign, $(\pm)^{(i)}$, depends on the direction of the spin at the site $i$ relative to the spin at the nearest neighbor site for each $\text{^1}H$-site concerned. It is thus necessary to know the three dimensional (3D) spin structure to perform the summation. Taking into account the spiral symmetry of the crystal structure and the three-fold periodicity along the $c$-axis, we adopted the model of spin structure as shown in Fig. 11:\(^5\) It is assumed that the neighboring Cu$^{2+}$ ions on the adjacent chains are interacting antiferromagnetically with each other through a super-exchange coupling mediated by a dimer of the DCNQI molecules in between. The reason to consider a dimer instead of a single molecule to mediate the exchange interaction is that this is the only way to fit to the three-fold periodicity along the chain. Then we can derive a three dimensional arrangement of the spins by setting “right” and “left” spins alternately along the route of interaction. In this case, the magnetic moments on a chain along the $c$-axis are all parallel.\(^5\)

The summation in eq. 6 was carried out for $7 \times 7 \times 7$ magnetic sites (approximately within a cube of 60 Å). We assumed that each magnetic Cu$^{2+}$ site has $\mu = g_\perp \mu_B S$ with $g_\perp = 2.078$\(^5\) and $S = 1/2$ at absolute zero. The full angular dependence (Fig. 6) was measured at 4.2 K, so that we finally reduced the calculated values by a factor 1.20 in order to take account of the

Fig. 11. Relative orientation of the ordered magnetic moments at adjacent Cu$^{2+}$ sites.
temperature dependence of the local moment as shown in Fig. 9. The calculated angular dependence of the pair separation is shown by the solid lines in Fig. 7. Essential features are very well reproduced. Note that there is no adjustable parameter except the ambiguity in the origin of the abscissa.

The observed value of the maximum line separation of $H_A$ is somewhat smaller (by $\sim 17\%$) than the calculated one. On the contrary, the observed $H_C$ is larger than the calculation. Possible reasons of these quantitative discrepancies are listed as follows: i) We used the lattice parameter obtained at room temperature. 4) The distance between the magnetic Cu$^{2+}$ and the nearest neighbor 'H should be different at low temperatures. ii) We assumed that the spin was located at a Cu site as a point. It may be possible that part of the magnetic moment spread out on the DCNQI molecule. iii) It is also possible that the spin density on the DCNQI molecule is modified due to the super-exchange coupling through Cu$^{2+}$-DCNQI dimer-Cu$^{2+}$ discussed above. 5) iv) The localized moment at the Cu$^{2+}$ site may be remarkably reduced by the zero point motion of spin waves in the antiferromagnetic system (spin contraction$^{16,17}$).

At the moment, we do not know which is the most responsible for the discrepancy. We need more information to refine the agreement with the observed results.

§5. Conclusive Remarks

In summary, the magnetic structure in the antiferromagnetic state of the selectively deuterated (DMe-DCNQI-d$_2$)$_2$Cu was investigated from microscopic points of view. i) The antiferromagnetic moments are localized at Cu$^{2+}$ site and are regularly ordered with a three-fold periodicity along the stacking c-axis; ii) the easy axis is in the ab-plane and the c-axis is the hard axis; iii) a model of the three dimensional arrangement of the magnetic moments, proposed in the previous publication is found to explain the experimental results very well. These are quite consistent with the macroscopic data thus far obtained. 5,8) Since the external field larger than the spin-flop field was used in the present measurement, the real direction of the easy axis for the antiferromagnetic order was not determined in spite of the use of a single crystal sample. An important information on this aspect has been obtained by an independent experiment of antiferromagnetic resonance (AFMR), 18) which suggests that the principal axes for the anisotropic energy corresponds to the symmetry axes of the distorted tetrahedron of the CN-groups surrounding the Cu$^{2+}$-site. Further analysis of the AFMR will be published separately.

Acknowledgments

The authors thank Mr. K. Takagawa for technical assistance on the experiment and Professor K. Kanoda and Dr. M. Tamura for useful discussions.

References

15) V. Jaccarino: Magnetism, ed. G. T. Rado and H.

