MAGNETIC STRUCTURE IN ANTIFERROMAGNETIC STATES OF A MOLECULAR CONDUCTOR, \((\text{DMe-DCNQI-d}_7)_2\text{Cu}\)


Department of Physics, Gakushuin University, Mejiro, Tokyo 171, Japan
*Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan
+Department of Chemistry, Toho University, Funabashi, Chiba 274, Japan

Deuteration of the quasi-one-dimensional d-π conductor, \((\text{DMe-DCNQI})_2\text{Cu}\), was found to make its metallic state unstable at low temperatures; the title compound exhibits a metal–insulator transition at 79K and an antiferromagnetic order at 7K. \(^1\text{H–NMR}\) and AFMR measurements have been made to investigate the antiferromagnetic state of this compound. The three-fold periodicity (–Cu\(^{2+}\)–Cu\(^{+}\)–Cu\(^{+}\)–) along the chain (c-axis) has been confirmed by \(^1\text{H–NMR}\) lineshapes. The angular dependence of the lineshape reveals that the c-axis is the hard-axis. The AFMR measurements show that the easy-axis lies along \(<110>\) direction: there exist two crystallographically equivalent domains in the antiferromagnetic order.

PACS numbers: 75., 73.20.Dx

1. INTRODUCTION

The Cu salt of DMe-DCNQI (DMe-DCNQI: dimethyl(dicyanoquinodiimine) and its analogues have attracted our interests because of their unique electronic structures [1]; the DMe-DCNQI molecules stack to form one-dimensional conducting π-bands and the stacks are connected with each other through Cu atoms. The non-integer valence of Cu (\(+4/3\)) in the metallic states suggests that the Cu 3d-bands intersect the Fermi level. The three-dimensional interaction through the Cu 3d-orbitals is considered to stabilize the metallic states of \((\text{DMe-DCNQI})_2\text{Cu}\) down to low temperatures. The metallic state becomes unstable under pressure; applying pressure brings them into an insulating states where a band gap opens at the Fermi level of π-bands. The insulating state is characterized by the appearance of magnetic Cu\(^{2+}\) moments and the three-fold superlattice along the stacking axis. Recently, the selective deuteration of DMe-DCQNI molecule produces the same effect as applying pressure [2]. It enables us the systematic investigation of the phase transition of this materials at ambient pressure. The title salt, where 7 of 8 proton sites are replaced with deuterons, undergoes a metal–insulator transition at 79K. We found antiferromagnetic (AF) order at 7K by \(^1\text{H–NMR}\) relaxation and EPR measurements. The detailed magnetic structure has not been clarified so far. In this paper, we present a possible magnetic structure of the title compound on the basis of the experimental results of \(^1\text{H–NMR}\) lineshapes and antiferromagnetic resonances (AFMR).

2. EXPERIMENTAL

The \(^1\text{H–NMR}\) lineshape measurements of the single crystal sample were performed by a conventional cw method using phase sensitive detection. We investigated the dispersion part of the resonance to avoid the saturation effect, since \(^1\text{H}\) nuclei in the AF phase have rather long \(T_1\) with large inhomogeneity. The AFMR measurements were carried out at 4.5K, using an X-band (9.06 GHz) ESR spectrometer.

3. RESULTS AND DISCUSSION

While \(^1\text{H–NMR}\) dispersion was a single sharp line above \(T_N\), an abrupt increase of the linewidth has been observed just below \(T_N\). At low
temperatures, the resonance line splits into six lines. It is attributed to the magnetic order of \( \text{Cu}^{2+} \) with threefold periodicity \((-\text{Cu}^{2+}-\text{Cu}^{+}-\text{Cu}^{2+})\) along the \(c\)-axis. There appear three kinds of \(1^\text{H}\) sites which feel different local fields due to \(\text{Cu}^{2+}\) magnetic moments. The satellite spacings changes as a function of the angle between the external field and the crystallographic axes. The angular dependence of the satellite width at 4.2K is shown in Fig. 1. The magnetic field was rotated in the \(a-b\) plane. If we assume that the \(c\)-axis is the hard-axis, and that the external field of 1.15T is larger than the anisotropy field, each of the satellite spacing (the nearest neighbor contribution) is given by the following equation as,

\[
\Delta H = \frac{3\mu}{r^3} \sin^2\theta |\sin 2\varphi|,
\]

where \(\mu\) is the magnetic moment, \(r\) is the distance between \(1^\text{H}\) and \(\text{Cu}^{2+}\), and \(\theta\) and \(\varphi\) is defined in the inset of Fig. 1. This \(|\sin 2\varphi|\) dependence is consistent with the experimental results. A preliminary estimate of the moment at the Cu-site from the maximum satellite spacing gives about 80% \(\mu_B\).

The AFMR has been observed below \(T_N\) where the EPR signal disappeared. The angular dependence of the resonant field at 4.5K is shown in

\[\text{Fig. 1. Angular dependence of the satellite spacings of } ^1\text{H}-\text{NMR dispersion at } 4.2\text{K.}\]

\[\text{Fig. 2. Angular dependence of antiferromagnetic resonance field in } a-b \text{ plane at } 4.5\text{K.}\]

\[\text{Fig. 2. The external static field was rotated in the } a-b \text{ plane. It takes a minimum at about } 45^\circ, \text{indicating the easy-axis lies along about } <110> \text{ direction. It is difficult, however, to explain the } 90^\circ \text{ periodicity of the angular dependence. The most probable explanation is that the contributions of two crystallographically equivalent domains of the antiferromagnetic order are superposed. The anomalous pattern of the resonance fields around } a \text{ or } b-\text{axis has not been clear so far.}\]

\[\text{ACKNOWLEDGEMENTS}\]

The authors would like to thank Messrs. K. Takagawa, N. Fujii and Miss T. Nobutoki for help with the experiments. This work is supported in part by the Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture, Japan (No.03302017).

\[\text{REFERENCES}\]