ESR study of DMTCNQ salt

Shuichi Kawamata [a,1], Takekazu Ishida [a], Toyonari Sugimoto [b]
[a] *Department of Physics & Electronics, Osaka Prefecture University, Sakai 599-8531, Japan*
[b] *Research Institute for Advanced Science and Technology, Osaka Prefecture University, Sakai 599-8531, Japan*

Abstract

Electron spin resonance (ESR) experiments with 15 GHz microwave have been done between 1.5 and 300 K for $(\mathrm{AsMe}_4)_2\mathrm{DMTCNQ}_3$ single crystals, where Me and DMTCNQ stand for methyl and dimethyl-tetracyanoquinodimethane, respectively. The crystal has one-dimensional structure in which the DMTCNQ molecules stack along the *b*-axis. Two kinds of resonance line are found. Although the main resonance line is observed in whole measured temperature range, the other resonance line appears only above 225 K. The magnetic field direction dependence of the line width for main one follows the dipole calculation which reflects one dimensional character of localized spin. However, that for the other one does not show the one dimensional localized spin character. The results suggest the coexistence of localized spins and carrier electrons above 225 K.

Key words: organic material ; electron spin resonance ; one dimensional magnetic property ; TCNQ molecule

1. Introduction

As a famous acceptor molecule, tetracyanoquinodimethane (TCNQ), composes a lot kind of charge transfer salts, a 2.5-dimethyltetracyanoquinodimethane (DMTCNQ) molecule can also become a radical anion, $\mathrm{DMTCNQ}^{-\cdot}$ in the salt [1]. $(\mathrm{AsMe}_4^+\mathrm{DMTCNQ}^{-\cdot})_2\mathrm{DMTCNQ}$ is one of DMTCNQ salt, where Me stands for methyl. This salt exhibits both ferromagnetic behavior and high conductivity at room temperature [2]. The salt has one-dimensional crystal structure in which the DMTCNQ molecules stack along the *b*-axis. What is very characteristic in the structure is a composition of two different columns. While radical $\mathrm{DMTCNQ}^{-\cdot}$ (A site) and neutral DMTCNQ (B site) stack alternately in one column (AB column), all molecules are radical $\mathrm{DMTCNQ}^{-\cdot}$ (C site) in another column (CC column) [2].

In this paper, electron spin resonance (ESR) with 15 GHz microwave by using a single crystalline $(\mathrm{AsMe}_4)_2\mathrm{DMTCNQ}_3$ is reported for the first time.

2. Results and Discussion

The preparation of single crystals is described elsewhere [2]. Temperature dependencies of the g-value and line width, ΔH_{P-P}, were measured between 1.5 and 300 K for the magnetic field, H, parallel to a, b and c^* axis. Magnetic field direction dependencies of the g-value and ΔH_{P-P} were measured at 100 and 295 K. A signal of Mn^{2+} impurity ions in CaCO_3 was measured simultaneously as a reference.

For $H//a$ and $H//c^*$, one resonance line is observed in whole measured temperature range. For $H//b$ which is parallel to the chain direction, two resonance lines are observed above 225 K, while there is only one resonance line below 225 K. Figure 1 shows the magnetic field direction dependencies of ΔH_{P-P} for the ab, bc^* and c^*a planes at 295 K. Solid and open circles indicate ΔH_{P-P} for the main resonance and that for the extra resonance which appears only above 225 K, respectively. Solid lines indicate calculated ΔH_{P-P} taking account to the dipole interaction between localized spins normalized by the maximum value. The magnetic field direction dependence of the main one al-

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[1] E-mail: kawamata@pe.osakafu-u.ac.jp

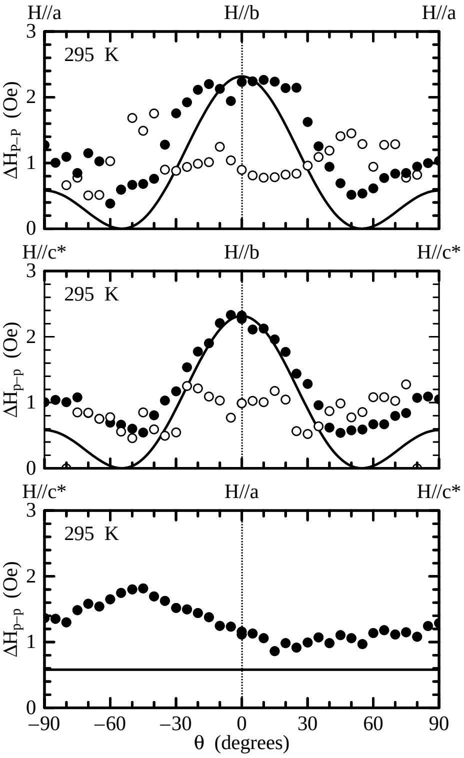

Fig. 1. Angular dependencies of line width, ΔH_{P-P}, for the ab, bc^* and c^*a planes. Solid and open circles indicate data for the main resonance and those for the extra resonance, respectively. Solid lines indicate calculated one due to the dipole interaction.

most follows the calculated ΔH_{P-P} which reflects one-dimensional localized spin character along the b-axis. Almost the same angular dependencies for the main resonance are also obtained at 100 K. The result reveals that the main resonance is caused by the localized electrons. On the other hand, that of the extra resonance does not follow the calculated ΔH_{P-P}. It suggests that the extra resonance above 225 K is due to the itinerant electrons. Smaller value of ΔH_{P-P} can be explained by the motional narrowing. This results, which suggest the coexistence of the localized spins and the carrier electrons, are consistent with the electrical resistance report [2]. The resistance is almost independent of the temperature above 225 K, although its temperature dependence shows semiconductor-like behavior below 225 K. In the CC column, electrons are expected to be localized due to the on-site Coulomb interaction because all molecules are radical. On the other hand, the AB column is more likely to become conductive because radical and neutral molecules stack alternately as the TCNQ molecule case in which the high conductivity is usually obtained by the neutral TCNQ and radical $\mathrm{TCNQ}^{-\cdot}$ mixed salts [3]. Therefore, the AB column is considered to become conductive above 225 K.

Figure 2 shows the temperature dependencies of ΔH_{P-P} for $H//a$, $H//b$ and $H//c^*$. Open circles indicate ΔH_{P-P} for the signal which appears only above 225 K. For each magnetic field direction, ΔH_{P-P} enhances below 60 K with decreasing temperature. The g-value for $H//b$ show a little decrease below 60 K with decreasing temperature, while there is not any specific temperature dependence of the g-value for $H//a$ and $H//c^*$. It is possible that antiferromagnetic correlation in one dimensional chain occurs below 60 K.

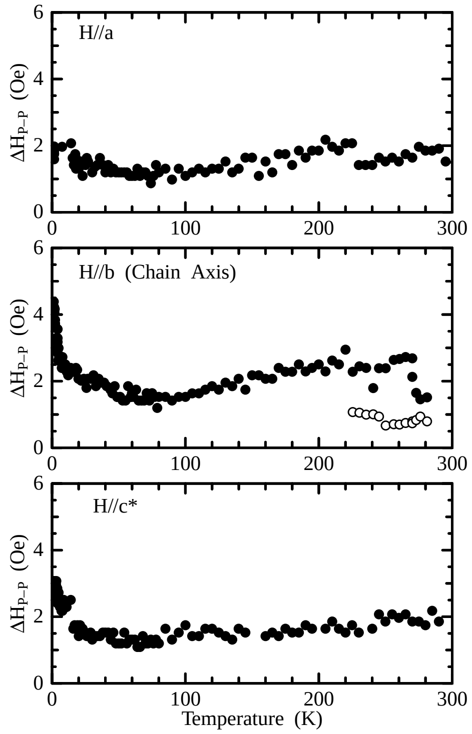

Fig. 2. Temperature dependencies of line width for $H//a$, $H//b$ and $H//c^*$. Solid and open circles indicate data for the main resonance and those for the extra resonance, respectively.

In conclusions, the ESR data of $(\mathrm{AsMe_4})_2\mathrm{DMTCNQ_3}$ show that the electrons partly become itinerant at above 225 K while they are localized at low temperatures. The result is consistent with the high conductivity at room temperature.

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