ESR study of the charge ordering in $(\mathrm{TMTTF})_2X$

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Abstract

ESR studies of the quasi-one-dimensional organic conductors, $(\mathrm{TMTTF})_2\mathrm{ReO}_4$, were carried out. The ESR linewidth shows an discontinuous drop at 154 K, and its anisotropy also changes. In the low temperature phase, the electronic dipoles contribute to the ESR linewidth. We discuss the possible charge ordering patterns from the microscopic point of view.

Key words: organic conductor; TMTTF; ESR; charge order

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1. Introduction

The recent discoveries of the charge ordering and/or charge disproportionation states in quasi-two-dimensional organic conductors, θ-type BEDT-TTF compounds, are attracting much attention. [1–4] As for the TMTTF compounds, the insulating states at low temperatures have been believed as Mott-Hubbard insulating phases since strong dimerization of the donor molecules might reduce the system half-filled. However recent reports of ^{13}C NMR and ac-conductivity for $(\mathrm{TMTTF})_2M\mathrm{F}_6$ (M = P, As, Sb) compounds suggest existence of inequivalent TMTTF sites at low temperatures. [5,6] Moreover, in the previous ^{1}H NMR investigation for the magnetic structure of the commensurate spin density wave (C-SDW) phase of $(\mathrm{TMTTF})_2X$ (X = Br, SCN), it was proposed for the ordering pattern along the stacking axes that -up-0-down-0-up- is more likely than -up-up-down-down- expected in large U systems. [7–9] Several theatrical investigations are pointing out the importance of the long-range Coulomb interaction to stabilize the -up-0-down-0-up- state. [10–12] These results strongly suggest possible charge ordering also in the paramagnetic states of $(\mathrm{TMTTF})_2X$, and present a question about validity of the simple Mott-Hubbard insulator scenario.

In order to clarify the charge localized states, we performed accurate ESR measurements. In this paper, we focus on the topics about one of $(\mathrm{TMTTF})_2X$ compounds, $(\mathrm{TMTTF})_2\mathrm{ReO}_4$. This compound undergoes a spin-singlet transition at 154 K. The resistivity shows a minima at around the transition temperature. The possible charge ordering and its pattern of $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ are discussed from a microscopic point of view.

2. Experimental

The TMTTF molecules, and crystals of $(\mathrm{TMTTF})_2$-ReO_4 have been prepared according to the previous reports. [13,14] Rectangular plate-like crystals were prepared by the electrochemical oxidation of TMTTF using KReO_4 and 18-crown-6 ether in a acetonitrile solution under a constant current of 1.0 μA.

The ESR measurements were carried out for a single crystal using an X-band spectrometer, Bruker ESP-300E, with a rectangular cavity: TM_{110}. The temperature range of the ESR measurements was between 300 K and 4 K. We applied a least squares method for the analyses of the observed ESR absorption derivative curves. In the high temperature metallic region,

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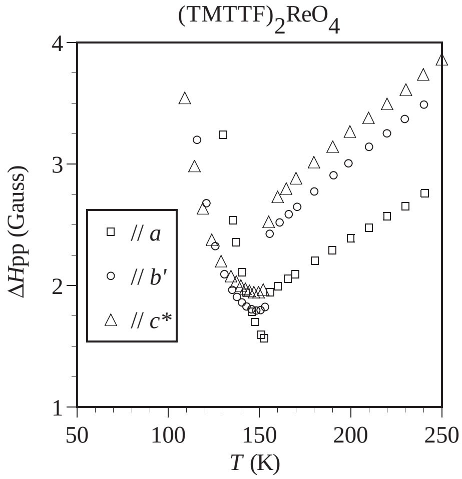

Fig. 1. Temperature dependence of the peak-to-peak ESR linewidth, $\Delta H_{\rm pp}$, of $({\rm TMTTF})_2{\rm ReO}_4$ for a single crystal.

Dysonian-like line shapes were observed. We assumed a small mixture of a dispersion component to the absorption signal and determined the peak-to-peak linewidth and resonance field for the pure-absorption component.

3. Results and Discussion

Temperature dependence of the peak-to-peak ESR linewidth, $\Delta H_{\rm pp}$, of $({\rm TMTTF})_2{\rm ReO}_4$ applying the external static field along the three orthogonal crystal axes is shown in Fig. 1. In the high temperature paramagnetic region, the $\Delta H_{\rm pp}$ is the largest when it is applied along the c^* axis, and smallest along the a axis. The $\Delta H_{\rm pp}$ decreases as the temperature decreases for all directions in the paramagnetic metallic phase. This behavior is the same as those of the typical organic conductors, and indicates that phonon scatterings contribute to the electron spin relaxation.

At 154 K, the ESR signal intensity suddenly decreases, associating with the spin-singlet transition. The $\Delta H_{\rm pp}$ shows an discontinuous drop at 154 K. The sudden 'stepwise' jump suggests that the 154 K anomaly is a transition of first-order, although we did not observe clear hysteresis behavior. Below the transition temperature, the $\Delta H_{\rm pp}$ increases as the temperature decreases. It should be also noted that the anisotropy of the $\Delta H_{\rm pp}$ also changes: The $\Delta H_{\rm pp}$ is the largest when the static field is applied along the *b*' axis, and the absolute values are almost the same for the a^* and c axes in the low-temperature phase.

In the high temperature phase, the $\Delta H_{\rm pp}$ follows the standard anisotropic behavior. On the other hand, the $\Delta H_{\rm pp}$ shows characteristic angular dependence of the system with dipole-dipole interaction. Considering the anisotropy of the ESR linewidth, we can estimate the possible charge ordering pattern in the low temperature phase. If we assume the charge ordering pattern -O-O-o-o- along the stacking axes (O and o indicate the charge rich and poor sites, respectively), we can explain the experimental results, $\Delta H_a > \Delta H_{b'}$. A possibility of the ordering pattern -O-O-o-o- is ruled out. This result is consistent with the recent X-ray investigation. [15] We carried out ESR measurements for other $({\rm TMTTF})_2X$ compounds. Detailed experimental results and discussions will be reported elsewhere.

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