Charge ordering in $\alpha$-(BEDT-TTF)$_2$I$_3$

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Abstract

$^{13}$C-NMR measurements were performed to the quasi two-dimensional organic conductor $\alpha$-(BEDT-TTF)$_2$I$_3$, which exhibits metal-insulator transition at 135 K ($=T_{MI}$) at ambient pressure. The relaxation rate $T^{-1}$ has two components below $T_{MI}$ indicating two nonequivalent sites. $T$-dependence of the lineshape clearly indicates that there exist two differently charged BEDT-TTF molecules below $T_{MI}$.

Key words: Nuclear magnetic resonance spectroscopy, Metal-insulator phase transitions, Organic conductors based on radical cation and/or anion salts

1. Introduction

A large number of organic conductor has been synthesized until today. Among them, the BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) family is one of the most intensively studied systems. They form 2 : 1 cation radical salts with layered structure of conducting BEDT-TTF sheets separated by insulating anion sheets. $\alpha$-(BEDT-TTF)$_2$I$_3$ is a typical salt of the BEDT-TTF family.

There are four BEDT-TTF molecules denoted as A, A', B and C in a unit cell. The conducting layer is constructed by two donor columns along $\alpha$-axis. A and A' form one of the columns and B and C the other. Reflecting the crystal structure, two dimensional semi-metallic Fermi surface is expected by band calculation. However a metal-insulator (M-I) transition occurs at 135 K ($=T_{MI}$) at ambient pressure [1]. Spin susceptibility decreases abruptly below $T_{MI}$ indicating a non-magnetic insulator [2].

A lot of studies are made by now, but the origin of this M-I transition is not understood yet. To make clear this point, we have carried out the $^{13}$C-NMR measurements.

2. Experimental

We synthesized single crystals of the title compound with BEDT-TTF molecules, in which only the central double-bonded carbon site was enriched by $^{13}$C isotopes. We have made $^{13}$C-NMR measurements for a single crystal. A magnetic field of about 8.2 T (corresponding resonance frequency is 88 MHz) was applied perpendicular to the conducting layer. The spectra and relaxation rate were measured using a spin-echo method.

3. Result and discussion

The relaxation rate, $T^{-1}$, is plotted in Figure 1. In the high temperature region, $T^{-1}$ obeys a Korringa relation which is expected for a metallic system. However we observed two components below $T_{MI}$ intensity of which is nearly the same.

Fig 2 shows the temperature dependence of the $^{13}$C-NMR spectra. In the metallic phase ($T > T_{MI}$), the spectrum has rather complicated structure which is considered as doublet plus quartet [3]. We expect that if the charge is equally populated on BEDT-TTF molecules, the spectrum should be more simple structure. Therefore the possibility of
charge disproportionation is suggested.

The spectra are composed of four peaks below $T_{MF}$. We found that these are two doublets with different $T_1^{-1}$. The separation of each doublet is exactly the same as the value expected for the dipolar interaction on the BEDT-TTF molecules. $T$-dependence of the position of these doublets is clearly different. The doublet with longer relaxation time is almost temperature-independent. However the other doublet shows large shift as temperature is lowered. These results clearly indicate that there exists charge rich and poor molecules.

The arrangement of these sites in the molecular layer can be determined from the measurements rotating the magnetic field in the layer.

4. Conclusion

We have made $^{13}$C-NMR experiments on a single crystal of $\alpha$-(BEDT-TTF)$_2$I$_3$ above and below of the M-I transition temperature. In the insulating phase, temperature dependence of the spectra and $T_1^{-1}$ clearly indicate the charge ordering with charge rich and poor BEDT-TTF molecular sites. In the metallic phase, the spectra is rather complicated suggesting the charge disproportionation. $T_1^{-1}$ was found to follow the Korringa relation.

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References

