Conduction Mechanism of Charge-Transfer Complexes Based on Hyperconjugated Compounds

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Recently, we synthesized a charge-transfer complex $(EtHAC)_2I_3$ to realize a three-dimensional metallic band structure based on the non-planar hyperconjugated molecule EtHAC.[1] Despite the nearly identical lattice constants, some of the single crystals of the complex exhibited non-metallic behavior. This study explores what makes such qualitative differences in the electrical properties. Regarding the angular-dependence of linewidths (Γ) in electron spin resonance (ESR), the insulating crystals exhibit different angular-dependences depending on the rotation axes, while the metallic crystals exhibit quantitatively similar angular-dependence irrespective of the rotation axes (**Fig. 1**). These observations suggest that the metallic carriers in $(EtHAC)_2I_3$ possess a three-dimensional character. [2]

The electrical resistivity measurements provide further evidence for the distinction between metallic and non-metallic behavior based on the anisotropy in the ESR spectra. Anomalies attributed to the ethyl group disorder, often observed around 200 K, were interpreted as phenomena independent of the metallic properties of the sample. Insulating samples exhibited steeply increasing resistivity below 200 K, while metallic samples exhibited unusally low resistivity with small temperature dependence (**Fig. 2**). This contrast suggests a fundamental shift in the conduction mechanism occurring around 200 K. Additionally, the non-metallic samples exhibited ESR spectra that appear to be characteristic of a charge-ordering phase transition, which is thought to be associated with a metal-insulator transition. We further investigate the overall conduction mechanism paying particular attention to the behavior around 200 K.

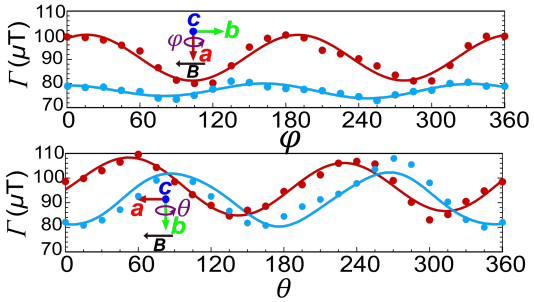

Fig 1. Magnetic field(***B***)-angular-dependence of ESR linewidths in metallic and insulating single crystals of $(EtHAC)_2I_3$ (Red: Metal, Blue: Insulator)

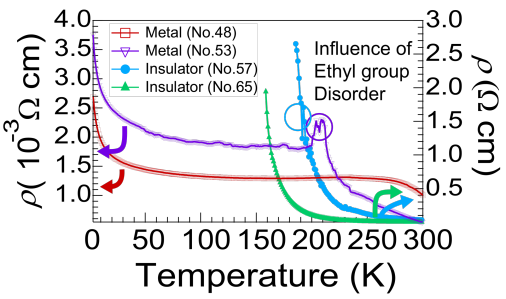

Fig 2. Temperature dependence of electrical resistivities of metallic and insulating $(EtHAC)_2I_3$

1) Y. Sasaki *et al*., Molecules, **2020**, 25.11: 2486.
2) M. Ikeda *et al*., Submitted