

IV-C Microscopic Investigation of Molecular-Based Conductors

Molecular based conductors are one of the most extensively studied materials in the field of solid state physics. Their fundamental properties have been very well clarified: The development of the understanding of the electronic structure enables us systematic investigations of these materials. At the same time, it is true that there still remain several unsolved questions in the molecular based conductors.

To clarify the low temperature electronic states, we performed the static susceptibility, EPR, ^1H - and ^{13}C -NMR measurements for molecular based conductors.

IV-C-1 Low-Temperature Electronic States in $(\text{EDT-TTF})_2\text{AuBr}_2$

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Magnetic investigation was carried out at low temperatures in a one-dimensional 1/4-filled system, $(\text{EDT-TTF})_2\text{AuBr}_2$ by performing SQUID, EPR, and ^1H -NMR measurements. The electronic phase is discussed for $(\text{EDT-TTF})_2\text{AuBr}_2$, which undergoes an antiferromagnetic transition at 16 K followed by a resistivity minimum. We observed an anomalous second-peak of the NMR spin-lattice relaxation rate in the magnetic phase, suggesting a stable incommensurate SDW in a 1/4-filled system.

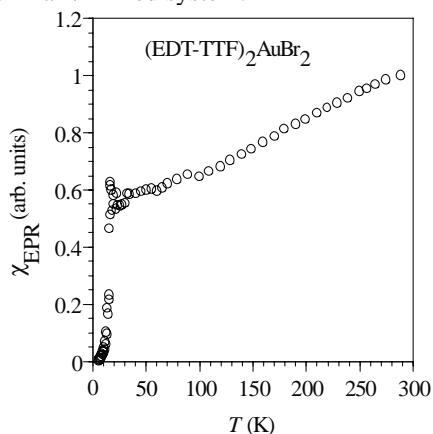


Figure 1. Temperature dependence of the spin susceptibility, χ_{EPR} , of $(\text{EDT-TTF})_2\text{AuBr}_2$ determined by EPR measurements.

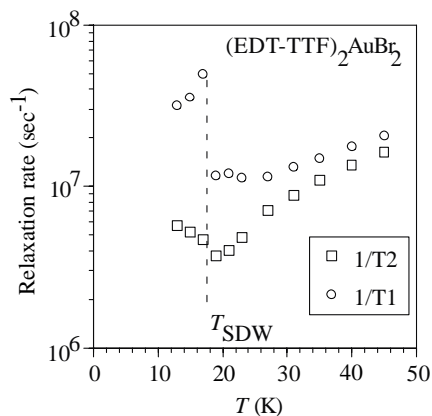


Figure 2. The temperature dependence of the EPR spin-lattice relaxation rate, T_1^{-1} , (circle) and the spin-spin relaxation rate, T_2^{-1} , (square).

IV-C-2 Low Temperature Electronic States of β' -type $\text{Pd}(\text{dmit})_2$ Compounds

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Research of metal dithiolene complexes $M(\text{dmit})_2$ is one of major trend in the development of molecular based conductors with new functions. Although several metallic compounds even at ambient pressure are observed in $\text{Ni}(\text{dmit})_2$ compounds, most of $\text{Pd}(\text{dmit})_2$ compounds show paramagnetic non-metallic behavior at ambient pressure. In order to clarify the mechanism of the charge localization of β' -type $\text{Pd}(\text{dmit})_2$ compounds, we have carried out electron spin resonance measurements for β' -type $\text{Pd}(\text{dmit})_2$.

We found that most of them except one compound undergo antiferromagnetic transition. Although they are isostructural and with little differences in lattice parameters, the EPR linewidth, ΔH_{pp} , and the antiferromagnetic transition temperature, T_N , show a huge sample dependence. We found a close relation between the T_N and inter-stack interaction (Figure.1). Since the crystal structure of the $\text{Pd}(\text{dmit})_2$ system is based on the stack of strongly dimerized $\text{Pd}(\text{dmit})_2$ molecules, the conduction band is considered to be formed by the two-dimensional half-filled HOMO band. The EPR g -values of β' -type $\text{Pd}(\text{dmit})_2$ are found to be beyond one radical description which is a good approximation for conventional molecular based conductors; we should consider the wave-function $\text{Pd}(\text{dmit})_2$ supermolecules. These experimental facts are evidences from the view point of magnetic investigation that this family is a Mott-Hubbard insulator with dimer as a unit. In order to understand more detailed electronic structure, we synthesized ^{13}C substituted $\text{Pd}(\text{dmit})_2$ molecules, and ^{13}C -NMR investigation are performed. The electronic structures of a series of molecular conductors based on $\text{Pd}(\text{dmit})_2$ are discussed from microscopic points of view.

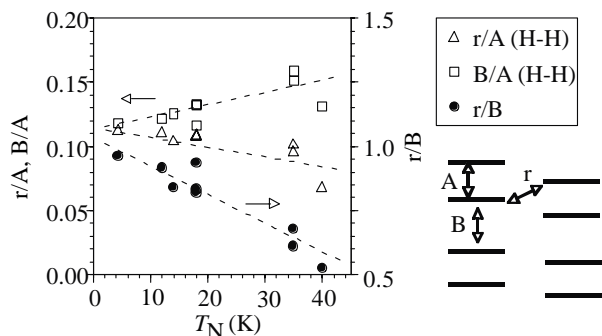


Figure 1. Relationship between the inter-dimer interaction versus the T_N . Previous results determined by $^1\text{H-NMR}$ are also included in this figure. The parameters, A , B and r , which are shown in the schematically shown in insets, are same in previous report. The Broken line is a guide to the eye.

IV-C-3 Magnetic Investigation of Organic Conductors Based on TTP Derivatives

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Most of TTP based organic conductors possess stable metallic phases. It is widely believed that the extended π orbital reduces on-site Coulomb interaction. To clarify the electronic states of the low-temperature phases, we performed $^1\text{H-NMR}$ measurements for $(\text{BDT-TTP})_2\text{SbF}_6$. Figure 1 show the temperature dependence of the $^1\text{H-T}_1^{-1}$ of the $(\text{BDT-TTP})_2\text{SbF}_6$. The $^1\text{H-T}_1^{-1}$ exhibits a characteristic temperature dependence. A large enhancement with a peak around 160 K is well fitted by the BPP type relation, indicating a possible relaxation by molecular motion. But no simple explanation can be offered at present, since the BDT-TTP molecule does not seem to possess internal freedom. Between 20 and 100 K, the $^1\text{H-T}_1^{-1}$ shows a T-linear temperature dependence, suggesting Korringa-like relation. The magnitude of the $(T_1T)^{-1}$ of 6.9×10^{-4} ($\text{sec}^{-1}\text{K}^{-1}$) is comparable to that of a typical organic superconductor, β -(BEDT-TTF) $_2\text{I}_3$ (5.8×10^{-4} ($\text{sec}^{-1}\text{K}^{-1}$)). Below 20 K, the $^1\text{H-T}_1^{-1}$ starts to deviate from the Korringa-like behavior and shows a $T^{0.5}$ dependence. To investigate more detail, we carried out measurements operated at 196 MHz. As seen in the inset of Figure 1, low temperature results of the $^1\text{H-T}_1^{-1}$ show different behavior between 89.4 MHz and 196 MHz, although those above 20 K agree with each other. The deviation from the Korringa-like behavior seems to be suppressed at high frequency measurements. Moreover estimated ratio, T_1^{-1} (89.4 MHz)/ T_1^{-1} (196 MHz), of 1.39 at 12 K is close to the expected value of 1.48 assuming one-dimensional diffusive propagation of spin-excitation. In conclusion, our NMR measurements for two organic conductors based on TTP derivative tell that 1) the present salts are Q1D electronic system, and that 2) electronic correlation seems to be comparable to those of typical BEDT-TTF salts.

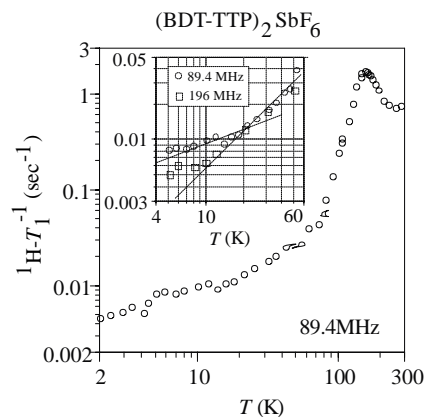


Figure 1. Temperature dependence of the $^1\text{H-NMR}$ spin-lattice relaxation rate, $^1\text{H-T}_1^{-1}$, of $(\text{BDT-TTP})_2\text{SbF}_6$ over the complete range of our investigation. The inset shows the low temperature region of the $^1\text{H-T}_1^{-1}$ (a) operated at 89.4 MHz (circle) (b) at 196 MHz (square).

IV-C-4 Possible Charge Disproportionation and New Type Charge Localization in θ -(BEDT-TTF) $_2\text{CsZn}(\text{SCN})_4$

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We have investigated the magnetic properties of the θ -(BEDT-TTF) $_2\text{CsZn}(\text{SCN})_4$. A large enhancement of the $^1\text{H-NMR-T}_1^{-1}$ and the spin susceptibility was observed below 20 K. The principal axes of the EPR g -tensor have been found to change their directions, keeping the principal values constant. The abrupt rotation of the axes has indicated a phase transition at 20 K. We have proposed a possible model of the electronic state of a quarter-filled two-dimensional system, θ -(BEDT-TTF) $_2\text{CsZn}(\text{SCN})_4$: In the high-temperature metallic region, a charge disproportionation seems to grow as temperature decreases. The low temperature insulating phase is essentially a state of charge localization where most of the sites are local spin-singlet. The low-temperature magnetism is originated from small number of unpaired local moments. To understand the unusual transition in a quarter-filled two-dimensional system, more works are required. We are preparing $^{13}\text{C-NMR}$ lineshape analysis.

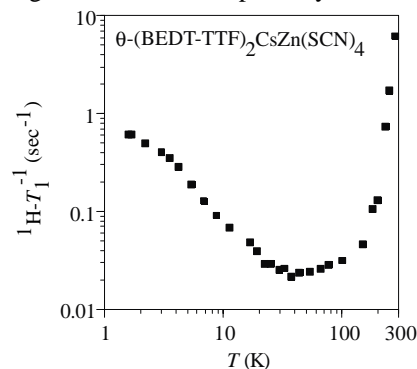


Figure 1. Temperature dependence of the $^1\text{H-NMR}$ spin-lattice relaxation, T_1^{-1} .