IV-C Microscopic Investigation of Molecular-Based Conductors

The aim of this research is to clarify the electronic states (charge and spin states) of molecular based compounds with curious electronic phases by microscopic point of view. Although the fundamental properties of molecular based conductors have been very well clarified, it is true that there still remain several unsolved questions in the molecular based conductors.

Microscopic investigations are advantageous for understanding the microscopic charge and spin states. To clarify the low temperature electronic states, we performed the ^{1}H, ^{13}C NMR, and ESR measurements for molecular based conductors.

IV-C-1 Possible Successive SDW Transition in (EDT-TTF)$_2$AuBr$_2$

NAKAMURA, Toshikazu

[*J. Phys. Soc. Jpn.* **69**, 4026 (2000)]

The low temperature magnetic properties in the quasi-one-dimensional system, (EDT-TTF)$_2$AuBr$_2$, were investigated by using ^{1}H-NMR and ESR techniques. (EDT-TTF)$_2$AuBr$_2$ undergoes an SDW transition at 16 K. At 6 K, an anomalous second-peak of ^{1}H-NMR spin-lattice relaxation rate, ^{1}H-T_1^{-1}, in the SDW phase has been observed. An additional increase of ^{1}H-NMR absorption line and gradual decrease of spin-spin relaxation rate, ^{1}H-T_2^{-1}, were observed below 6 K. The magnetic properties of the SDW phase observed in the present salt are discussed from microscopic points of view.

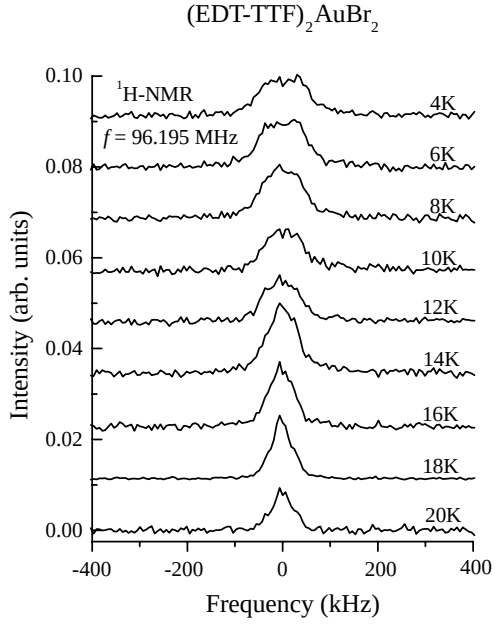

Figure 1. Temperature dependence of the ^{1}H-NMR absorption lines of powdered (EDT-TTF)$_2$AuBr$_2$ crystals.

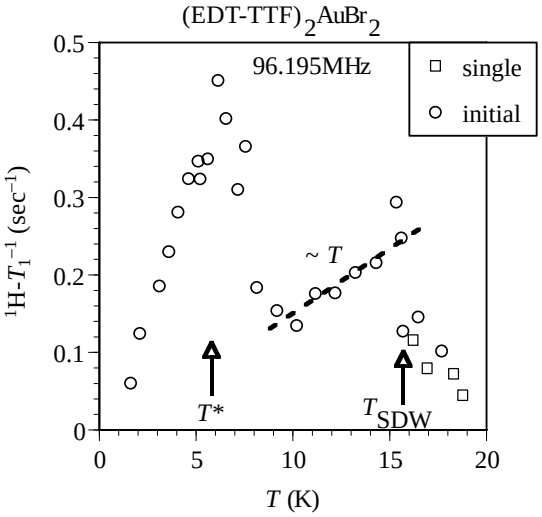

Figure 2. Temperature dependence of the ^{1}H-NMR spin-lattice relaxation rate, T_1^{-1}, in the SDW phase.

IV-C-2 Magnetic Investigation of Organic Conductors Based on TTP Derivatives

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[*Synth. Met.* **120**, 869 (2001)]

Magnetic investigation of organic conductors based on TTP derivatives, (BDT-TTP)$_2$SbF$_6$ and (EO-TTP)$_2$AsF$_6$, was carried out by ^{1}H-NMR measurements. The NMR spin-lattice relaxation rates, ^{1}H-T_1^{-1}, of the present salts deviate from the Korringa-like behavior at low temperatures. The low-temperature electronic states of the TTP family will be discussed from microscopic points of view.

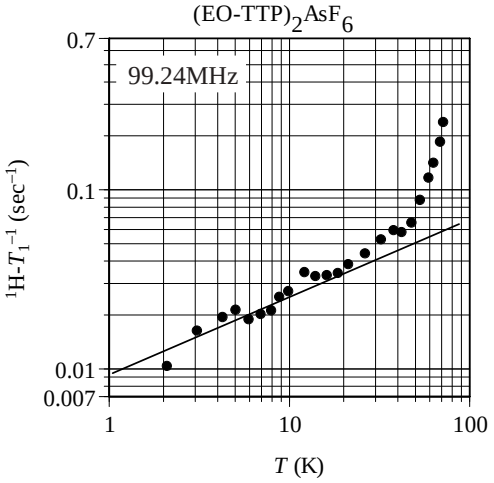

Figure 1. Temperature dependence of the ^{1}H-T_1^{-1} of (EO-TTP)$_2$AsF$_6$.

IV-C-3 Magnetic Properties of Organic Spin-Ladder Systems, (BDTFP)$_2X$(PhCl)$_{0.5}$

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[*Mol. Cryst. Liq. Cryst.* in press]

(BDTFP)$_2X$(PhCl)$_{0.5}$ (X = AsF$_6$, PF$_6$) are quasi-one-dimensional organic conductors with so-called two leg ladder structures; the inter-ladder interaction is one-order smaller than that in intra-ladder. Since there is a considerable dimerization within the column, the upper band is a half-filled.

Figure 1 shows the temperature dependence of the spin susceptibility of the PF$_6$ salt. Between 170 and 300 K, the spin susceptibility is almost temperature independent, but gradually increases as temperature decreases. The EPR signal intensity suddenly decreases below 170 K where the resistivity shows an abrupt jump. The EPR linewidth also shows anomaly; it abruptly decreases around 170 K, suggesting an abrupt change of the relaxation mechanism of the electron spins. It is proved that the low temperature phase of the PF$_6$ salt is spin-singlet.

Figure 2 shows the temperature dependence of the spin susceptibility of the AsF$_6$ salt. In the case of the cooling process, the spin susceptibility abruptly increases around 230 K, suggesting the existence of a phase transition. Below 200 K, the spin susceptibility of the AsF$_6$ salt shows a Curie-like enhancement. This hysteresis phenomenon indicates that the transition is of first order. The low temperature phases are undoubtedly different between the AsF$_6$ and PF$_6$ salts. Below 50 K, the spin susceptibility of the AsF$_6$ salt turns to decrease, indicating spin-gap behavior. It fits with Troyer's prediction for the undoped two-leg ladder. However an abrupt broadening of the EPR line indicates existence of a magnetic order at 14 K.

Although the electronic states of the PF$_6$ and AsF$_6$ salts at R. T. are very similar, those at low temperatures are quite different. Detailed investigations are now going on.

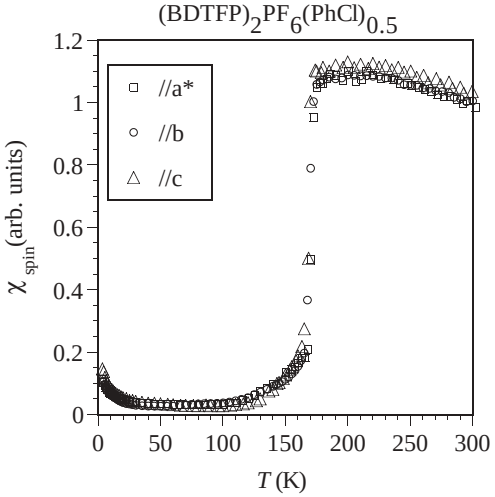

Figure 1. Temperature dependence of the spin susceptibility of (BDTFP)$_2$PF$_6$(PhCl)$_{0.5}$ determined by the EPR signal intensity of a single crystal.

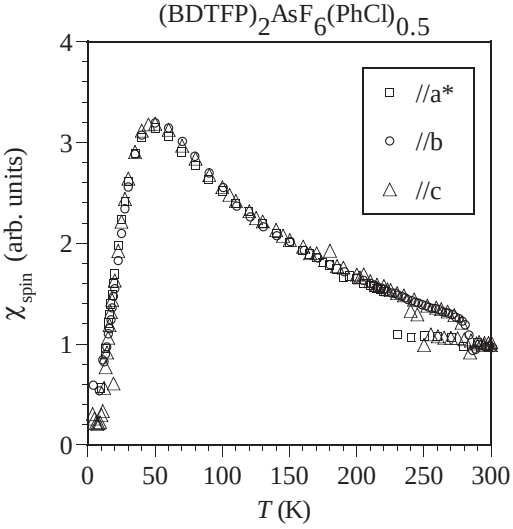

Figure 2. Temperature dependence of the spin susceptibility of (BDTFP)$_2$AsF$_6$(PhCl)$_{0.5}$ determined by the EPR signal intensity of a single crystal.

IV-C-4 EPR Investigation of the Electronic States in β'-type [Pd(dmit)$_2$]$_2$ Compounds (Where dmit is the 1,3-dithia-2-thione-4,5-dithiolato)

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([1]Gakushuin Univ.; [2]Univ. Tokyo; [3]Inst. Phys. Chem. Res.)

[*J. Mater. Chem.* in press]

Magnetic investigations of organic conductors, β'-type [Pd(dmit)$_2$]$_2$, have been performed by Electron Paramagnetic Resonance (EPR) measurements. We found that most of them except one compound underwent antiferromagnetic transitions. Although they are isostructural with little differences in lattice

parameters, their spin-spin correlations and antiferromagnetic transition temperatures show strong counter ion dependence. The EPR *g*-values of $Pd(dmit)_2$ cannot be explained within the framework of isolated radical description, which is a good approximation for conventional organic conductors. The electronic structures of a series of molecular conductors based on $Pd(dmit)_2$ at ambient pressure are discussed from microscopic points of view.

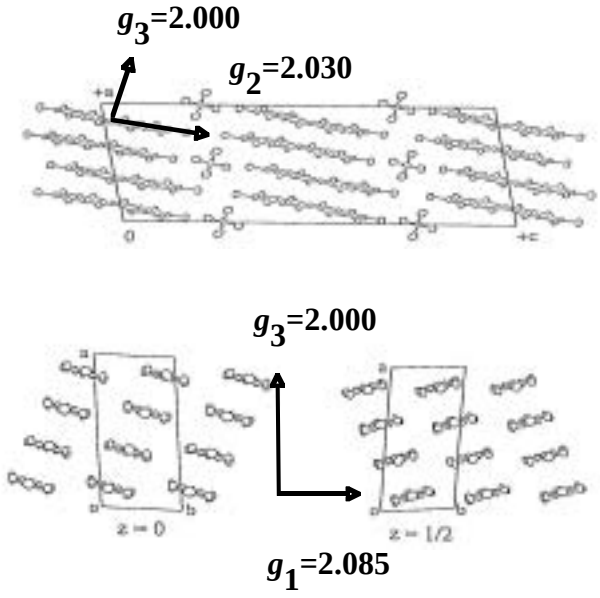

Figure 1. Determined principal axes and values β'-Et_2Me_2P-$[Pd(dmit)_2]_2$ on the actual crystal structure.

IV-C-5 Microscopic Investigation of Itinerant and Local Spins System, $(CHTM\text{-}TTP)_2TCNQ$

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([1]Kyoto Univ.; [2]Okayama Univ.)

$(CHTM\text{-}TTP)_2TCNQ$ is a new organic conductor developed by Kyoto university group. This compound is composed of segregated donor (CHTM-TTP) and acceptor (TCNQ) layers. The CHTM-TTP molecules stack to form one-dimensional columns. On the other hand, there is little interaction between the TCNQ molecules. This salt shows metallic behavior down to 30 K with abrupt jump around 240 K. In order to clarify the low temperature electronic phases of this salt, we performed magnetic investigation.

Figure 1 shows the temperature dependence of the spin susceptibility determined by the EPR signal intensity. Between 240 K and 300 K, the spin susceptibility shows a gradual increase as the temperature decreases. At 240 K and 170 K, the spin susceptibility decreases abruptly. The principal values of the *g*-tensor change their absolute values both at the transition temperatures. It cannot be explained within the framework of one spin picture . These observations lead us to a conclusion that effective local moments on TCNQ decrease at 240 K, and that disappear perfectly below 170 K.

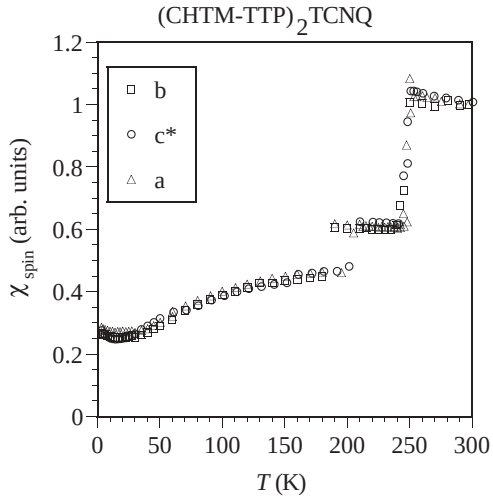

Figure 1. Temperature dependence of the spin susceptibility of $(CHTM\text{-}TTP)_2TCNQ$ determined by the EPR signal intensity of a single crystal.