IV-B 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 detailed electronic structures of molecular based compounds. To clarify the low temperature electronic states, we performed the NMR, and ESR measurements for molecular based conductors.

IV-B-1 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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[*J. Mater. Chem.* **11**, 2159 (2001)]

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.

IV-B-2 NMR Study of Charge Localized States of $(TMTTF)_2Br$

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[*J. Phys. Chem. Solids* **63**, 1259 (2002)]

^{13}C NMR study was performed for a quasi-one-dimensional organic conductor $(TMTTF)_2Br$ using a single crystal in which two central carbon sites of TMTTF molecules were labeled with ^{13}C. To investigate the relation between the charge localization around 100 K and its magnetic ground state from the microscopic point of view, we measured the NMR spectra and nuclear relaxation. We found slight broadening of the spectra above the magnetic phase transition temperature (T_N ~ 15 K). We discuss this anomaly with the newly measured data of uniform susceptibility and ESR.

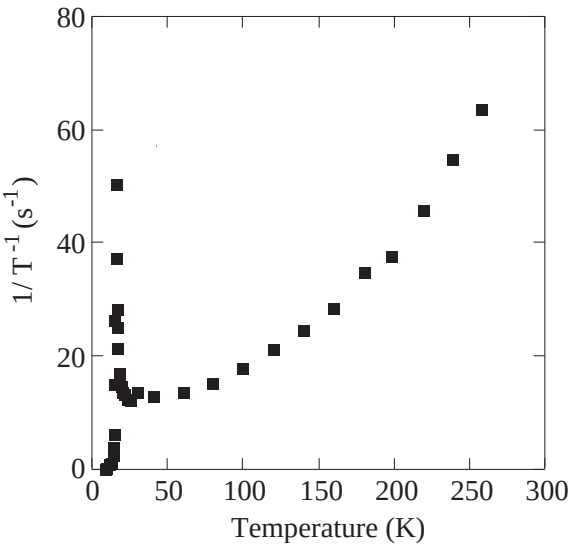

Figure 1. Temperature dependence of spin lattice relaxation rate $1/T_1$ of ^{13}C NMR. The values are deduced by fitting the experimental recovery data with a single exponential.

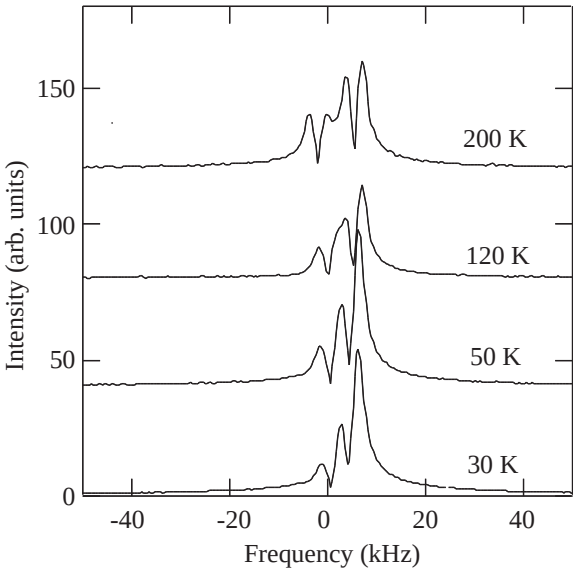

Figure 2. Temperature dependence of ^{13}C NMR spectra of $(TMTTF)_2Br$ above 30 K. The horizontal axis indicates the deviation from 87.25 MHz.

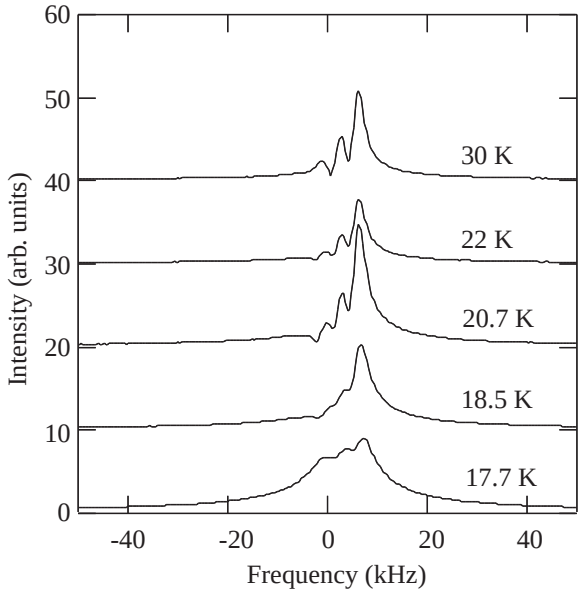

Figure 3. Temperature dependence of the ^{13}C NMR absorption lines between 17 K and 30 K.

IV-B-3 Magnetic Investigation of Possible Quasi-One-Dimensional Two-Leg Ladder Systems, $(BDTFP)_2X(PhCl)_{0.5}$ (X = PF_6, AsF_6)

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[*J. Phys. Soc. Jpn.* **71**, 2022 (2002)]

ESR and ^{1}H-NMR investigations of the quasi-one-dimensional organic conductors, $(BDTFP)_2X(PhCl)_{0.5}$ (X = PF_6, AsF_6), were carried out. The low-temperature physical properties of the title compounds are quite different from each other, although those at R.T. are very similar. The PF_6 salt undergoes a spin-singlet transition around 170 K. On the other hand, the AsF_6 salt shows a discontinuous transition of first order around 230 K, in association with an abrupt jump in the spin susceptibility. The AsF_6 salt shows spin-gap behavior below 50 K, but it undergoes an antiferromagnetic transition at 14 K. The low-temperature electronic states of the title compounds are discussed by microscopic point of view.

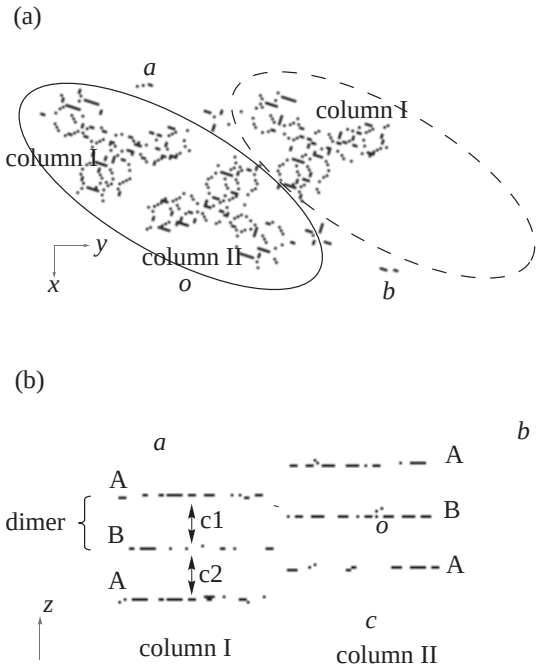

Figure 1. Crystal structure of $(BDTFP)_2X(PhCl)_{0.5}$: (a) possible two-leg ladder structures, (b) dimerization along the stacking axes.

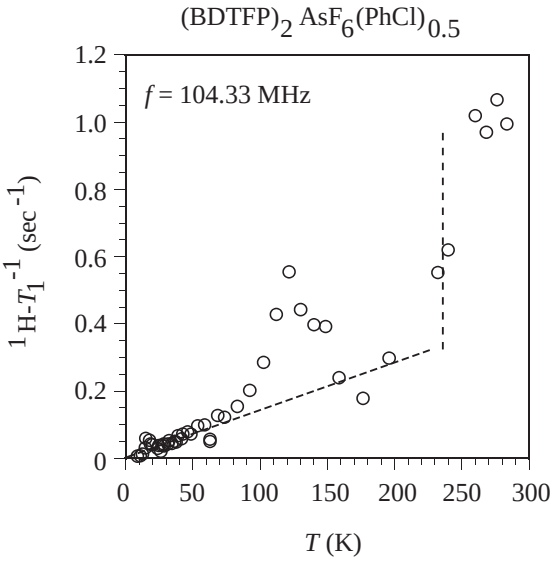

Figure 2. Temperature dependence of the ^{1}H-NMR spin-lattice relaxation rate, ^{1}H-T_1^{-1}, of $(BDTFP)_2AsF_6(PhCl)_{0.5}$ for a single crystal.

IV-B-4 Microscopic Investigation of a New Two-Component Organic Conductor with Itinerant and Localized Spins: $(CHTM\text{-}TTP)_2TCNQ$

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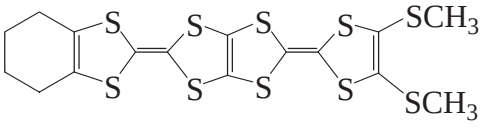
[*J. Phys. Soc. Jpn.* in press]

Low-temperature electronic phases in a new two-

component organic conductor, a segregated-stack charge-transfer salt called $(CHTM\text{-}TTP)_2TCNQ$, are investigated. The ESR *g* tensor analyses indicate that there exist itinerant CHTM-TTP spins and localized TCNQ spins at R.T. The temperature dependence of the physical parameters reveals that this salt undergoes two drastic, successive phase transitions at low temperatures. The effective moment of the localized TCNQ spins decreases at the 245 K transition and completely disappears at the transition around 195 K. These curious physical properties are explained by the drastic changes in the electronic states of the two different types of spins. The spin susceptibility was decomposed into the contribution of each of the two spin species by using ESR, ^{1}H-NMR, and static susceptibility analyses. We present a microscopic investigation of the two-spin system with itinerant and localized moments.

(a)



CHTM-TTP

(b)

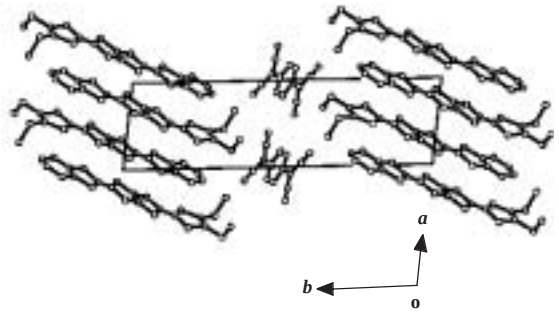


Figure 1. (a) Molecular structure of CHTM-TTP. (b) Crystal structure of $(CHTM\text{-}TTP)_2TCNQ$ at R.T.

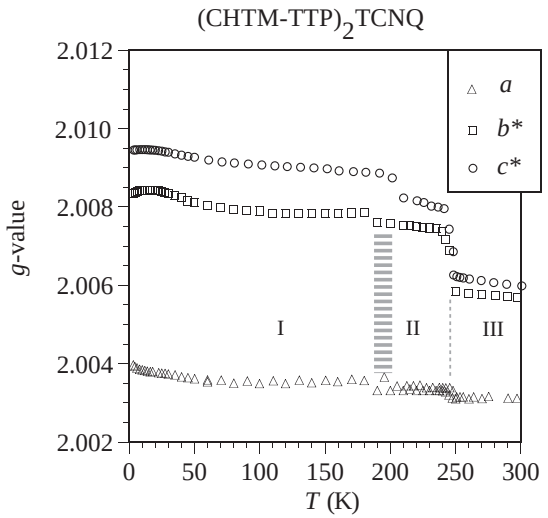


Figure 2. Temperature dependence of the *g* values of $(CHTM\text{-}TTP)_2TCNQ$ applying the external static field along the *a* (triangle), *b** (square), and *c** (circle) crystal axes.

IV-B-5 ESR Study of the Charge Ordering States in $(TMTTF)_2X$

NAKAMURA, Toshikazu

ESR investigations were performed for a series of organic conductors, $(TMTTF)_2X$ (X = SbF_6, AsF_6, PF_6, ReO_4, ClO_4, SCN, Br). The ESR linewidth shows abrupt jumps or humps in the paramagnetic insulating region. The $(TMTTF)_2X$ compounds are roughly divided into three groups in the aspect of the anisotropy of the ESR linewidth at low-temperatures. We discuss the low-temperature charge distributed pattern from the microscopic point of view.

Figure 1 show the temperature dependence of the peak-to-peak ESR linewidth, ΔH_{pp}, of $(TMTTF)_2ReO_4$. The angular dependence of the ΔH_{pp} for the *c***a* plane at 300 K, 170 K and 110 K is shown in the inset of Figure 1. While the ΔH_{pp} reveals the standard anisotropic behavior in the metallic region, that at 110 K follows the formula for dipole-dipole interacted spins. This fact indicates that the electronic dipoles contribute to the ESR linewidth in the low temperature region. Considering the anisotropy of the ESR linewidth, we can estimate the charge distribution patterns in the low temperature phase. According to the experimental result, $\Delta H_a >> \Delta H_{b'} \sim \Delta H_{c*}$, the possible charge ordering pattern is –O–O–o–o– along the stacking axes (O and o indicate the charge rich and poor sites, respectively) with the wave-number, Q = (1/2, 0, 1/2).

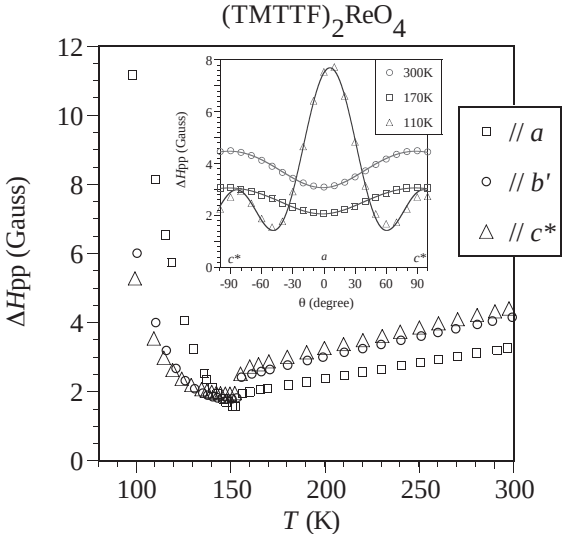


Figure 1. Temperature dependence of the peak-to-peak ESR linewidth, ΔH_{pp}, of $(TMTTF)_2ReO_4$ for a single crystal. The inset shows the angular dependence of the ΔH_{pp} at 300 K, 170 K and 110K. The static magnetic field applied in the *c***a*-plane.