

# Magnetic Resonance Studies for Molecular-Based Conductors

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Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

## 1. Anomalous Temperature Dependence of $g$ -Tensor in Organic Conductor, $(\text{TMTTF})_2\text{X}$ ( $\text{X} = \text{Br}$ , $\text{PF}_6$ and $\text{SbF}_6$ )

The magnetic properties of organic conductor  $(\text{TMTTF})_2\text{X}$  ( $\text{X} = \text{Br}$ ,  $\text{PF}_6$  and  $\text{SbF}_6$ ), where TMTTF is tetramethyltetrathiafulvalene, were examined by electron spin resonance (ESR) spectroscopy, X-ray diffraction (XRD) of the single crystals, and quantum-chemical calculation of the  $g$ -tensor. In the case of salts with bulky counter anions such as the  $\text{PF}_6$  and  $\text{SbF}_6$ , an anomalous temperature dependence of the  $g$ -tensor was observed in the temperature range from 20 K to 296 K. This anomalous behavior of the  $g$ -tensor signifies the rotation of the principal axes as well as the shift of the principal values. The  $g$ -tensor of the Br salt is, however, temperature independent. No remarkable change in the intra-molecular structure as a function of temperature was observed for all salts. On the other hand, the distance between TMTTF and counter-anion molecules obviously decreases as the temperature decreases for the  $\text{PF}_6$  and the  $\text{SbF}_6$  salts, while thermal contraction is not remarkable for the Br salt. In order to clarify the origin of the

anomalous behavior of the  $g$ -tensor, we investigated the possibility of deformation of the wave-function by the counter-anion potentials using a quantum-chemical calculation for the actual crystal structures measured at low-temperatures. In this paper, we describe the first direct observation of the deformation of the frontier orbital by the counter anion potential for organic conductors. The intra-molecular spin-distribution as a function of temperature also is discussed from the microscopic point of view.

## 2. Electronic Properties of a TMTTF-Family Salt, $(\text{TMTTF})_2\text{TaF}_6$ : New Member Located on the Modified Generalized Phase-Diagrams

A new TMTTF-family salt,  $(\text{TMTTF})_2\text{TaF}_6$ , which has the largest octahedral (Oh) symmetry counter anion among the various salts in the TMTTF family, was prepared. X-ray, static magnetic susceptibility, Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR) measurements were carried out in order to investigate the electronic state of  $(\text{TMTTF})_2\text{TaF}_6$ . The unit-cell volume of  $(\text{TMTTF})_2\text{TaF}_6$  is larger than that of  $(\text{TMTTF})_2\text{MF}_6$  ( $M = \text{P}$ ,  $\text{As}$  and  $\text{Sb}$ ).  $(\text{TMTTF})_2\text{TaF}_6$  shows the highest charge-ordering phase transition temperature ( $T_{\text{CO}} \sim 175$  K) among TMTTF salts with the Oh-symmetry counter anion. These facts indicate that  $(\text{TMTTF})_2\text{TaF}_6$  is located on the most negative side in the generalized phase-diagram for TMTCF family salts.  $(\text{TMTTF})_2\text{TaF}_6$  undergoes an antiferromagnetic transition around 9 K. It turned out the phase diagram needs to be modified.

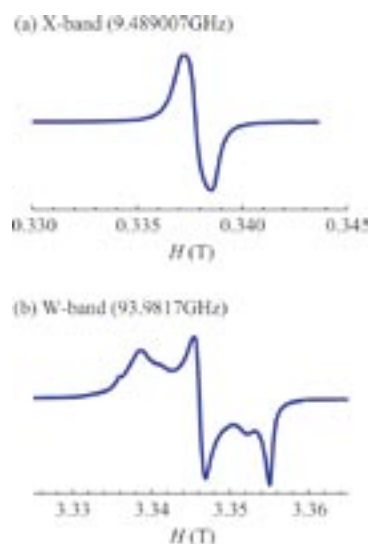
## 3. Spin-Dynamics in Vicinity of Phase Transition for Organic Conductor $(\text{TMTTF})_2\text{X}$

The spin dynamics in the vicinity of the spin-gap phase transition for the organic conductor  $(\text{TMTTF})_2\text{PF}_6$  were examined by pulsed-ESR spectroscopy. An anomaly in the

relaxation time was observed in the intermediate region between the ground state and the high-temperature phase and was associated with the charge re-orientation originating in the transverse magnetic interaction. The calculation of the overlap integrals implied considerable inter-chain interactions. The transverse magnetic interaction plays an important role of the spin-gap phase transition in  $(\text{TMTTF})_2\text{PF}_6$ .

#### 4. Novel Type of Carrier Generated System: Magnetic Investigations of TTF-Based Self-Doped Hydrogen-Bonding Conductor

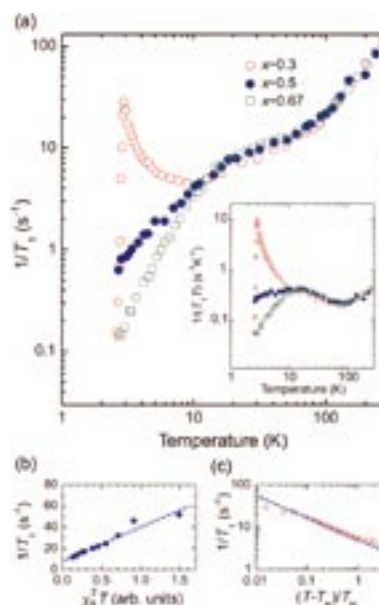
Magnetic investigations, including static magnetic susceptibility and high-field Electron Spin Resonance (ESR) measurements, were carried out for an organic conductor,  $(\text{TTF}^+\text{COO})[(\text{NH}_4^{+1})_{1-x}(\text{NH}_3)_x]$ . Anisotropic ESR parameters were determined for powder samples using a high-frequency W-band (93.9817 GHz) ESR spectrometer. The observed principal values of the  $g$ -tensor and quantum chemical calculation results indicate that the observed spin is distributed on quasi-hole-like TTF skeletons, and that the TTFCOO main-frame partially becomes a neutral radical. The temperature dependence of the spin susceptibility is well fitted with a Curie-Weiss term and an activation-type term, with the activation-type term dominant at high temperatures. The high absolute value of the spin susceptibility and the extremely small activation energy,  $\Delta$ , indicate that a quasi-degenerate (metallic) state is stabilized in  $(\text{TTF}^+\text{COO})[(\text{NH}_4^{+1})_{1-x}(\text{NH}_3)_x]$ , although the weakly temperature-dependent ESR linewidth indicates a localized characteristic. A novel type of carrier generation, self-doping, was discussed.



**Figure 1.** Typical ESR spectra for powder  $(\text{TTF}^+\text{COO})[(\text{NH}_4^{+1})_{1-x}(\text{NH}_3)_x]$  (at 100 K) using the (a) X-band (93.9817 GHz), and (b) W-band (93.9817 GHz), frequency regions.

#### 5. The Ground States and Critical Behavior in the Quasi-One-Dimensional Complexes $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$

$^{13}\text{C}$  NMR measurements were carried out to understand the chemical pressure effect on the ground state in quasi-one-dimensional (1D) organic complexes using the alloy system  $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$  ( $x \sim 0.3, 0.5, 0.67$ ). The temperature of the charge-ordering transition decreases with the concentration of  $\text{AsF}_6$ . Additional line splitting and the rapid increase in the spin-lattice relaxation rate,  $1/T_1$ , on cooling for the salt of  $x \sim 0.3$  indicates that the ground state of the salt is antiferromagnetic. In the  $x \sim 0.67$  alloy, the spin gap opens without antiferromagnetic spin correlations. The intermediate salt of  $x \sim 0.5$  is located in the vicinity of the quantum critical region between two phases at low temperatures. The quasi-1D correlation and antiferromagnetic critical behavior are discussed in terms of the power-law behavior of  $1/T_1$ .



**Figure 2.** a) Temperature dependence of  $1/T_1$ . The inset shows the temperature dependence of  $1/(T_1 T)$ . (b)  $1/T_1$  as a function of  $\chi_S^2 T$  for the alloy of  $x \sim 0.5$ . (c) Power-law behavior of  $1/T_1$  for the alloy of  $x \sim 0.3$  on approaching  $T_N$  by lowering temperature.

#### References

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#### Award

SUGIURA, Koichi; Tokai-Branch, Chemical Society of Japan Award.