Magnetic Resonance Studies for Molecular-Based Conductors

Department of Materials Molecular Science
Division of Electronic Properties

NAKAMURA, Toshikazu	Associate Professor
FURUKAWA, Ko	Assistant Professor
IWASE, Fumitatsu	IMS Fellow
SUGIURA, Koichi	Graduate Student
ABE, Hitomi	Secretary

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.[1)] 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. ^{13}C NMR Study of the Chemical Pressure Effect in $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$ ($x \sim 0.5$)

^{13}C NMR measurements of $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$ ($x \sim 0.5$) alloy were performed in order to understand the chemical pressure effect and the electronic state at low temperatures. The charge-ordering transition temperature is the intermediate value between those of SbF_6 and AsF_6 salts. The broadening of NMR spectra and the weak temperature dependence of the spin-lattice relaxation rate at low temperatures indicate that this salt is situated in the vicinity of the phase boundary between the spin-Peierls and antiferromagnetic phases.

2. ^{13}C NMR Investigation of Low-Temperature States in One-Dimensional Organic Cation Radical Salt, $(TMTTF)_2SbF_6$, under High Pressures

^{13}C nuclear magnetic resonance (NMR) measurements under the application of hydrostatic pressure were carried out on the one-dimensional organic conductor, $(TMTTF)_2SbF_6$, to investigate the competed antiferromagnetic and spin-singlet ground states. The charge-ordering (CO) transition temperature, T_{CO}, (155 K at ambient pressure), decreased to 100 K under a pressure of 5 kbar, and was suppressed above 8 kbar. Under pressures between 5 kbar and 14 kbar, the low-pressure side antiferromagnetic state (AF-I) was suppressed. At the same time, a spin-gap phase was stabilized. Above 17 kbar, another antiferromagnetic phase appeared below approximately 15~20 K. A possible reentrant antiferromagnetic phase diagram is discussed from a microscopic point-of-view.

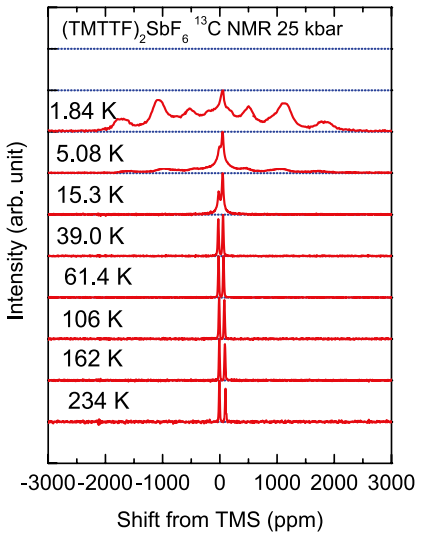

Figure 1. Temperature dependence of the ^{13}C NMR spectra of $(TMTTF)_2SbF_6$ under a pressure of 25 kbar.

3. Anomalous Temperature Dependence of *g*-Tensor in Organic Conductor, $(TMTTF)_2X$ (X = Br, PF_6 and SbF_6)

The magnetic properties of organic conductor $(TMTTF)_2X$ (X = Br, PF_6 and SbF_6), where TMTTF is tetramethyltetrathia-

fulvalene, 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 PF_6 and 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 PF_6 and the 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.

4. Spin-Dynamics in Vicinity of Phase Transition for Organic Conductor $(TMTTF)_2X$

$(TMTTF)_2PF_6$ shows unique electronic state with a charge ordering phase above the ground state. The spin dynamics in the vicinity of the spin-Peierls transition for the $(TMTTF)_2PF_6$ were examined and compared with those for the typical spin-Peierls materials, $MEM(TCNQ)_2$. The temperature dependence of the electron-spin relaxation rate, T_1^{-1} and T_2^{-1}, in the vicinity of the spin-Peierls transition was measured by pulsed-ESR spectroscopy. The FID signal was successfully detected and the relaxation rate for the condensed matter could be estimated. In the typical spin-Peierls system, $MEM(TCNQ)_2$, decrease of the spin-lattice relaxation and increase of the spin-spin relaxation were observed below the T_{sP}. On the other hand, an anomaly of the spin-spin relaxation rate was observed for the $(TMTTF)_2PF_6$ below the T_{sP}, which suggests the re-orientation of the charge. This behavior is not shown in typical spin-Peierls materials, and is peculiar to the spin dynamics of spin-Peierls materials with a charge ordering phase. This result is the first example of direct experimental estimation of the electron spin dynamics of the spin-Peierls transition.

5. ESR Investigation for Competed Electronic Phases in $(TMTTF)_2X$

A Quasi-one-dimensional conductors based on TMT*C*F (*C* = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-Peierls (sP), antiferromagnetic state (AF), incommensurate spin density wave (IC-SDW) and super-conductivity (SC), with applied pressures or counter anions, *X*. Findings of charge-ordering (CO) and related phenomena in $(TMTTF)_2X$ have attracted significant recent attention. We have also investigated the completed ground states and CO phenomena observed in the intermediated temperature region from the viewpoint of magnetic resonance.

Based on recent systematic transport measurements for $(TMTTF)_2X$ salts under ultra-high pressures, a possible modified generalized Pressure-Temperature phase diagram was proposed. However, this phase diagram is based on the preconceived idea that the spin-gap (spin-Peierls) phase, which is a quantum one-dimensional phase, is sandwiched between two antiferromagnetic phases. In a general sense, for conventional systems, antiferromagnetic phases are stabilized with finite inter-chain interactions with the application of pressure.

Therefore, in order to understand the whole phase diagram of the TMT*C*F-family salts, we prepared several TMTTF-family salts, such as $(TMTTF)_2TaF_6$ and $(TMTTF)_2I$, and carried out ESR measurements. Both salts undergo antiferromagnetic states, but the temperature dependences of the ESR properties are quite different. We discussed the competed electronic phases in $(TMTTF)_2X$ from a view of microscopic.

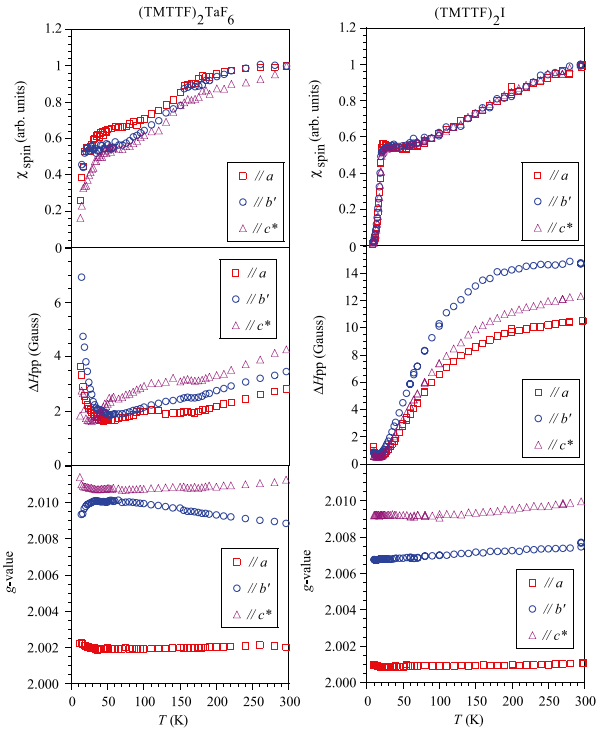

Figure 2. Temperature dependence of the ESR parameters, χ_{spin}, ΔH_{pp} and *g*-values, for $(TMTTF)_2TaF_6$ and $(TMTTF)_2I$.

References

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