

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.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. Another Commensurate Antiferromagnetic State in $(\text{TMTTF})_2\text{X}$: ^{13}C NMR Investigation of $(\text{TMTTF})_2\text{SbF}_6$

^{13}C nuclear magnetic resonance (NMR) investigations were performed on the one-dimensional organic conductor $(\text{TMTTF})_2\text{SbF}_6$ to clarify its electronic properties in the proximity of the ground states. An abrupt broadening of ^{13}C NMR absorption lines below 8 K ($T_N = 8$ K), confirmed a long-range antiferromagnetic phase transition. Below T_N , the absorption lines are composed of four distinct broad lines.

The ^{13}C NMR spin-lattice relaxation rates, $^{13}\text{C } T_1^{-1}$, for the distinct lines show critical enhancement just above T_N , and rapid decrease below T_N . These observations indicate that the ground state of $(\text{TMTTF})_2\text{SbF}_6$ is a commensurate antiferromagnetic phase. The amplitude of staggered magnetization, ρ , is comparable to $(\text{TMTTF})_2\text{Br}$, and on the order of 0.1 μ_B , according to the splitting of ^{13}C NMR lines at 3 K. However the angular dependence of the ^{13}C NMR shifts shows slight differences between $(\text{TMTTF})_2\text{SbF}_6$ and $(\text{TMTTF})_2\text{Br}$.

2. ^{13}C NMR Study of the Chemical Pressure Effect in $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$ ($x \sim 0.5$), and Physical Pressure Effect for $(\text{TMTTF})_2\text{SbF}_6$

Recently ISSP group discover superconductivity in $(\text{TMTTF})_2\text{SbF}_6$ and $(\text{TMTTF})_2\text{AsF}_6$ salts under ultra high pressures.^{2,3)} If we remind the ground states of SbF_6 and AsF_6 are spin-Peierls (sP) and antiferromagnetic (AF), respectively, the so-called generalized phase diagram should be modified (AF-I-sP-AF-II). Curiously enough, the one-dimensional sP phase is sandwiched by two AF phases. And it is also an open question whether QCP is likely or unlikely. Hence, We performed ^{13}C NMR measurements for $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$ ($x \sim 0.5$) alloy, and $(\text{TMTTF})_2\text{SbF}_6$ under pressure

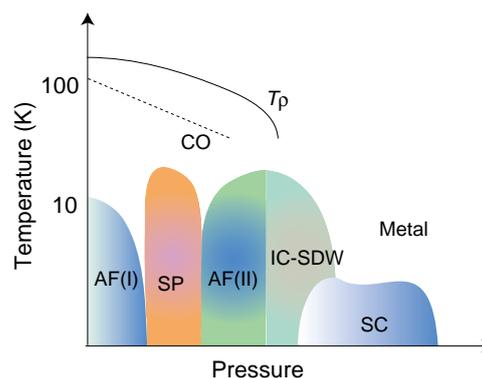


Figure 1. Modified generalized phase diagram for one-dimensional organic conductors, $(\text{TMTCF})_2\text{X}$.

in order to clarify following issues: 1) Does Quantum Critical phenomena exist between the sP and AF Phase boundary? 2) Is the sP phase actually sandwiched by two AF phase? 3) Are AF-I and AF-II of the same origin or not?

As for $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$ ($x \sim 0.5$), the charge-order transition temperature is the intermediate value between the critical temperatures of SbF_6 and AsF_6 . At low temperatures, we observed the characteristic behavior toward the

spin-Peierls phase transition. However, the temperature dependence of the spin-lattice relaxation rate is weak suggesting that this salt is situated in the vicinity of the phase boundary between the spin-Peierls and antiferromagnetic phases.

In the case of $(\text{TMTTF})_2\text{SbF}_6$, we observed clear phase change from AF to sP under 5 kbar. This observation supports the modified generalized phase diagram.

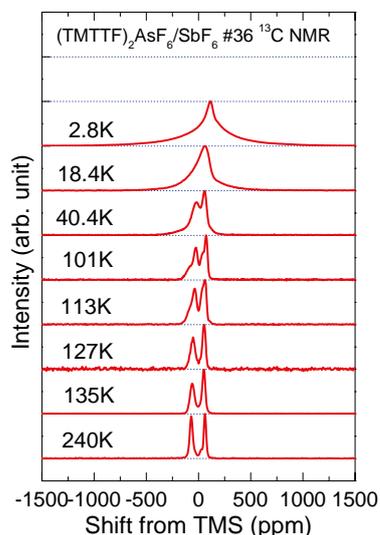


Figure 2. ^{13}C NMR spectra of $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$ ($x \sim 0.5$). The shift origin is TMS.

3. ESR Investigation of Novel Low-Dimensional Conductors, $(\text{TMTTF})_2\text{TaF}_6$ and $(\text{TMTTF})_3\text{Ta}_2\text{F}_{11}$

The electronic properties of one-dimensional organic conductor $(\text{TMTTF})_2X$ were extremely investigated by a lot of researchers because of the variety of the electric properties. These electronic properties were drastically changed by external pressures or variety of counter anions (chemical pressure). In fact, the counter anion size is recognized as an important factor to emerge various type phases such as sP (spin-Peierls), SDW (spin density wave), CO (charge-order), AF (antiferromagnetic) and SC (superconductor).

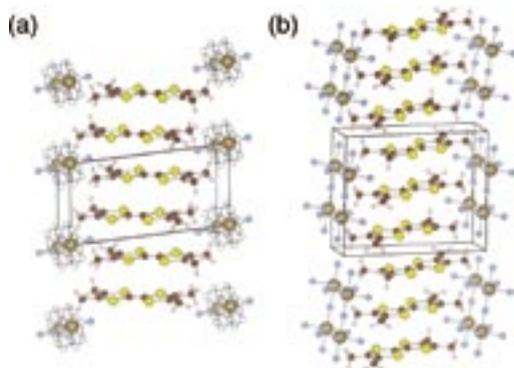


Figure 3. Crystal Structure of novel organic conductors, $(\text{TMTTF})_2\text{TaF}_6$ and $(\text{TMTTF})_3\text{Ta}_2\text{F}_{11}$.

Recently, we obtained novel organic conductors, $(\text{TMTTF})_2\text{TaF}_6$ and $(\text{TMTTF})_3\text{Ta}_2\text{F}_{11}$, by electrochemical oxidation. The lattice parameters of $(\text{TMTTF})_2\text{TaF}_6$ are expected to be the largest among $(\text{TMTTF})_2X$ family, and $(\text{TMTTF})_2\text{TaF}_6$ is beyond the pristine Jérôme phase diagram.¹⁾ Hence, the electronic properties of $(\text{TMTTF})_2\text{TaF}_6$ are not clarified and attracted much attention. It should be noted that the band-structure of $(\text{TMTTF})_3\text{Ta}_2\text{F}_{11}$ is different from those of typical organic conductors, $(\text{TMTTF})_2X$ salts, since $(\text{TMTTF})_3\text{Ta}_2\text{F}_{11}$ is a 3:1 salt. In this study, we carried out ESR measurements, and discuss the electronic states from the temperature dependence of the spin susceptibility, linewidth and g -value.

4. ESR Study of Spin Dynamics for Dye-Sensitized Solar Cell

In dye-sensitized solar cells (DSSC),⁴⁾ dye molecules are excited from the ground state S to the excited state S^* by photo energy. The electron transfer from the excited dye molecules to the electrode plays an important role of the photoelectric transfer characteristic in DSSC. A various type of dye molecules were investigated. Time-resolved ESR measurements give us to detailed information of the photoelectric transfer characteristic. The aim of the present study is to reveal the relationship between the photoelectric transfer characteristic and the spin dynamics of electron in DSSC. The spin dynamics of the various organic dye molecules such as the eosin-Y was investigated by time-resolved ESR spectroscopy with laser photolysis (Nd:YAG 2nd harmonics, 532 nm). We discuss the spin dynamics of the various organic dye molecules with TiO_2 .

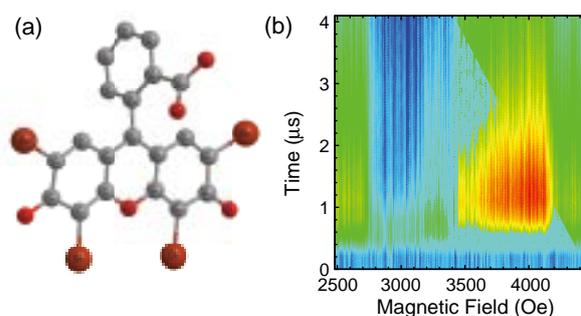


Figure 4. Molecular structure of eosin-Y, and time-resolved ESR spectroscopy of eosin-Y with laser photolysis.

References

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