Magnetic Resonance Studies for Functional Molecular-Based Solids

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Keywords Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

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.

Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Nakamura, K. Furukawa, T. Terauchi and Y. Kobayashi, " Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate," *Phys. Status Solidi RRL* **9**, 480–484 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Curious Electronic Phases and ESR Behaviors in One-Dimensional Organic Conductors (TMT*C*F)$_2$*X*

One-dimensional conductors based on (TMT*C*F)$_2$*X* (*C* = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-singlet (SS), commensurate antiferromagnetic state (C-AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, *X*. Moreover, findings of charge-ordering (CO) and related phenomena in (TMTTF)$_2$*X* have attracted significant recent attention.

(TMTTF)$_2$Br undergoes antiferromagnetic transition at 16 K (T_N). But it is located on the proximity between C-AF and IC-SDW phase in the generalized phase diagram. Previously, we examined the magnetic structure of the antiferromagnetic state of (TMTTF)$_2$Br by ^{1}H-NMR spectroscopy at 4.2 K. We clarified that the wave-number of the antiferromagnetic state is commensurate Q = (1/2, 1/4, 0) with amplitude 0.14μ_B/molecule at 4.2 K.[1)] The commensurate antiferromagnetic state of (TMTTF)$_2$Br was also confirmed by ^{13}C-NMR measurements. Recently anomalous ^{13}C-NMR spectra change was observed in (TMTTF)$_2$Br below 4.2 K.[2)] This observation suggests possible successive phase transition around 4.2 K. Hence we also investigated antiferromagnetic resonance (AFMR) of a single crystal of (TMTTF)$_2$Br. The X-band ESR experiments were carried out using Bruker Elexsys 500 with Oxford Cryostat E910. The temperature range was between 1.5 K and 10 K. Figure 2 shows the angular dependence of the antiferromagnetic resonance (AFMR) modes (normal mode and spin-flop mode) at 4.8 K and 1.5 K. The AFMR modes seem to enhance at 1.5 K, indicating development of the magnetic moment of the AF sub-lattices even at low-temperatures ($T << T_N/2$). Temperature dependence of the two AFMR modes also shows anomalous increase below 5 K. According to the detailed analysis of the AFMR experiment results, the shift of the AFMR field suggests change of the magnetization of the AF sub-lattice (namely, the amplitude of the AF).[3)] Possible sub-phases in the antiferromagnetic state are discussed.

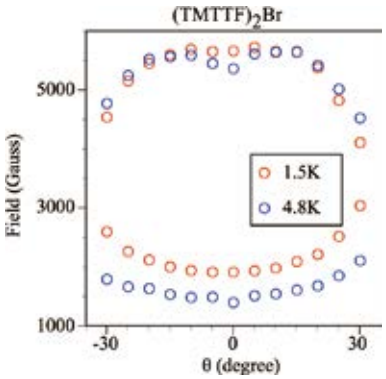

Figure 2. Angular dependence of the anti-ferromagnetic resonance in (TMTTF)$_2$Br (easy-intermediate plane: 9.5 GHz).

2. Effect of Spin–Orbit Interaction and Topological Gap for ESR Spectra in Low-Dimensional Organic Conductors

Recently theoretical investigation by Oshikawa proposed that strong spin–orbit interaction causes additional ESR satellite signal and *g*-shift in 1D metallic system.[4)] So, we reexamined detailed X-band ESR spectra (satellite, line-shape, line-width) for low-dimensional metallic systems. Firstly, we focused on a 1D organic conductor (TMTSF)$_2$ClO$_4$, which shows stable metallic state down to 1 K. Since the TMTSF molecule contains heavy selenium elements, there are considerable spin–orbit interactions. When we apply the static magnetic field along 1D conducting direction (H_0//a), a tiny satellite peak was appeared below 12 K. In the case of H_0//c*, we cannot observed any satellite peak. We also performed 2D metallic system, BEDT-TTF salts. A series of BEDT-TTF salts with low-symmetry shows anomalous *g*-shift at low-temperatures. We discuss relationship between the tiny band gap and anomalous ESR behavior observed in low-dimensional metallic systems.

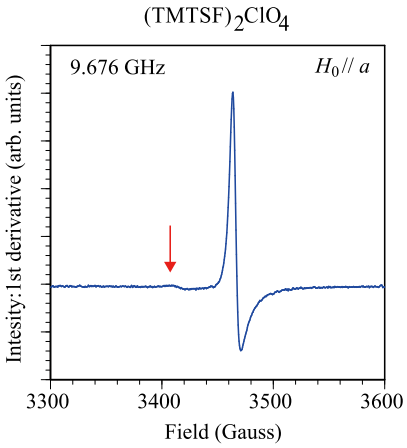

Figure 3. ESR spectra of (TMTSF)$_2$ClO$_4$ at 8 K with the static magnetic field along 1D conducting direction (H_0//a). A tiny satellite peak was appeared below 12 K.

These works were supported by a Grant-in-Aid for Scientific Research B (No. 20340095) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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