Magnetic Resonance Studies for Functional Molecular-Based Solids

Department of Materials Molecular Science
Division of Electronic Properties

NAKAMURA, Toshikazu
Associate Professor
[t-nk@ims.ac.jp]

Education
1987 B.S. Kyoto University
1995 D.S. Kyoto University

Professional Employment
1992 Assistant Professor, Gakushuin University
1998 Associate Professor, Institute for Molecular Science
2003 Associate Professor, The Graduate University for Advanced Studies

Award
2017 The 22nd Outstanding Paper Award of the Physical Society of Japan

Member
IMS Research Assistant Professor
ASADA, Mizue
Secretary
YAMASAKI, Yumi

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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.

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

Selected Publications

- S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).
- T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

1. Magnetic Resonance Investigation for Possible Antiferromagnetic Sub-Phase in $(TMTTF)_2Br$

The ground state of $(TMTTF)_2X$ has been believed to be the C-AF(II) phase in the generalized phase diagram so far. Actually, the electronic state of $(TMTTF)_2Br$ at 4.2 K is clarified as a commensurate antiferromagnetic state with wave vector Q = (1/2, 1/4, 0), and the spin configuration is –up–0–down–0–. We performed AFMR and ^{2}D-NMR measurement to understand ground state of $(TMTTF)_2Br$. AFMR measurements shows the increase of the staggered magnetization of the sub-lattice below 4 K. As for ^{2}D-NMR, the nuclear quadrupole relaxation was dominant through electric field gradient. According to the ^{2}D-NMR spectra, the peak number decreases and broad back ground appear at 4 K, suggesting that charge (spin) configuration changes to inhomogeneous or incommensurate. Considering the AFMR and ^{2}D-NMR experimental results, the possible explanation of 4 K anomaly observed in $(TMTTF)_2Br$ is commensurate to incommensurate successive phase transition. Although the step-like 4 K anomaly observed in AFMR support a homogeneous phase transition, we cannot rule out the possibility of homogeneous effect such as discomesuration state at present. At least, we can say that a phase ϕ change anomaly of antiferromagnetic spin configuration occurs around 4 K. It is also very surprising and intriguing, the sub-magnetic phase detected in the present work appears at a temperature around $T_N/4$. Similarly $(TMTSF)_2X$ salts undergo sub-phases at $T_{SDW}/3$ in which the coexistence between CDW and SDW. Further investigation is ongoing, and supports from theoretical approaches for spin and charge distribution are awaited.

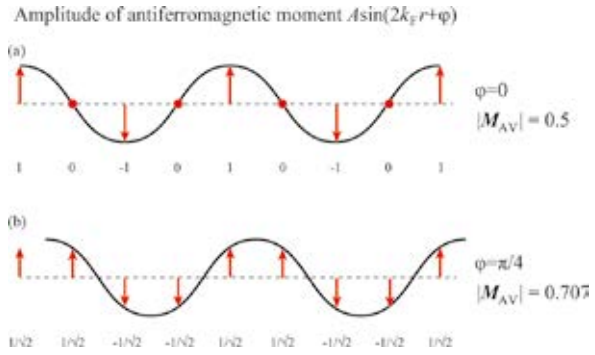

Figure 2. Schematic antiferromagnetic spin configuration for 1/4-filled 1D system along the 1D chain. (a) Spin configuration assuming the antiferromagnetic amplitude follows $A\sin(2k_Fr+\phi)$ with $\phi = 0$. The magnetic structure of $(TMTTF)_2Br$ at 4.2 K is thought to have this configuration. (b) Spin configuration assuming $A\sin(2k_Fr+\phi)$ with $\phi = \pi/4$.

2. Possibility of Dielectric Material: Nuclear Magnetic Resonance of Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex

Since the discovery of mixed-valence compounds such as the Creutz-Taube type complex, the development of mixed-valence compounds and the spectroscopic study of the mixed-valence state have advanced significantly. Investigations into dinuclear and one-dimensional mixed-valence compounds such as those in the diethylbiferrocenium families and halogen-bridged platinum mixed-valence complexes have been particularly significant. The discovery of one-dimensional partial oxidation mixed valence platinum complexes has led to the development of organic conductor research. As for rare earth mixed valence compounds, the electronic properties of (resonance inner 4*f* orbitals) have been attracting much attention. These compounds gave us rich and interesting physical phenomena such as heavy fermion, Kondo-lattice, unconventional superconductivity and non-Fermi liquid. Their fundamental characteristics and electronic nature have been clarified through extensive study. On the other hand, along with the progress of recent research, it is also a fact that new and interesting unresolved problems exist as follows. Possible topological Kondo insulators in rare earth mixed valence compounds have been proposed and discussed. Extensive studies have been carried out for electronic phases in exotic systems such as manganite, magnetite, copper oxide, and so on.

However, recent developments of mixed valence phenomena mainly focus on intermetallic compounds and oxides. There are few studies on electronic states in metal complexes and molecular compounds. The recent progress in charge-ordering and multiferroic phenomena in the field of solid-state physics enhances the desire to redevelop interesting materials. Mixed-valence compounds offer interesting characteristics, such as multi-redox potential, spin-multiplet configurations, a variety of possible building blocks, and potential inter-molecular interactions. Moreover, from the viewpoint of material science, materials that can assume unique valence states and magnetic properties are strongly desired. There is growing momentum toward the research and development of mixed-valence compounds from an electronic functionality point of view. We are interested in systems with moderate valence fluctuations, because intermediate valence and spin states are advantageous for use in electromagnetic switching devices.

Recently, a series of oxo-bridged dinuclear ruthenium mixed-valence complex was systematically synthesized and characterized in three distinct redox states. We focus on the air-stable $[RuORu]^{5+}$ ($Ru^{3+}ORu^{4+}$) complex, and on a description of its electronic properties.

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