Magnetic Resonance Studies for Functional Molecular-Based Solids

Department of Materials Molecular Science
Division of Electronic Properties

NAKAMURA, Toshikazu
Associate Professor
(–March, 2019)
[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

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.

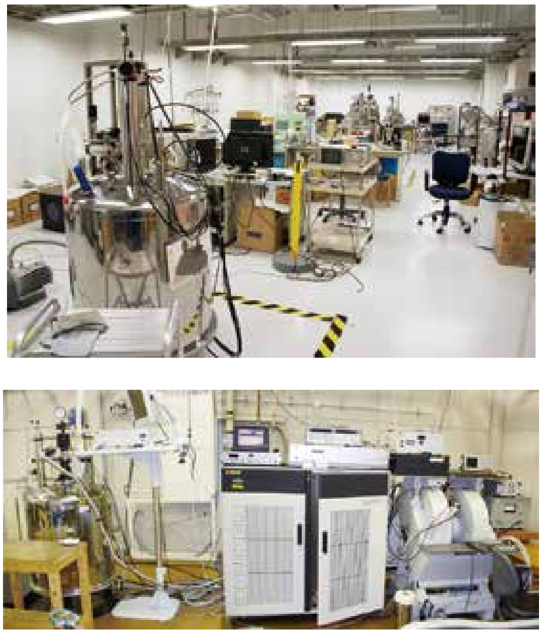

Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

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

Solid-state broad line ^{1}H-NMR (nuclear magnetic resonance) and ESR (electron spin resonance) were performed for an oxo-bridged dinuclear ruthenium $[\mathrm{RuORu}]^{5+}$ ($\mathrm{Ru}^{3.5+}\mathrm{ORu}^{3.5+}$) mixed-valence complex. The ^{1}H-NMR spin–lattice relaxation rate T_1^{-1} was significantly enhanced, to below 100 K with a peak at approximately 33 K. The T_1^{-1} peak temperature was frequency-independent, indicating that this anomaly is a possible phase transition. Below approximately 40 K, an abrupt decrease of ^{1}H-NMR spin–spin relaxation time T_2 provides evidence of the appearance of inequivalent ^{1}H-sites (sudden decrease in symmetry). ESR spectra suddenly disappeared above 35 K. The electronic properties and possible charge ordering ($\mathrm{Ru}^{3+}\mathrm{ORu}^{4+}$) states in this mixed-valence compound are discussed from a microscopic point of view.

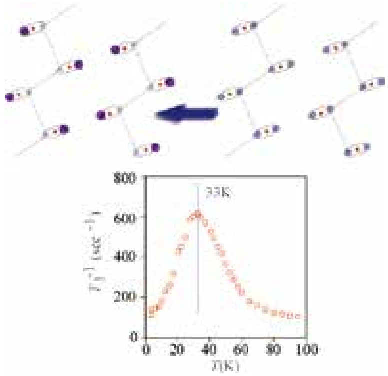

Figure 2. Temperature dependence of the ^{1}H-NMR spin–lattice relaxation rate T_1^{-1} of the $[\mathrm{RuORu}]^{5+}$ complex. A schematic diagram of the *ac*-plane: The inter-molecular Ru–Ru interactions between each dinucleus are described here. Possible schematic charge configuration within the *ac*-plane below 33 K. Color code: Ru^{3+}, dark blue; Ru^{4+}, gray; $\mathrm{Ru}^{3.5+}$, blue; O, red.

2. Effect of Cu Intercalation and Pressure on Excitonic Interaction in 1*T*-TiSe$_2$

1*T*-TiSe$_2$ has a semimetallic band structure at room temperature and undergoes phase transition to a triple-*q* charge density wave (CDW) state with a commensurate superlattice structure ($2a \times 2a \times 2c$) below $T_c \approx 200$ K at ambient pressure. This phase transition is caused by cooperative phenomena involving electron–phonon and electron–hole (excitonic) interactions, and cannot be described by a standard CDW framework. By Cu intercalation or the application of pressure, this phase transition temperature is suppressed and superconductivity (SC) appears. However, it is not clear what kinds of order parameters are affected by these two procedures. We investigated the crystal structure of $\mathrm{Cu}_x\mathrm{TiSe}_2$ and pressurized 1*T*-TiSe$_2$ around the SC state by synchrotron x-ray diffraction on single crystals. In the high-temperature phase, the variation of structural parameters for the Cu intercalation and application of pressure are considerably different. The relationship between the critical points of the CDW phase transition and the SC dome are also different. The excitonic interaction appears to play an important role in the P–T phase diagram of 1*T*-TiSe$_2$, but not in the x–T phase diagram.

3. Honeycomb Lattice Type CDW Formed by Cooperative Interaction in Cu Intercalated 1*T*-TiSe$_2$

1*T*-TiSe$_2$ has attracted attention as an excitonic insulator. However, since the phase transition accompanying superlattice peaks has the *q*-vector connecting the Fermi surfaces of the three-dimensional shape of hole- and electron-pockets, it also suggests the CDW state due to the electron–phonon interaction. In order to understand the electronic state at the low-temperature, the control of chemical potential was attempted by electronic doping by Cu^+ intercalation. It has been found that phase transition occurs as a cooperative phenomenon between the honeycomb lattice type CDW corresponding to the nesting vector and the ordered state of the Cu^+ ions between TiSe$_2$ layers at a specific doping amount. The behavior of Cu^+ ions in highly doped regions suggests the two-dimensional liquid–solid state transition from the temperature dependence of the x-ray diffuse scattering.

4. Synthesis of a Protected Ribonucleoside Phosphoramidite-Linked Spin Label via an Alkynyl Chain at the 5' Position of Uridin

New spin-labeled nucleosides and an efficient synthetic route for the modified uridine amidite were developed. The spin-labeled part was the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) group, and TEMPO was linked via an alkynyl chain at the 5 position of uridine. Three typical protecting groups, such as the *t*-butyldimethylsilyl (TBDMS) group at 2′, the dimethoxytrityl (DMTr) group at 5′, and the phosphoramidite group at 3′, were introduced to induce an automated nucleic acid synthesizer. The TEMPO group at the 5 position in the uridine structure affected the introduction of the bulky protecting groups, such as the DMTr group at the 5′ position and the TBDMS group at the 2′ position. The EPR data revealed the presence of a nitroxy radical in the structure of synthetic nucleoside compounds; however, RNA synthesized by an automated synthesis using TEMPO linked uridine phosphoramidite bulding block which was protected by TBDMS at 3′ and DMTr at 5′ was EPR silent.

References

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