Magnetic Resonance Studies for Functional Molecular-Based Solids

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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


Solid-state broad line $^1$H-NMR (nuclear magnetic resonance) and ESR (electron spin resonance) were performed for an oxo-bridged dinuclear ruthenium [RuORu]$^{5+}$ (Ru$^{3.5+}$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 (Ru$^{3+}$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 [RuORu]$^{5+}$ complex. A schematic diagram of the $ac$-plane: The inter-molecular Ru–Ru interactions between each dinuclear are described here. Possible schematic charge configuration within the $ac$-plane below 33 K. Color code: Ru$^{3+}$, dark blue; Ru$^{4+}$, gray; Ru$^{3.5+}$, blue; O, red.

2. Effect of Cu Intercalation and Pressure on Excitonic Interaction in 1$^7$-TiSe$_2$

1$^7$-TiSe$_2$ has a semimetallic band structure at room temperature and undergoes a phase transition to a triple-$q$ compound at approximately 33 K. Color code: Ru$^{3+}$, dark blue; Ru$^{4+}$, gray; Ru$^{3.5+}$, blue; O, red.

The SC dome are also different. The excitonic interaction appears to play an important role in the $P$–$T$ phase diagram of 1$^7$-TiSe$_2$, but not in the $x$–$T$ phase diagram.

3. Honeycomb Lattice Type CDW Formed by Cooperative Interaction in Cu Intercalated 1$^7$-TiSe$_2$

1$^7$-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 amide 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 to the 5’ position of uridine. Three typical protecting groups, such as the tert-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 nitroxyl radical in the structure of synthetic nucleoside compounds; however, RNA synthesized by an automated synthesis using TEMPO linked uridine phosphoramidite building block which was protected by TBDMS at 3’ and DMTr at 5’ was EPR silent.

References