

IV-B Magnetic Resonance Studies for Molecular-Based Conductors

Molecular based conductors are one of the extensively studied materials. The development of the understanding of the electronic phases of these materials enables us systematic investigations of low-dimensional highly correlated electrons systems. Competition of the electronic phases in molecular based conductors has attracted much attention. Magnetic resonance investigations are powerful investigations to understand the fundamental electronic properties, because they are microscopic and also dynamical measurements. The investigations of such electronic phases by means of magnetic resonance measurements are important to understand the unsolved fundamental problems in the field of solid state physics.

In this project, we performed the multi-frequency- (X-, Q- and W-bands) and pulsed-ESR, and broad-line NMR measurements for molecular based conductors to understand the electron spin dynamics in the low temperature electronic phases.

IV-B-1 Charge Disproportionation in (TMTTF)₂SCN Observed by ¹³C NMR

FUJIYAMA, Shigeki; NAKAMURA, Toshikazu

[Phys. Rev. B **70**, 045102 (6 pages) (2004)]

The results of the ¹³C NMR spectra and nuclear spin-lattice relaxation rate $1/T_1$ for the quasi-one-dimensional quarter-filled organic material (TMTTF)₂SCN are presented. Below the anion ordering temperature (T_{AO}), a new broad line appears in the NMR spectra and the intensity of the distinct line owing to the inner carbon site from the inversion center is almost halved. The remarkable difference in the temperature dependence of $1/T_1$ below T_{AO} for the two sharp lines corresponding to outer and inner carbon sites shows the development of a local electronic state. Our simple model of a charge configuration based on the electrostatic interaction between the SCN anions and TMTTF molecules is consistent with our observation of a local gap for the spin excitation. Nevertheless, we reveal that only the electrostatic interaction is insufficient to reproduce the observed divergence of the frequency shift and the linewidth of the newly appearing broad line stemming from the charge-accepting inner site at a much lower temperature than T_{AO} .

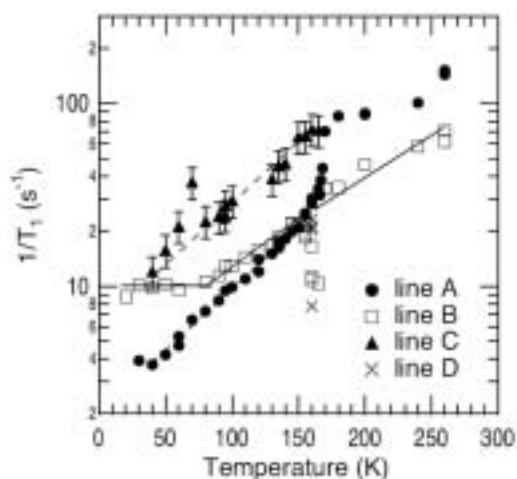


Figure 1. Nuclear spin-lattice relaxation rates for distinct lines. The solid and dashed lines are guides to the eye.

IV-B-2 Redistribution of Electronic Charges in the Spin-Peierls State in (TMTTF)₂AsF₆ Observed by ¹³C NMR

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[J. Phys. Soc. Jpn. in press]

We report the results of ¹³C NMR spectra and nuclear spin lattice relaxation rate $1/T_1$ for a quasi-one-dimensional quarter-filled organic material (TMTTF)₂-AsF₆, which undergoes charge ordering ($T_{CO} = 102$ K) and spin-Peierls phase transitions ($T_{SP} = 12$ K). The ratio of two $1/T_1$ for the charge accepting and donating sites which grows from T_{CO} finally saturates in approaching T_{SP} , that indicates an opening of single gap for the spin excitation spectra. At T_{SP} , however, doubly split NMR lines from inequivalently charged molecules merge originated from the variation in charge densities. This shows a rearrangement of the charge configuration in the spin-Peierls state.

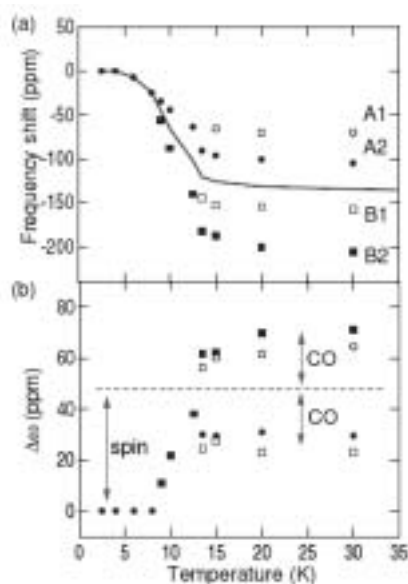


Figure 1. (a) The peak positions in the vicinity and below T_{SP} . (b) The gaps between the peak positions and the averaged frequency denoted as the solid line in (a). The dashed line shows the spin contribution to $\Delta\omega$.

IV-B-3 Deuteration Effect and Possible Origin of the Charge-Ordering Transition of (TMTTF)₂X

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[*J. Phys. Soc. Jpn.* in press]

ESR, NMR and X-ray measurements were performed for pristine and fully perdeuterio-TMTTF, TMTTF-*d*₁₂ salts. Significant enhancement by deuteration of the charge-order phase transition temperature, *T*_{CO}, was observed in ESR measurements for all (TMTTF)₂X salts measured. No obvious relation between the SbF₆ anion motion and the TMTTF charge-order was found by ¹⁹F NMR. We also performed single crystal X-ray measurements to understand the deuteration effects and temperature dependence of the crystal structure. A possible relationship between the *T*_{CO}'s and crystallographical parameters is proposed. The deuteration effects and possible origin of the charge-ordering transition of TMTTF salts are discussed.

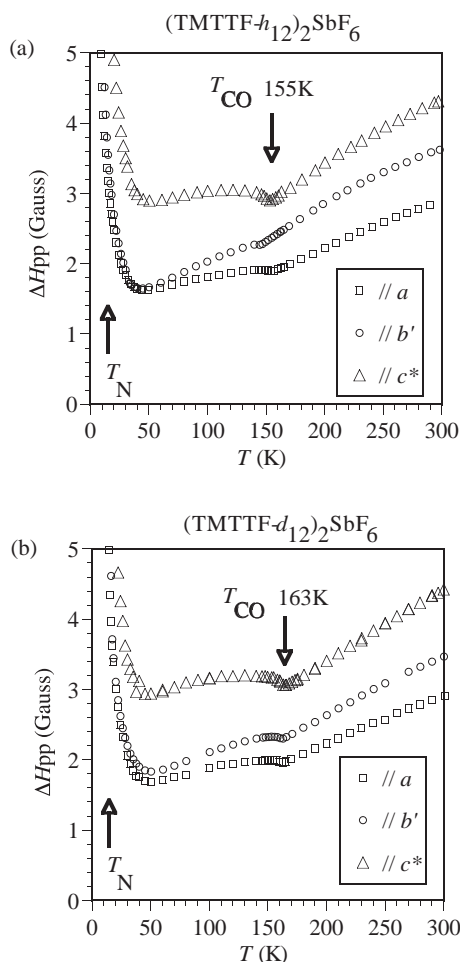


Figure 1. Temperature dependence of the ESR linewidth, ΔH_{pp} , of (a) pristine, (TMTTF-*h*₁₂)₂SbF₆ and (b) deuterated, (TMTTF-*d*₁₂)₂SbF₆.

IV-B-4 Redistribution of Electronic Charge in (TMTTF)₂ReO₄: ¹³C NMR Investigation

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FURUKAWA, Ko

[*J. Low Temp. Phys.* in press]

¹³C NMR measurements were performed for a one-dimensional organic conductor, (TMTTF)₂ReO₄. An intermediate charge-ordering (CO) phase has been found firstly for a TMTTF salt with a T_d-symmetry counter anion: The NMR parameters indicate two inequivalent molecules with unequal electron densities below 225 K. Moreover, the spin-singlet transition associated with ReO₄ anion ordering was confirmed at around 158 K by ¹³C NMR measurements. A drastic change of NMR parameters below 158 K also indicates a redistribution of the electronic charge at the anion ordering temperature.

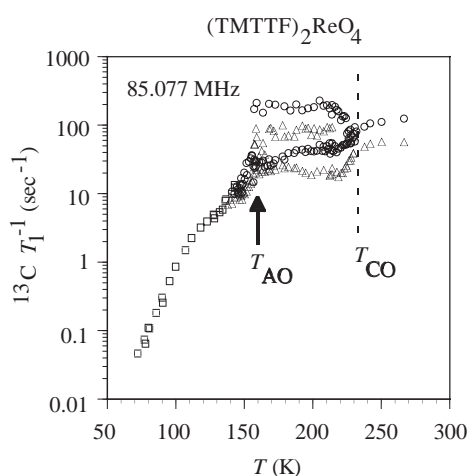


Figure 1. Temperature dependence of the ¹³C NMR spin-lattice relaxation rate, $^{13}\text{C } T_1^{-1}$, of (TMTTF)₂ReO₄.

IV-B-5 Spin Structure of Organic Conductors (TMTTF)₂X

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NAKAMURA, Toshikazu

Organic conductors, (TMTTF)₂X (*X* = Br, SbF₆, and PF₆), are examined by electron spin resonance (ESR) spectroscopy, X-ray diffraction and theoretical calculation of *g*-tensor. In the case of the counter anions with octahedral symmetry, the anomalous change of the principal values and axes of the *g*-tensor, which were determined by the angular dependence of *g*-values, were observed in the temperature range from 20 K to the room temperature. However, the *g*-tensor was temperature independence in the Br salt. The temperature variation of the crystal structure for both salts is performed by X-ray diffraction. No obvious change of the molecular structure is observed in both salts. In the octahedral counter anion salts, the distance between the TMTTF molecules and the counter anion shrank due to the bulk counter anion as the temperature decreased. In order to interpret the anomalous *g*-shift, the theoretical calculation of the *g*-tensor based on the DFT-GIAO method is carried out. The relationship between the spin and the crystal structure will be discussed.

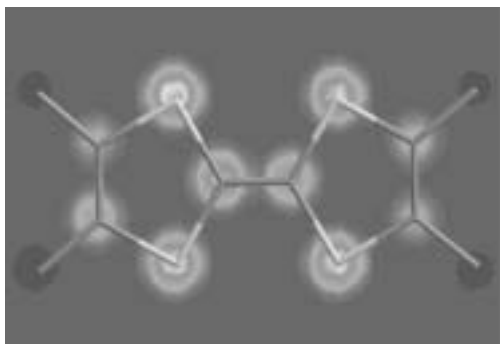


Figure 1. Spin density of the TMTTF radical determined by the DFT-GIAO method.

IV-B-6 Multi-Frequency ESR Measurements for (TMTTF)₂X

HARA, Toshifumi; FURUKAWA, Ko;
NAKAMURA, Toshikazu

TMTTF family salts are now attracted attention by the recent progress of the charge ordering (CO) investigations. Recently, we proposed the possible charge ordering configurations for each of (TMTTF)₂X salts according to the difference of the ESR linewidth anisotropy at low temperatures. The CO configurations of (TMTTF)₂X are roughly divided into three groups, and this classification is consistent with the results determined by other measurements. However the origin of the charge ordering phenomena is not clarified, and the quantitative understanding of the ESR linewidth is not succeeded so far. So we performed multi-frequency (X- [10GHz], Q- [30GHz], and W-bands [100GHz]) ESR measurements for one of typical TMTTF salts, (TMTTF)₂SbF₆, which shows the charge ordering transition at 154 K. The ESR linewidth determined by the W-band measurement is obviously larger than that by X-band below the charge ordering transition. We discuss the low temperature electron spin dynamics from the ESR point of view.

IV-B-7 Extremely Slow Charge Fluctuations in the Metallic State of the Two-Dimensional Molecular Conductor θ -(BEDT-TTF)₂RbZn(SCN)₄

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[*Phys. Rev. Lett.* **93**, 216405 (4 pages) (2004)]

Large charge disproportionation has been confirmed in the metallic state of a 1/4-filled organic conductor θ -(BEDT-TTF)₂RbZn(SCN)₄ by means of ¹³C-NMR analysis on a selectively ¹³C-enriched single crystal sample. By comparing the homogeneous and inhomogeneous linewidths, the temperature dependence of the extremely slow dynamics of charge fluctuations has been determined first. The exotic nature of the metallic state of this salt is discussed.

IV-B-8 Sliding Spin-Density Wave of (TMTSF)₂PF₆ Studied with Narrow-Band Noise

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[*Phys. Rev. B* **70**, 214201 (13 pages) (2004)]

We report narrow-band noise (NBN) due to sliding motions of the spin-density wave (SDW) condensate at 2.0 K in three samples of (TMTSF)₂PF₆ and the magnetic-field effects. Typical NBN spectra coming from the saw-toothed-wave current oscillations are clearly observed. The periodic peaks due to the 4k_F-charge-density wave (CDW) collective excitation are found, together with the SDW moving with a faster velocity, revealing that the sliding mode of the SDW is coupled with 4k_F-CDW fluctuations. Observation of the interference peaks gives evidence of spatially non-uniform dc current carried by the deformable SDW in domains. At large currents the NBN spectrum drastically changes with increasing current and depends on applied magnetic field, suggesting a dynamical phase transition from the plastic-flow phase to the moving-solid phase. In the moving-solid phase the frequencies of the periodic peaks decrease with increasing current because the spatial coherency grows rapidly. The current oscillations in this phase are interpreted in terms of the coexistence of the 2k_F-CDW collective excitation with the phason.

IV-C Synchrotron X-Ray Diffraction Experiments and MEM Analyses for Single Crystals of Organic Conductors

By recent development of aggressive experimental and theoretical researches, electronic phases of organic conductors have been clarified so far. The remarkable anisotropy (low-dimensionality), small band-width and flexibility of the lattice are the characteristics of organic conductors. In most cases, band-structures of organic conductors are deduced with frontier orbitals (the highest occupied molecular orbital: HOMO as for a donor molecule, for example) estimated by molecule orbit calculations applying the tight-binding approximation. The Fermi surfaces calculated above correspond very well with that estimated from quantum vibration and/or angular dependence magneto-resistance experiments. Consistency with first principle calculations is also good. These facts

indicate that most of physics phenomena can be explained within the framework that the frontier orbital can be treated as if one rigid atomic orbital in an alkaline metal. The main aims of this project are, 1) to study whether there is a change of symmetry of frontier orbitals (electric charge distribution in molecules), which is believed to be rigid so far, at phase transitions, and 2) to investigate possible relation between the detailed electric charge distribution in molecules and the electronic phases. Of course, the tight-binding approximation with a rigid frontier orbital is firm to be very good approximation. However, there are several experimental results which suggest a change of electric charge distribution in the molecule in some systems. We performed synchrotron X-ray diffraction experiments and MEM (The Maximum Entropy Method) analyses to investigate the electric charge distribution of molecules for such interesting systems.

This project is partially supported by Grant-in-Aid for Creative Scientific Research Collaboratory on Electron Correlation-Toward a New Research Network between Physics and Chemistry- (13NP0201) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

IV-C-1 Low-Temperature Charge-Ordering State of (TMTTF)₂PF₆

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As for the charge-ordering problem which is one of the recent hot topics, electronic charge configurations at low temperatures are clarified so far by several groups containing us. The importance of the long-range Coulomb interaction is pointed out by theoretical researches. TMTTF family salts have been attracting attention due to observations of their charge-ordering (CO) phenomena. ¹³C NMR indicates the existence of inequivalent TMTTF sites at low temperatures, and dielectric permittivity measurements show ferroelectric behaviors for (TMTTF)₂MF₆ (*M* = P, As, Sb) salts. We also proposed that the variation of charge-ordering patterns such as –O–O–o–o– and –O–o–O–o– along the stacking axes for a series of TMTTF salts by ESR linewidth analyses. However, as for the research of the charge-ordering, the electric charge distribution in the molecule was ignored so far. Hence we performed synchrotron X-ray diffraction measurements and MEM analyses to investigate the electric charge distribution of molecules and to understand the low-temperature charge-ordering state of (TMTTF)₂PF₆. Figure shows the charge distribution of

(TMTTF)₂PF₆ at R.T. Further investigations are now underway.

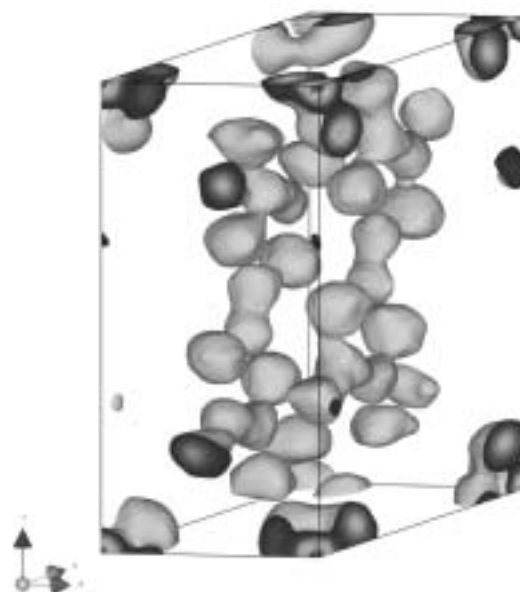


Figure 1. Charge distribution of (TMTTF)₂PF₆ at R.T. determined by synchrotron X-ray diffraction measurements and MEM analyses.

IV-D EPR Study toward Molecular Biology as Microscopic and Selective Probes Measurements

The structure analyses of the material related to fundamental biology are now hot topics. Especially synchrotron X-ray measurements attract much attention since they can provide detail of the structural information. However, X-ray measurements can be applied only for crystalline material, the resolution is not so good. On the other hand, EPR measurements are advantageous because they are microscopic and selective probes and they can provide dynamical information. Hence, we performed the multi-frequency- and pulsed-ESR for such kind of materials to understand the local structure and possible mechanism of several biological processes.

IV-D-1 First Detection of the Multiline Signal from the S_2 -State Manganese Cluster of Photosystem II by Single-Crystal W-Band EPR Spectroscopy

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[J. Phys. Chem. B submitted]

The multiline signal from the S_2 -state manganese cluster in the oxygen evolving complex of photosystem II (PSII) was observed in single crystals of a thermophilic cyanobacterium *Thermosynechococcus vulcanus* for the first time by W-band (95 GHz) electron paramagnetic resonance (EPR), as shown in the figure. The single-crystal spectra were reasonably interpreted by spectral simulation with the hfc parameters appropriate for a trimer-monomer structure of the cluster. The use of PSII single crystals allowed us to determine precisely the g -tensor of the cluster. The principal values of the tensor indicated that the Mn(III) ion in the cluster exists in an approximate axial symmetry. This work demonstrated that single-crystal experiments are crucial to detect the distinct resolved hfs of the S_2 state at W-band.

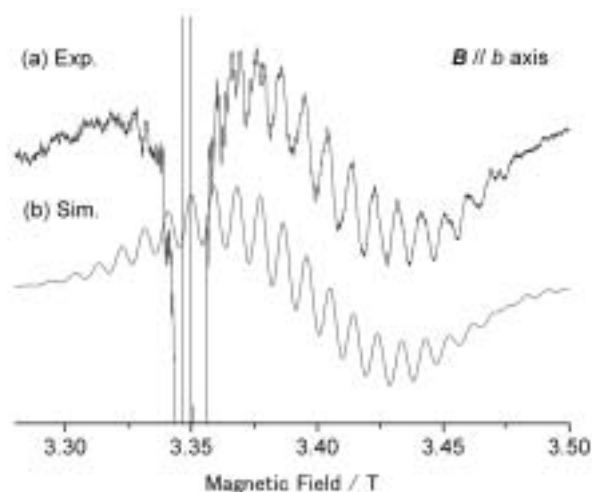


Figure 1. (a) Light-minus-dark W-band EPR spectra observed at 6 K for the S_2 state in single crystals of PSII from *T. vulcanus*. (b) The best-fit simulation of (a). The crystallographic b -axis was approximately parallel to the direction of the magnetic field.