

IV-B Magnetic Resonance Studies for Molecular-Based Conductors

Magnetic resonance measurements may be mature techniques as devices of the so-called chemical analyses. However, from the viewpoint of the solid state material science, magnetic resonance measurement is challenging area still in under the special condition such cases as the extreme low temperature, strong magnetic field, high pressure, electric field, optical response and so on. Moreover they are advantageous for studying the fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. 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. 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 Deuteration Effect and Possible Origin of the Charge-Ordering Transition of $(\text{TMTTF})_2\text{X}$

FURUKAWA, Ko; HARA, Toshifumi; NAKAMURA, Toshikazu

[*J. Phys. Soc. Jpn.* **74**, 3288–3294 (2005)]

ESR, NMR and X-ray measurements were performed for pristine and fully perdeuterio-TMTTF, $\text{TMTTF-}d_{12}$ salts. Significant enhancement by deuteration of the charge-order phase transition temperature, T_{CO} , was observed in ESR measurements for all $(\text{TMTTF})_2\text{X}$ salts measured. No obvious relation between the SbF_6 anion motion and the TMTTF charge-order was found by ^{19}F 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.

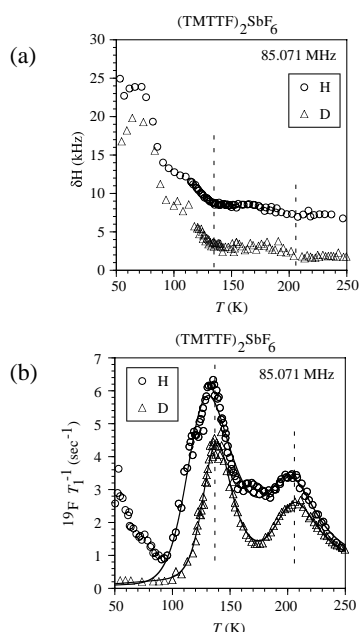


Figure 1. Temperature dependence of ^{19}F NMR, (a) absorption full width at half maximum (FWHM) linewidth, δH , and (b) spin-lattice relaxation rate, $^{19}\text{F} T_1^{-1}$, of $(\text{TMTTF-}h_{12})_2\text{SbF}_6$ (circle) and $(\text{TMTTF-}d_{12})_2\text{SbF}_6$ (triangle). The solid lines are fitted results using the BPP equation.

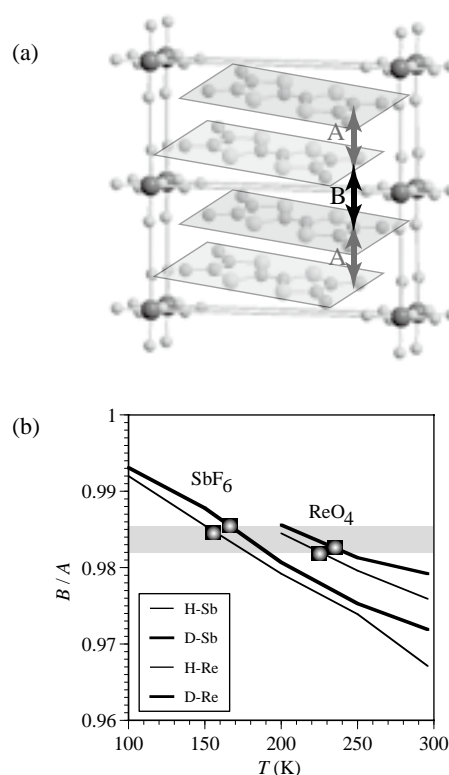


Figure 2. Crystal structure and definition of the inter-molecular distances, A and B , of $(\text{TMTTF})_2\text{SbF}_6$. Temperature dependence of inter-molecular distances and their ratio of $(\text{TMTTF-}h_{12})_2\text{SbF}_6$, $(\text{TMTTF-}d_{12})_2\text{SbF}_6$, $(\text{TMTTF-}h_{12})_2\text{ReO}_4$ and $(\text{TMTTF-}d_{12})_2\text{ReO}_4$. The measured points (every 50 K) are interpolated with a straight line. Solid circles correspond to T_{CO} 's for each of salts.

IV-B-2 ^{13}C NMR Analyses of Successive Charge Ordering in $(\text{TMTTF})_2\text{ReO}_4$

NAKAMURA, Toshikazu; FURUKAWA, Ko; HARA, Toshifumi

[*J. Phys. Soc. Jpn.* **75**, 013707 (4 pages) (2006)]

^{13}C NMR measurements were performed for a one-dimensional organic conductor, $(\text{TMTTF})_2\text{ReO}_4$. The existence of an intermediate charge ordering (CO) phase was clarified for a TMTTF salt with a Td symmetry counter anion by the ^{13}C NMR absorption line and spin-lattice relaxation rate, ^{13}C T_1^{-1} . The ^{13}C NMR spectra, which are characteristic of nuclei in equivalent molecules at room temperature, indicated two inequivalent molecules with unequal electron densities below 225 K. Moreover, the spin-singlet transition associated with ReO_4 anion ordering was confirmed at around 158 K by ^{13}C NMR. The ^{13}C NMR lines show a marked change at 158 K. The possible redistribution of the electronic charge at the anion ordering temperature as well as the origin of the charge ordering phenomena are discussed.

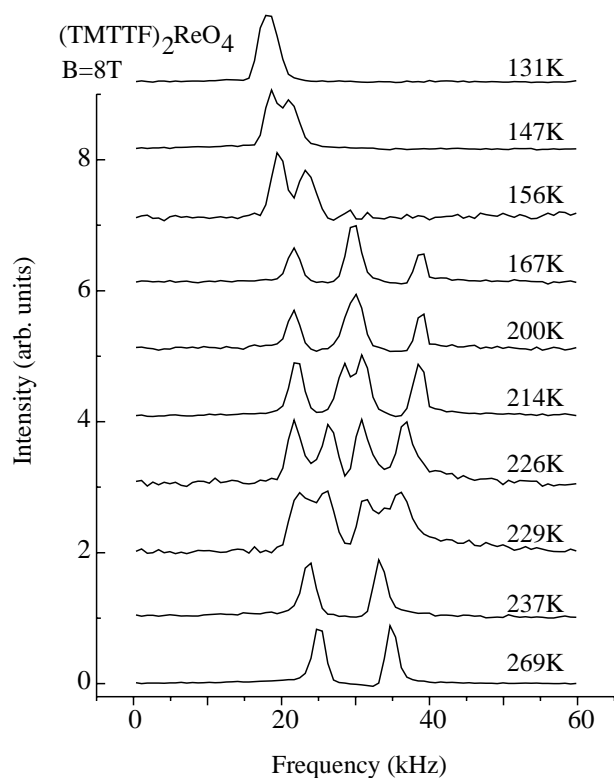


Figure 1. Temperature dependence of ^{13}C NMR spectra of $(\text{TMTTF})_2\text{ReO}_4$. Measurements were performed at the so-called magic-angle configuration.

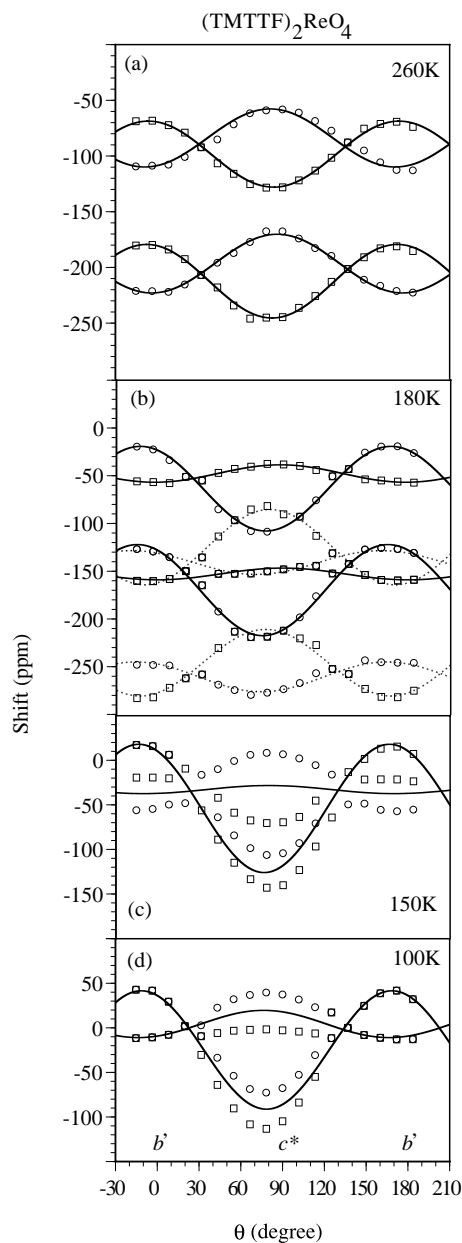


Figure 2. Angular dependence of resonance frequency of ^{13}C NMR in $(\text{TMTTF})_2\text{ReO}_4$. A single crystal of $(\text{TMTTF})_2\text{ReO}_4$ was rotated within the $b'c^*$ plane perpendicular to the external static magnetic field. The solid and dashed lines are included as guides to the eye, but are the least-squares fits to the measured data assuming the $3\cos^2\theta - 1$ formulae.

IV-B-3 Redistribution of Electronic Charges in the Spin-Peierls State in $(\text{TMTTF})_2\text{AsF}_6$ Observed by ^{13}C NMR

FUJIYAMA, Shigeki; NAKAMURA, Toshikazu

[*J. Phys. Soc. Jpn.* **75**, 014705 (7 pages) (2006)]

We report ^{13}C NMR spectra and nuclear spin lattice relaxation rate $1/T_1$ for a quasi-one-dimensional quarter-filled organic material $(\text{TMTTF})_2\text{AsF}_6$, which undergoes charge ordering ($T_{\text{CO}} = 102$ K) and spin-Peierls phase transitions ($T_{\text{SP}} = 14$ K). The ratio of two $1/T_1$ for the charge accepting and donating TMTTF sites which

grows from T_{CO} finally saturates in approaching T_{SP} , indicating one spin correlation function even in the charge ordered state. Below T_{SP} , however, the doubly split NMR lines from inequivalently charged molecules merge into one line, originated from the variation in charge densities. This shows that a rearrangement of the charge configuration occurs at T_{SP} .

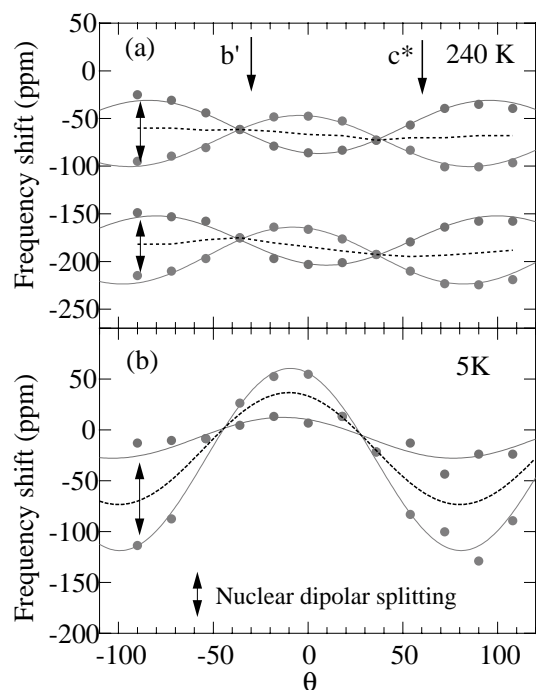


Figure 1. Angular dependence of the peak positions of the NMR spectra rotated in the b - c plane at 240 K (a) and 5 K (b).

IV-B-4 The Effect of Deuteration on the Transition into a Charge Ordered State of $(TMTTF)_2X$ Salts

NAD, Felix^{1,2}; MONCEAU, Pierre²; NAKAMURA, Toshikazu; FURUKAWA, Ko
(¹Inst. Rad. Elec., Russia; ²CNRS, France)

[*J. Phys.: Condens. Matter* **17**, L399–L406 (2005)]

From dielectric permittivity measurements, we show that deuteration yields a large increase of the transition temperature for the charge ordered state of $(TMTTF)_2X$ ($X = AsF_6, SbF_6, ReO_4$) salts. We propose an explanation of this phenomenon, suggesting that deuteration induces a modification of the $(TMTTF)_2X$ crystal unit cell.

IV-B-5 Magnetic Properties of Hexa-*peri*-hexabenzocoronene Nanotube Investigated by Magnetic Resonance

HARA, Toshifumi; FURUKAWA, Ko; NAKAMURA, Toshikazu; YAMAMOTO, Yohei¹; KOSAKA, Atsuko¹; FUKUSHIMA, Takanori^{1,2}; AIDA, Takuzo^{1,2}
(¹ERATO-SORST; ²Univ. Tokyo)

The discovery of electric conductive carbon nanotube

materials has expanded interest in exploring novel materials for functional electronic devices. Recently, new type nanotubular objects has been developed by Aida and co-workers with novel HBC (hexa-*peri*-hexabenzocoronene) amphiphiles bearing hydrophilic oxyalkylene chains and lipophilic dodecyl chains. These HBC molecules stack to form a well-defined nanotube with a helical array of a large number of π -stacked HBC units. By chemical oxidation using iodine, the HBC nanotube turns to show highly electrical conductive behavior.

In order to understand the origin of the carrier and the electronic properties, ESR and 1H NMR measurements were carried out for the iodine doped HBC nanotube. The drastic increases of the ESR intensity with the iodine doping indicates that the carrier possesses a spin-freedom. In the initial phase of doping, a narrow ESR line was observed. After additional several hours of doping, another broad ESR lines appear, and the intensity of it overcomes that of the narrow lines. The spin susceptibility evaluated from the broad ESR line shows a temperature independent behavior down to 140 K. The ESR linewidth decreases with lowering temperature. These observations are typical phenomena of itinerant spins. Below 140 K, the spin susceptibility turns to show the Curie-like behavior, following an hump of ESR linewidth. The drastic change of the ESR parameters suggests a possible semiconductor to insulator transition (or crossover) in this nanotubular system. In this paper, we describe magnetic properties of the HBC nanotube and discuss the nature of the electronic phases from a microscopic point of view.

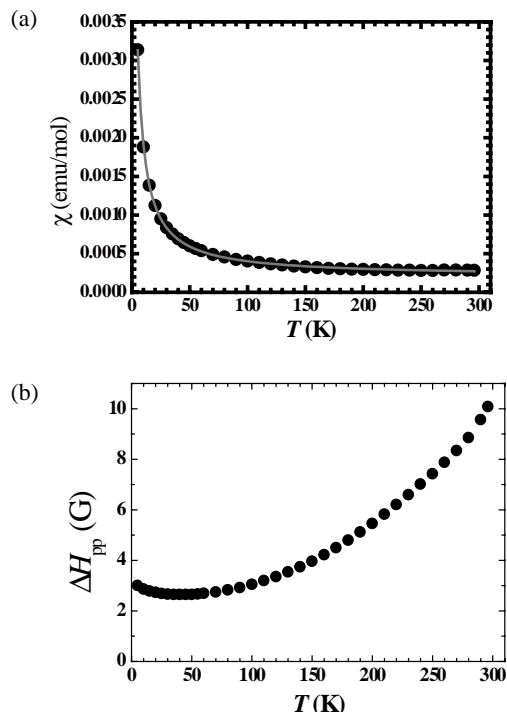


Figure 1. Temperature dependence of the spin susceptibility and ESR linewidth of the iodine doped HBC nanotube.

IV-B-6 X-Ray Structural Study of Charge and Anion Orderings of TMTTF Salts

NOGAMI, Yoshio¹; ITO, Takayoshi¹; YAMAMOTO,

Kenichiro¹; IRIE, Naoaki¹; HORITA, Shintaro¹;
KAMBE, Takashi¹; NAGAO, Nobuaki¹; OSHIMA,
Kokichi¹; IKEDA, Naoshi²; NAKAMURA,
Toshikazu
(¹Okayama Univ.; ²JASRI)

[*J. Phys. IV France* **131**, 39–42 (2005)]

High resolution X-ray structure analyses and electronic structure calculation revealed the condition for the charge ordering (CO) observed in the (TMTTF)₂X (Fabre) salts. The phase diagram of the electronic states including 2k_F and 4k_F CO has been proposed associated with magnitudes of molecular dimerization and tetramerization.

IV-B-7 Depinning of the Spin-Density Wave in (TMTTF)₂Br under Pressure

NOMURA, Kazushige¹; ISHIMURA, Kazunori¹;
FUJIMOTO, Kazuteru¹; MATSUNAGA, Noriaki¹;
NAKAMURA, Toshikazu; TAKAHASHI, Toshihiro²;
SAITO, Gunzi³
(¹Hokkaido Univ.; ²Gakushuin Univ.; ³Kyoto Univ.)

[*J. Phys. IV France* **131**, 111–114 (2005)]

We have investigated the sliding motion of the SDW in the organic compound (TMTTF)₂Br under the pressure with the measurement of the non-linear conductivity. Below the SDW transition temperature T_{SDW} , we observed the sharp increase of conductivity with the clear threshold electric field E_T , associated with the depinning of the SDW. For the typical sample, the temperature dependence of E_T shows a peak around $0.3T_{SDW}$ in each pressure. In addition, the field hysteresis with the switching appears in the dc I - V characteristics around $0.3T_{SDW}$. The excess conductivity, dominated by the kinetic friction, shows a sharp increase below $0.3T_{SDW}$. These behaviors indicate that the sliding mechanism of SDW varies across $0.3T_{SDW}$, which is almost equal to the sub-phase transition temperature. This fact suggests that the transition at $0.37T_{SDW}$ is associated with both the magnetic and charge degrees of freedom.

IV-B-8 Pulsed ESR Measurements for (TMTTF)₂X

FURUKAWA, Ko; HARA, Toshifumi; NAKAMURA,
Toshikazu

It is well known that most of TMTTF salts undergo the charge ordering (CO) transitions in the paramagnetic phase. We already demonstrated the charge configuration pattern for several TMTTF salts. However it is not clear the relationship between the CO configurations and ground states. Actually, the (TMTTF)₂SbF₆ salts undergoes an antiferromagnetic phase, while the (TMTTF)₂PF₆ and (TMTTF)₂AsF₆ salts show spin-Peierls ground states. They have common CO configuration pattern at the paramagnetic phase. So it is interesting to investigate the charge configuration at around the spin-Peierls state. So we performed the pulsed ESR measurements for one

of typical TMTTF salts, (TMTTF)₂PF₆ and (TMTTF)₂-Br. The low temperature electron spin dynamics from the ESR point of view are discussed.

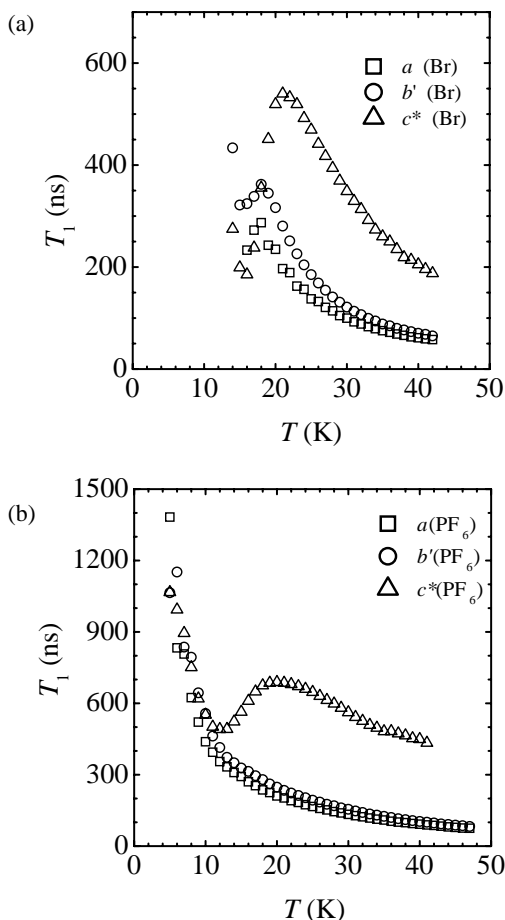


Figure 1. Temperature dependence of the ESR spin-lattice relaxation time, T_1 , for (TMTTF)₂Br (a) and (TMTTF)₂PF₆ (b).

IV-B-9 Synchrotron X-Ray Diffraction Experiments and MEM Analyses for the Charge-Ordering State of (TMTTF)₂PF₆

HARA, Toshifumi; FURUKAWA, Ko; NAKAMURA,
Toshikazu; KAKIUCHI, Toru¹; SAWA, Hiroshi²;
IZUMI, Fujio³
(¹SOKENDAI; ²KEK; ³NIMS)

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. The competition between the long-range Coulomb interaction and anion ordering are pointed out by experimental and theoretical investigations. However, there is no direct observation of the charge distribution for charge ordered states so far. Hence we performed synchrotron X-ray diffraction measurements and MEM

analyses (TMTTF)₂PF₆ at R.T. and 20 K. We observed apparent difference of the electric charge distributions between two TMTTF molecules in the original unit cell. This fact reveals that the charge order phase transition in (TMTTF)₂PF₆ is purely electronic one without apparent structural changes.

IV-B-10 g-Anisotropy of the S₂-State Manganese Cluster in Single Crystals of Cyanobacterial Photosystem II Studied by W-Band Electron Paramagnetic Resonance Spectroscopy

MATSUOKA, Hideto¹; FURUKAWA, Ko; KATO, Tatsuhisa²; MINO, Hiroyuki³; SHEN, Jian-Ren⁴; KAWAMORI, Asako⁵

(¹*IMS and Free Univ. Berlin*; ²*IMS and Josai Univ.*; ³*Nagoya Univ.*; ⁴*Okayama Univ.*; ⁵*Kwansei Gakuin Univ.*)

[*J. Phys. Chem. B* **110**, 13242–13247 (2006)]

The multiline signal from the S₂-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 (94 GHz) electron paramagnetic resonance (EPR). At W-band, spectra were characterized by the g-anisotropy, which enabled the precise determination of the tensor. Distinct hyperfine splittings (hfs's) as seen in frozen solutions of PSII at X-band (9.5 GHz) were detected in most of the crystal orientations relative to the magnetic field. In some orientations, however, the hfs's disappeared due to overlapping of a large number of EPR lines from eight crystallographic symmetry-related sites of the manganese cluster within the unit cell of the crystal. Analysis of the orientation-dependent spectral features yielded the following g-tensor components: $g_x = 1.988$, $g_y = 1.981$, $g_z = 1.965$. The principal values suggested an approximate axial symmetry around the Mn(III) ion in the cluster.