Joint Study Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint study programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

A. New Developments in Spin Science Using Pulsed and High-Frequency ESR

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In order to develop advanced ESR (electron spin resonance) spectroscopy for materials science, we performed functional materials studies, both on isolated molecules and on molecular assemblies. The following two topics were investigated: 1) We determined the molecular structure of novel systems such as N@C_{60}/C_{60} nano-whisker and their spin interaction using ESR spectroscopy, and explored the functionality of the complicated molecule system. 2) We carried out an analysis of spin dynamics for functional molecular assemblies, including molecular conductors and magnetic materials. We searched for cooperative phenomena involved in intra-molecule freedom, and new functional physical-properties originating in molecular assemblies.

A-1 Characterization of N@C_{60}/C_{60} Nano-Whisker by ESR

Endohedral N@C_{60} exhibits the spin ground state ($^4S_{3/2}$) due to the atomic nitrogen, which is located in the center of the fullerene cage. Because of the high symmetry, the guest nitrogen is subjected to isotropic environment and keeps the spherical symmetry of the free atom. The conventional spin relaxation processes are missing for the highly symmetric N@C_{60}, so even small deviation from the ideal structure like modification by crystal field can apparently be detected via interaction with the quartet spin.

C_{60} nano-whisker (NW) containing N@C_{60} was prepared by the crystal growth at the interface between toluene and isopropyl alcohol solutions. Comparing the spectrum of powder N@C_{60}/C_{60}, NW exhibited more enhanced broadening of ESR lines. The enhanced broadening reflects that the local symmetry at the nitrogen site in NW becomes lower than in C_{60} powder. ESR spectrum of N@C_{60}/C_{60} NW would give a good indicator of the solvation in the crystal growth process.

A-2 Spin and Lattice Dynamics near the Spin-Peierls Transition in Alkali-TCNQ

The dynamical nature of the spin-Peierls transition in K-TCNQ and Rb-TCNQ has been unveiled with the frequency and the temperature dependences of ESR line width and resonance positions. The spin-Peierls transition is governed by the competition of the thermal excitation and the exchange energy gain of singlet dimer formation in the half-filled Mott insulators, such as K-TCNQ.

With approaching temperature to the spin-Peierls transition T_{SP}, the singlet dimer of TCNQ molecules could be thermally excited to the triplet dimer in the singlet ground state. ESR observes the so-called "Pake-doublet" signals caused by the dipolar interaction between two electrons in an excited triplet dimer. With further approach to T_{SP}, the triplet dimer dissociates to the two isolated spin solitons with spin 1/2, resulting in the doublet ESR signals with the reduced peak separation due to the increased spin-spin distances on the dynamical average.

Thus, the separation of the doublet signals rapidly decreases near T_{SP}, accompanied with the maximum of the ESR line width which is dominated by the spin-lattice relaxation rate due to quasi-1D diffusion of the spin solitons. Therefore, these analyses of the frequency and the temperature dependences could provide ample information on the spin and lattice dynamics, important for the understanding of the phase transitions.

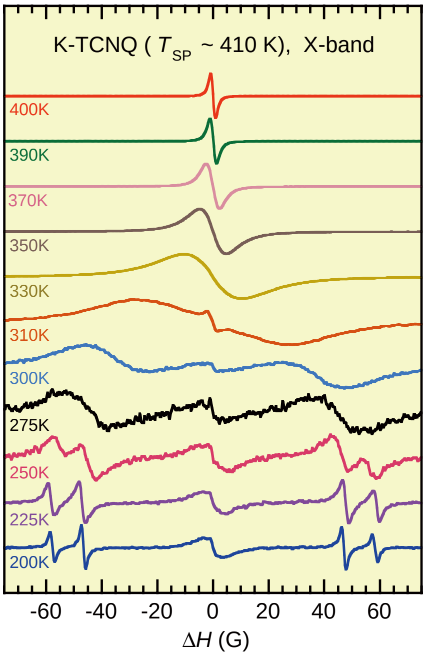

Figure 1. The temperature dependence of ESR spectra of K-TCNQ taken at X-band (~9.5 GHz). The center signals at $\Delta H = 0$ below 310 K might be originated by defects. Doublets correspond to the signal pairs around ±50 G or ±60 G.

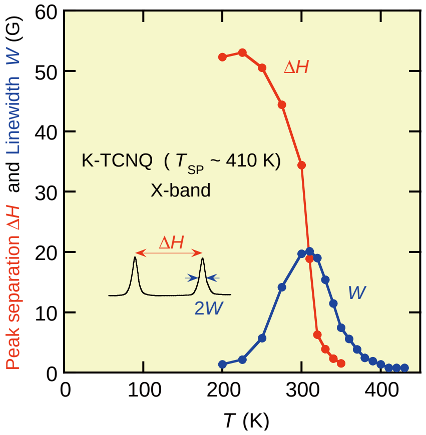

Figure 2. The temperature dependence of the peak separation for the outer doublet at ±60 G and the ESR linewidth. Note the steep disappearance of ΔH and the peak of ESR linewidth.

A-3 Spin-Dynamics Investigation by Pulsed-ESR for Phase Boundary between Spin-Peierls and Antiferromagnetic States in $(TMTTF)_2X$

$(TMTTF)_2SbF_6$ is considered to be located at the most negative pressure side in the generalized phase diagram of $(TMTCF)_2X$ at present. Observation of superconductivity in $(TMTTF)_2AsF_6$ (at 4.5 GPa) and $(TMTTF)_2SbF_6$ (6 GPa) under high pressure is also supporting this scenario. However, this model has produced a new unsolved problem: Another antiferromagnetic phase can be expected on the negative pressure side of the spin-Peierls phase according to ^{13}C NMR measurements for $(TMTTF)_2SbF_6$ under physical pressures. However, this phase diagram is based on the preconceived idea that a quantum one-dimensional spin-Peierls phase is sandwiched by two antiferromagnetic phases. In our knowledge, antiferromagnetic phases are stabilized with finite inter-chain interaction by applying pressure. It is also an open question whether the two antiferromagnetic phases (AF-I and AF-II) are of the same origin or not. To understand the P-T phase diagram of $(TMTCF)_2X$, we carried out pulsed-ESR measurements on $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$.

While the ESR spin-lattice relaxation rate, ESR-T_1^{-1}, of $(TMTTF)_2AsF_6$ shows an anomalous but spin-gap behavior below the spin-Peierls phase transition temperature, T_{SP}, the ESR-T_1^{-1} behavior of $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$ (x ~ 0.5) does not follows a conventional gap behavior suggesting that this salt is situated in the vicinity of the phase boundary between the spin-Peierls and antiferromagnetic phases.

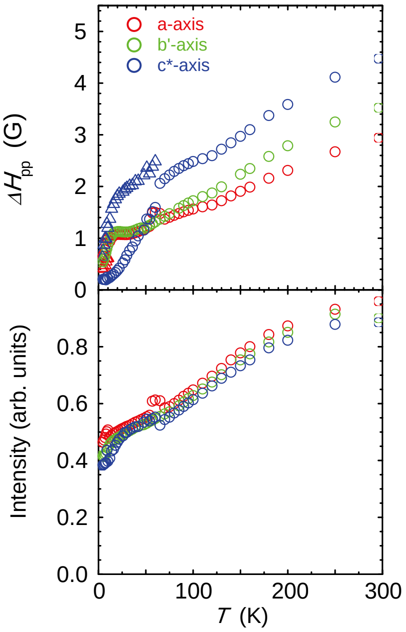

Figure 3. (left) Temperature dependence of the ESR linewidth, ΔH_{pp}, and integrated intensity (relative spin susceptibility) for $(TMTTF)_2$-$[(AsF_6)_x(SbF_6)_{1-x}]$ (x ~ 0.5) determined by CW-ESR measurements.

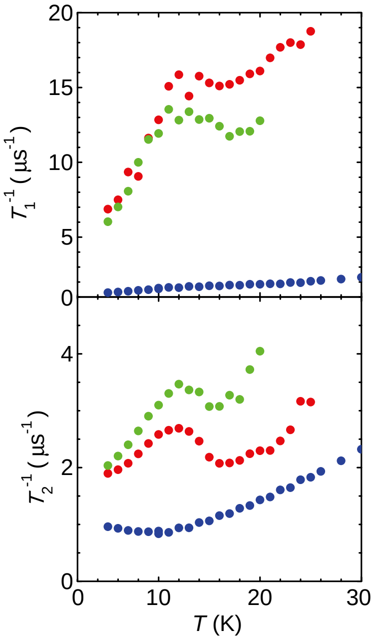

Figure 4. (right) Temperature dependence of the ESR spin-lattice relaxation rate, T_1^{-1}, and spin-spin relaxation rate, T_2^{-1}, for $(TMTTF)_2$-$[(AsF_6)_x(SbF_6)_{1-x}]$ (x ~ 0.5) determined by pulsed-ESR measurements.

B. Construction of the Research Methodology for Biomolecular Sensing System

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Although more than 50% of genome drag discovery targets are the membrane proteins, there is no efficient biosensors necessary for screening. Patch clamp using a pipette is a well known and established technique for ion channel current measurements. However, it is not suitable for the screenings due to that it requires a high level of skills and the system scale down is difficult. In this work we are developing a new incubation type planer ion channel biosensor using Si substrates suitable for neural cell function analysis.

B-1 Development of Incubation Type Si-Based Planar Ion Channel Biosensor[1)]

A new planar-type ion channel biosensor with the function of cell culture has been fabricated using silicon on an insulator substrate as the sensor chip material. Coating of the sensor chip with fibronectin was essentially important for cell incubation on the chip (Figure 1a and 1b). Although the seal resistance (R_s) was quite low (~7 MΩ) compared with the pipette patch-clamp gigaohm seal, the whole-cell channel current of the transient receptor potential vanilloid type 1 (TRPV1) channel expressing HEK293 cells was successfully observed (Figure 1c), with a good signal-to-noise ratio, using capsaicin as a ligand molecule. The good agreement between calculated and measured values of R_s indicates that the model of the gap between cell and substrate surface and the assumed value of the cleft thickness, 75 nm, are good approximations.

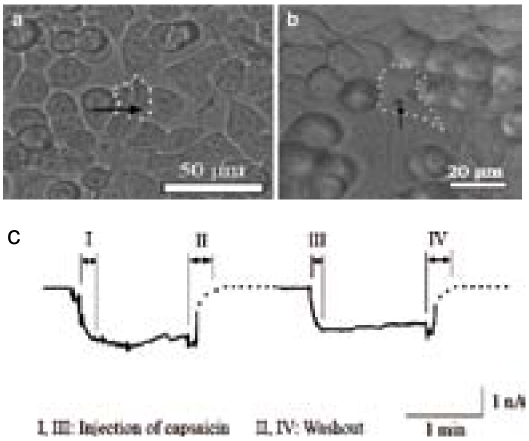

Figure 1. (a, b) Optical microscope images of HEK293 cells spreading on the pores of the planar-type ion channel biosensor. The seal resistance were (a) 6.3 MΩ, and (b) 8.4 MΩ (confluent cells). The arrows show the positions of the pores. The white dotted lines show the cells spreading on the pores. Round cells are sitting on the spreading cells. (c)Whole-cell current of TRPV1-transfected HEK-293 cell measured for the sample of (b) activated by repeated capsaicin (0.5 μmol l^{-1}) applications. Desensitization in the extracellular solution containing Ca^{2+} is observed. Holding voltage is −30 mV. Data are not shown for the dotted line region, where the signal is significantly disturbed by the noise induced by washout operations.

B-2 Development of Light Gated Ion channel Biosensor

The network function between neuronal cells has been investigated using an artificial signal input and output detection. In the investigation of the electrically excitable cells, photostimulation provides a versatile alternative to electrode stimulation. Channel of the excitable cell by the photo stimulation is especially useful in constructing the neural network analysis device. In the present work, we have expressed Chlamydomonas reinhardii channelrhodopsin 2 (ChR2) on the cell membrane of a kind of excitable cell C2C12, and measured the basic characteristics of the photo-response. ChR2 has a light absorbance peak at 460 nm and forms a non-selective cation channel, the gating of which is triggered by the photoisomerization of the all-trans retinal to 13-cis configuration. To investigate the photo-response characteristics of ChR2-expressed C2C12 cell, we have constructed the incubation type planer ion channel biosensor by putting a single C2C12 cell on the micropore of the Si substrate and successfully observed the light-gated whole cell channel current.

Reference

1) T. Urisu, T. Asano, Z. Zhang, H. Uno, R. Tero, H. Junkyu, I. Hiroko, Y. Arima, H. Iwata, K. Shibasaki and M. Tominaga, *Anal. Bioanal. Chem.*, published online, 2008.

(2) Research Symposia

(From Oct. 2007 to Sep. 2008)

Dates	Theme	Chair
Aug. 29–31, 2007	Self-Organization in the Material and Biological Systems: New Frontiers in Intergrated Research	**TOMINAGA, Masahide** **SAITO, Shinji**
Dec. 4– 5, 2007	New Development of Coordination Photochemistry by Fusing of Photofunctionality and High Reaction Selectivity	**SUZUKI, Takayoshi** **KAWAGUCHI, Hiroyuki**
Dec. 17–19, 2007	Advanced ESR Investigations for Noble Functionalities of Molecular Materials	**MIZOGUCHI, Kenji** **NAKAMURA, Toshikazu**
Mar. 10–11, 2008	Photosynthesis from Molecular Perspectives	**SUGIURA, Miwa** **NAGATA, Toshi**
Jun. 23, 2008	Preparatory Meeting for Molecular Science Summer School	**TAKEDA, Akihiro** **HISHIKAWA, Akiyoshi**
Jul. 18–19, 2008	Creation and Application of Functional Metal Complexes Based on Rational Design of Supporting Ligands —From Biological Systems to Catalysts and Devises—	**ITO, Shinobu** **AONO, Shigetoshi**

(3) Numbers of Joint Study Programs

Categories		Oct. 2007–Mar. 2008	Apr. 2008–Sep. 2008	Total
Special Projects		0	2	2
Research Symposia		3	2	5
Research Symposia for Young Researchers		–	1	1
Cooperative Research		47	46	93
Use of Facility	Instrument Center	28	25	53
	Equipment Development Center	6	4	10
Use of UVSOR Facility		77	70	147
Use of Facility Program of the Computer Center				146*

* from Apr. 2007 to Mar. 2008