Charge and Magnetic Orderings in Triangular Lattice Antiferromagnet $InFe_2O_4$

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$InFe_2O_4$ belongs to the RFe_2O_4 family where R is trivalent cation (R = In, Yb, Lu, Er, or Y). In the rhombohedral crystal structure of this compound as shown in Fig. 1, the double layers of FeO_5 bipyramids make two-dimensional triangular lattices and are separated by RO_6 octahedra. Since the numbers of Fe^{2+} and Fe^{3+} ions are equal in the triangular lattice, the coexistence of charge and magnetic frustrations is expected. However, despite the potential fascinating properties, $InFe_2O_4$ had not been investigated well because of the difficulty in sample preparation.

We succeeded in preparing high-quality $InFe_2O_4$ samples by a solid state reaction from In_2O_3, Fe and Fe_2O_3 in a vacuum sealed tube. Although a small amount of Fe_3O_4 was included as an impurity, it was magnetically separated.

Mössbauer spectroscopy (γ // c) showed that Fe ions took average valence of 2.5+ above 250K, while it changed into 3+ and 2+ below 210K. Temperature dependence of the dielectric constant showed a peak around 230K, suggesting the charge ordering in Fe layer at this temperature.

Magnetic measurement showed that $InFe_2O_4$ magnetically ordered at 230K (Fig.2). The magnetization behavior below the ordering temperature suggests that this $InFe_2O_4$ is a ferrimagnet. All experimental results indicate that charge and magnetic orderings in $InFe_2O_4$ occur simultaneously.

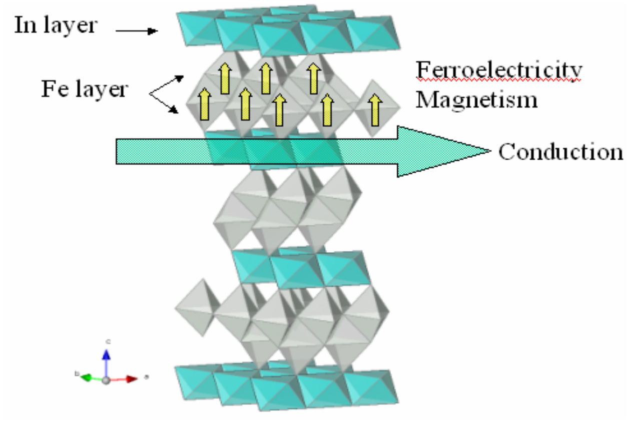

Fig.1 Crystal structure of $InFe_2O_4$

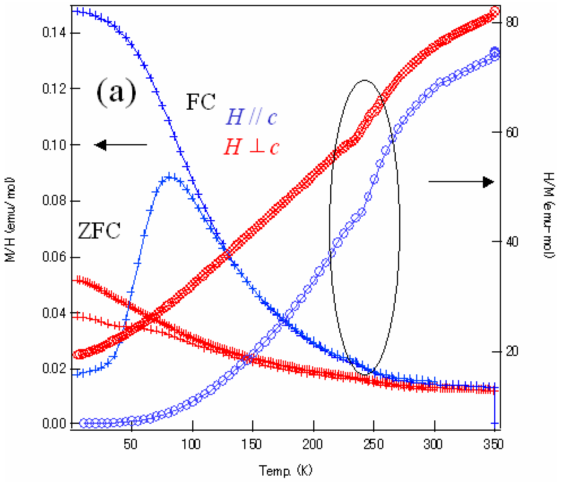

Fig.2 MT plot for oriented $InFe_2O_4$

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Magnetization and Heat Capacity of a Layered Perovskite (CuBr)$Sr_2Nb_3O_{10}$

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Topotactic chemistry provides opportunities to rationally create new magnetic materials having structures which are not form by conventional solid-state reactions Recently, a spin liquid with a finite spin gap of $\Delta/k_B = 26.7$ K has been observed in a double-layered perovskite of Dion-Jacobson type (CuCl)$LaNb_2O_7$ with a $S = 1/2$ square lattice obtained by the ion-exchange reaction between $RbLaNb_2O_7$ and $CuCl_2$ at low temperatures [1].

In this work, a triple-layered perovskite (CuBr)$Sr_2Nb_3O_{10}$ (Fig.1) with an $S = 1/2$ square lattice similar to the (CuCl)$LaNb_2O_7$ structure was successfully prepared by the ion-exchange reaction between $RbSr_2Nb_3O_{10}$ and $CuBr_2$. To investigate the physical properties of this compound, the magnetic susceptibility, high-field magnetization, and heat capacity measurements were performed. The heat capacity measurements in zero magnetic field have revealed two peaks at 7.3K and 9.1K, indicating successive phase transitions. Applying magnetic field, we have observed the two peaks in the heat capacity merge into one around 3 T. Furthermore, we have found that the magnetization curve at 4.2K shows a plateau at 1/3 of the full magnetization below 8 T, which is quite unusual for square lattice antiferromagnets. The magnetic phase diagram as well as the origin of the 1/3 magnetization plateau are discussed. Further experiments are in progress.

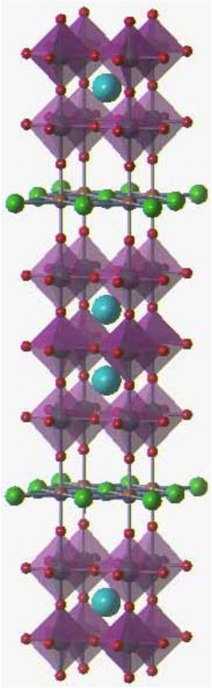
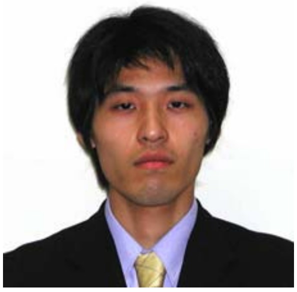


Fig.1 Crystal structure of (CuBr)$Sr_2Nb_3O_{10}$

Reference

[1] H. Kageyama et al., J. Phys. Soc. Jpn. 74 (2005) 1702.



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(Sr,Ca)$FeO_{2.5+\delta}$: Crystal Growth, Structure Analysis and Chemical Reactivity

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Oxides with high oxygen ionic transport and high electronic conductivity have attracted considerable attention in the last decade. This is mainly related to their potential application as electrodes for solid oxide fuel cells or batteries, membranes for oxygen separation and electrocatalysis. For this reason an intensive search for new oxides showing high oxygen mobility already at moderate temperatures has been stimulated in the last decade. In this respect, nonstoichiometric perovskite-type oxides are particularly interesting as they are able to undergo a reversible topotactic oxygen intercalation reaction *via* electrochemical oxidation in an aqueous alkaline electrolyte already at room temperature.

In this context, we are at present investigating oxygen deficient compounds (Ca,Sr,Ba)(Co,Fe)$O_{2.5}$ and especially (Sr,Ca)$FeO_{2.5+\delta}$. $SrFeO_{2.5}$ shows a Brownmillerite-type structure with iron equally distributed on tetrahedral and octahedral sites. It can be oxidized electrochemically or by soft chemistry methods at ambient temperature up to $SrFeO_3$ showing a cubic Perovskite structure. If the electrochemical oxidation is carried out in a galvanostatic mode, one can easily control the charge transfer and the reaction kinetics, allowing to follow this oxygen intercalation reaction on a reasonable time scale by diffraction methods or spectroscopy. This makes $SrFeO_{2.5+\delta}$ very interesting for a more general understanding of the oxygen intercalation reaction mechanism and to explore its phase diagram at room temperature as a function of the oxygen stoichiometry. Important structure and valence changes (oxidation from Fe (III) to Fe (IV)) occur during the oxygen intercalation, which implies a high oxygen ion conductivity. The reaction formula can be written as:

$$SrFeO_{2.5} + \delta\, O^{2-} \leftrightarrow SrFeO_{2.5+\delta} + 2\delta e^- \; (\delta_{max.} = 0.5).$$

The substitution of Sr by Ca leads to the isostructural $CaFeO_{2.5}$ phase, but in this case no significant oxygen ion conductivity is observed at room temperature. The different chemical reactivity of the Sr and Ca homologue system is not understood up to now and it is one aim of our investigations.

We will here report on the oxygen intercalation mechanism into $SrFeO_{2.5}$, which has been investigated on polycrystalline electrodes by *in situ* neutron powder diffraction on D1B (ILL, Grenoble, F) and by *in situ* X-ray absorption spectroscopy in transmission mode, in specially constructed electrochemical cells (BM29, ESRF, Grenoble, F). Complementary we will also report on single crystal structure analysis carried out by neutron diffraction (HEIDI, FRM2 Munich, D)on large high quality single crystals made with the help of a mirror furnace (TSFZ method).

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Single Crystal Growth of Dion-Jacobson Phases for the Magnetic Study of Two-Dimensional Square-Lattice System

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Topotactic chemistry offers a strategy for the rational design of magnetic materials. It is found that ion-exchange reactions between Dion-Jacobson type compounds $ALaB_2O_7$ (A = Li, Rb, Cs; B = Nb, Ta) and metal-halides MX_2 (M = Fe, Cu, etc…; X = Cl, Br) give a series of new magnets with a two-dimensional square lattice $(MX)LaB_2O_7$ (see Fig. 1). These compounds exhibit a large variety of magnetic properties. Among them, $(CuCl)LaNb_2O_7$, possibly having competing magnetic interactions, has a spin-singlet ground state with the spin gap of 2.3 meV, providing the first realization of the spin-liquid behaviour in the S = 1/2 square system [1].

Unfortunately, only powder samples of $(CuCl)LaNb_2O_7$ are available so far, which limits our understanding of the magnetic properties. It is thus important to grow single crystals of $(CuCl)LaNb_2O_7$. For this purpose, several techniques for growing crystals of mother compounds, e.g. $RbLaNb_2O_7$, have been used and developed. After several trials, single crystals of $RbLaNb_2O_7$ were successfully grown by using a flux method. A mixture of $RbLaNb_2O_7$ and $RbCO_3$ in a mass ratio 1 : 15 was heated up to 1050°C in 2 h, maintained during 48 h and then cooled down to room temperature in 12 h. Thin plate single crystals with typical dimensions of $0.5\times0.5\times0.03$ mm^3 have been obtained. For the next step, we are investigating ion-exchangeability of the crystal with $CuCl_2$.

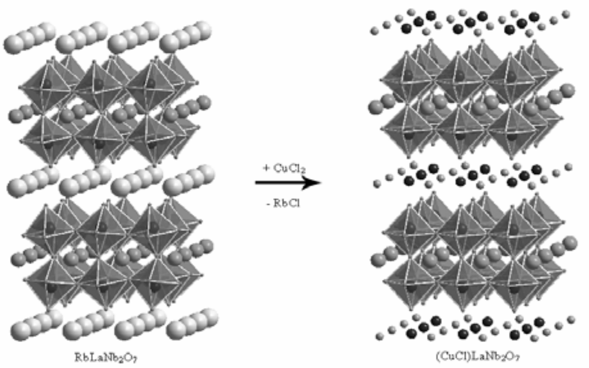

Fig. 1 Ion-exchange reaction

Reference

[1] H. Kageyama et al., J. Phys. Soc. Jpn. 74 (2005) 1702.

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Multiferroic Thin Film of Bi_2MnNiO_6 with an Ordered Double-Perovskite Structure Prepared by a Pulsed Laser Deposition Method

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Multiferroic materials, in which ferromagnetic and ferroelectric orders coexist, have attracted lots of attention from the viewpoints of technological applications as well as fundamental physics. Despite their usefulness, however, multiferroic materials are rare in nature and none of them have been used for practical applications due to small response to an external field.

A new multiferroic material, Bi_2NiMnO_6 (BNMO) with a double-perovskite structure, was recently found in our laboratory. Since this BNMO is a metastable at ambient pressure but is stabilized under high pressure, it should be interesting to stabilize this compound in a thin film form by using epitaxial strain. We report synthesis and multiferroic properties of epitaxially grown BNMO thin films.

In this study, we use a PLD (pulsed laser deposition) method (Fig.1) for making thin films. In this method, ablated oxide materials by pulsed laser beam are deposited on substrates. A great advantage of this technique is that the chemical composition of the film is very close to that of the ceramic target, thus the composition of the film can be easily controlled. We have succeeded in synthesizing multiferroic BNMO thin films epitaxially grown on $SrTiO_3$ substrates. *M-H* curve shows a large moment of ferromagnetically coupled Ni^{2+} and Mn^{4+} spins as shown in Fig.2 *P–E* measurement reveals ferroelectricity of this film. The experimental results clearly indicate that the double-perovskite BNMO thin films grown on $SrTiO_3$ show multiferroic properties.

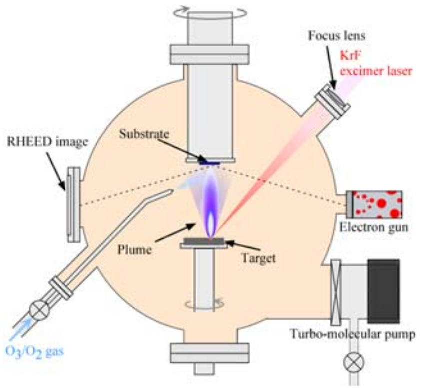

Fig.1. Schematic diagram of PLD method.

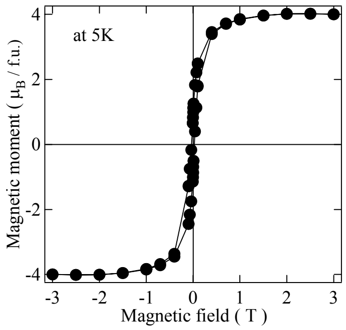

Fig.2. Magnetic field dependence of the magnetization at 5K.

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One-dimensional Chain Structure of the Tl/Ge(111)-3×1 Surface

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Reconstructed semiconductor surfaces induced by metal adsorption have gained much attention because of interesting physical properties particular to low-dimensional systems. Adsorption of thallium onto the Ge(111) surface induces two phases at room temperature [1]. The 3×1 surface at 1/3 ML has a one-dimensional chain structure, as observed on the alkali-metal induced 3×1 surfaces. The single-domain Tl/Ge(111)-3×1 surface was investigated by scanning tunneling microscopy (STM), angle-resolved photoelectron spectroscopy (ARPES) and dynamical low-energy electron diffraction (LEED) analysis.

The STM image of the 3×1 structure in Fig. 1 shows two atomic rows along the $[1\bar{1}0]$ direction. For this structure we propose the structure model shown in Fig. 2. In this model, a honeycomb-like chain of Ge adatoms and rows of Tl atoms run along the $[1\bar{1}0]$ direction. Our dynamical LEED analysis shows that this structure model is a likely candidate for the atomic structure of this surface.

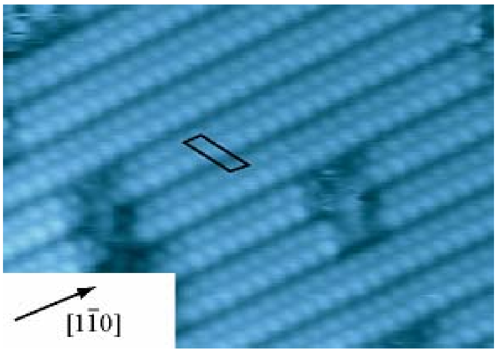

Fig.1 High-resolution STM image of the Tl/Ge(111)-3×1 structure (140×100 Å ;V_t=-0.3 V, 0.6 nA). A 3×1 unit cell is drawn on the image.

ARPES measurements were compared with first-principles band calculations performed using this structure model. The observed surface bands were assigned to surface states of the chain reconstruction.

For a more thorough understanding of the electronic and atomic structure of this surface, further analyses of the ARPES and dynamical LEED data are now in progress.

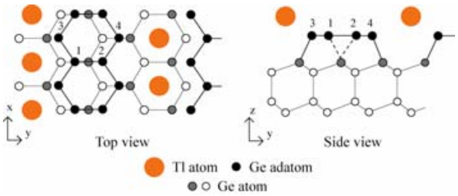

Fig.2. The modified HCC structure model of the Tl/Ge(111)-(3×1) surface.

Reference

[1] C. Castellarin-Cudia et al., Surf. Sci. 491, 29 (2001).

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Magnetic Ratchet Effect in Submicron Magnetic Wires with Asymmetric Notches

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We investigated the depinning process of a magnetic domain wall (DW) from an asymmetric notch artificially introduced into a submicron magnetic wire [1]. It was shown that the depinning field of the DW from the asymmetric notch depended on the propagation direction of the DW, and that the DW moved more easily in the direction along which the slope of the asymmetric notch was less inclined. Thus, the asymmetric notch works as an asymmetric potential barrier against the propagation of a magnetic DW. This phenomenon should be called a "*magnetic ratchet effect*". Moreover, we investigated the current-driven DW motion due to the spin transfer effect in the magnetic wire with asymmetric notches [2]. It was confirmed that the magnetic ratchet effect could be generated not only by a magnetic field but also by an electric current through the magnetic wire. In this contribution, we report a study on the magnetic ratchet effect in submicron magnetic wires with asymmetric notches.

Samples were fabricated by lift-off method in combination with electron beam lithography. Figure 1 shows a schematic illustration of a top view of the sample. The sample consists of an arched $Ni_{81}Fe_{19}$ wire with periodic asymmetric notches and two electrodes made of Au. Because of the arched shape of the NiFe wire, a magnetic DW can be introduced into a centre of the NiFe wire by applying an external magnetic field (H_{ext}) in one direction. A pulsed direct current was applied through the NiFe wire in order to drive the DW pinned by the asymmetric notch.

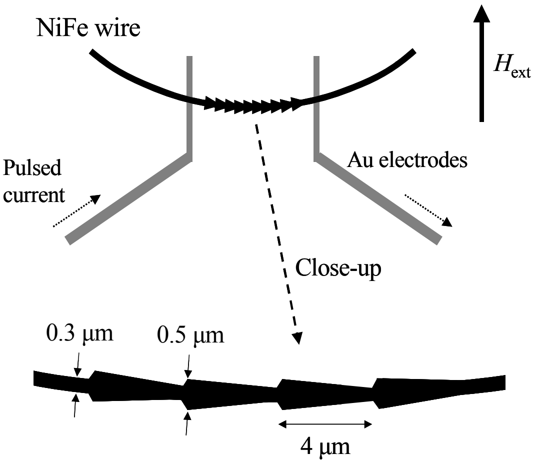

Fig. 1 Schematic illustration of the sample which consists of an arched NiFe wire with asymmetric notches and two electrodes made of Au.

References
[1] A. Himeno *et al.*, J. Appl. Phys. **97**, 066101 (2005).
[2] A. Himeno *et al.*, Appl. Phys. Lett. **87**, 243108 (2005).

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Photo Patternable Thin Film of Organic-Inorganic Hybrid Materials Prepared by Non-Aqueous Acid-Base Reaction

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A new family of organic-inorganic hybrid glasses prepared through non-aqueous acid-base reaction was recently reported. Orthophosphoric acid (H_3PO_4) and organic modified dichlorosilane ($RR'SiCl_2$) were used as the starting materials.[1] The hybrid glasses consisting of -P-O-Si-O-P- alternating copolymer structure could be obtained through the reaction, which are expected to be highly opto-functional materials because of high solubility of ionic molecules and metal ions. Especially, these hybrid materials are considered to be candidate materials for the active photonic devices. A large third nonlinear optical effect, surface plasmon resonance and so on resonance are expected for Au nano particles doped materials. The development of photo-patternable thin films using the silicophosphate materials seems to be one of the most important issues to make this new material applied to practical applications. The aim of the present study is to fabricate novel silicophosphate hybrid photo-patternable materials prepared through acid-base reaction by organo-chlorosilane, modified with vinyl-group and phosphoric acid.

Vinyl modified chlorosilane and orthophosphoric acid are used as starting materials to realize photo curable material. The obtained material from H_3PO_4-$MeViSiCl_2$ acid-base pair was a viscous liquid. ^{31}P NMR spectra indicated that linear chain of $–(P(OH)\text{-}O\text{-}Si(MeVi)\text{-}O)_n$- structure was obtained by the reaction. The silicophosphate liquid was used for spin coating to produce a photo curable transparent thin film. Free radical polymerization of vinyl group is expected to realize photo patterning. When the vinyl silicophosphate is doped with optical functional centers such as Au-nano particle, rare earth ions, and organic dyes, a highly functional photonic circuit is obtained.

Reference

[1] H. Niida, M. Takahashi, T. Uchino, T. Yoko, J. Mater. Res. 18 (2003) 1–3.

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Phase Separation in Alkoxy-Derived Silica System Containing Polyacrylamide

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By inducing phase separation parallel to the sol-gel transition of alkoxy-derived silica systems, gels having both macroporous and mesoporous structures can be obtained. The tendency of polymerization-induced phase separation can be controlled by the starting composition and reaction temperature. Relation between two parallel dynamics, i.e. formation of phase domains and sol-gel transition, determines final morphologies frozen in the gel network.

Tetramethylorthosilicate (TMOS) as a silica source, polyacrylamide (average MW=10,000) and aqueous nitric acid solution were mixed for hydrolysis at 0°C, and kept closed at 40°C. Polyacrylamide, which exhibits a strong hydrogen-bonding interaction with silica, was used as a phase-separation inducer. The gels thus prepared were dried at 40°C after solvent exchange by ethanol. Some of the dried gels were heat-treated at 570°C for 6 h. Characterization of the samples was carried out using a scanning electron microscope (SEM), nitrogen adsorption and TG-DTA.

From limited starting compositions, we obtained silica gels having continuous macroporous structure. Typical scanning electron micrographs are shown in Fig. 1. Several samples, which have high polyacrylamide concentrations, showed significantly different morphologies after the heat-treatment compared with that of dried state. At higher surfactant concentrations, after vigorous ethanol washing, pores measured by the nitrogen adsorption distributed in significantly large pore size regime (20-100nm). The aggregation state of silica-polyacrylamide hybrid network will strongly influence the final pore size distribution in the nanometer range.

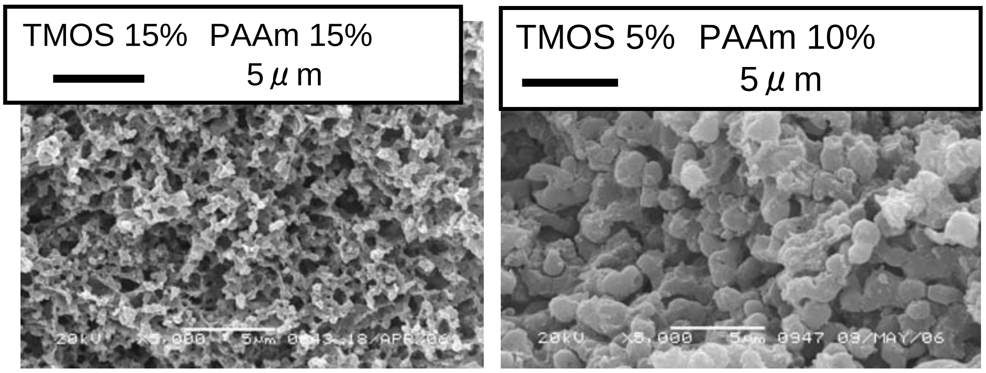

Fig.1 Typical scanning electron micrographs of non heat-treated gels.

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Porous Coordination Polymer with π Lewis Acidic Pore Surfaces

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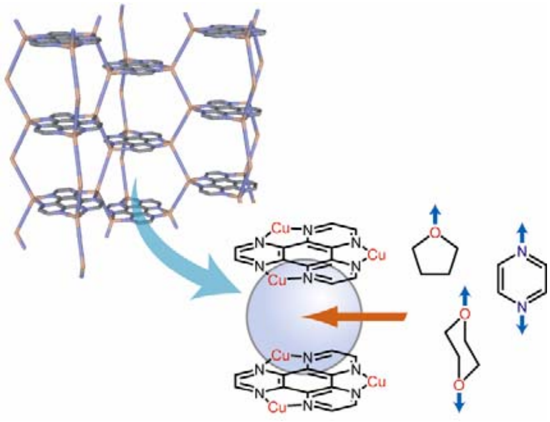
Noncovalent interactions involving aromatic rings play a fundamental role in many molecule-based crystals. In particular, the interaction of cation and aromatic rings (π-electrons) is characteristic of noncovalent binding forces, which is originated from electrostatic and cation-induced polarization. On the other hand, the interaction of electro deficient aromatic rings with anion or electronegative atom is quite rare in molecule-based crystals. Herein, we synthesized the novel host compound, $\{[Cu_3(CN)_3\ \{HAT\text{-}(CN)_3(OEt)_3\}]\cdot 3THF\}\}_n$ (**1**· THF) (HAT = hexaaza triphenyrene) , and observed the interaction of electro deficient π plane of HAT and electronegative atoms of guest molecules.[1]



Crystal structural analyses of **1**·THF reveal that the THF is included in cavity of **1** and the oxygen atom of THF interact with the π plane of HAT. The interaction of oxygen atom and HAT π plane is "electro deficient aromatic rings - electronegative atom" interaction. Furthermore, we synthesize **1**·pyz, which include pyrazine as a guest molecule. Thermogravimetric analyses, solid state NMR studying, and X-ray powder diffraction data reveal that **1**·pyz is more stable than **1**·THF. X-ray crystal structure of **1**·pyz shows that guest pyrazine is perpendicular to π plane and two nitrogen atoms of a pyrazine interact with the π planes of HAT in the cavity. The enhanced stabilities of **1**·pyz originate in that two-point interaction.

Reference

[1] D. Tanaka, S. Kitagawa et al., *Angew Chem. Int. Ed.*, *in press.*

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Study and Rationalization of the Magnetic Anisotropy in a Set of Pseudo-C_2v Ni^{II} complexes

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Since the discoverr of the single molecule magnet (SMM) behavior of the Mn_{12}ac in 1991, great efforts have been made to synthesize new molecular magnets with high blocking temperature, meaning clusters that have a high spin ground state and a non-negligible magnetic anisotropy. Among all the synthetic pathways, it is the step-by-step building approach, which consists in a rational assembly of anisotropic building blocks. Ni^{II} ions are promising candidates as building blocks because of their potential high magnetic anisotropy. To include such a mononuclear complex in the expected SMM-cluster, one needs to fully know its magnetic anisotropy and the parameters it depends on. Here, we focus on the case of a set of pseudo-C_{2v} complexes $Ni(bipy)_2X_2$ and we show that their magnetic anisotropy can be rationalized and tuned with simple chemical rules.

Reference:

J.-N. Rebilly, L. Catala, G. Charron, G. Rogez, E. Rivière, R. Guillot, P. Thuéry, A.-L. Barra and T. Mallah, *Dalton Trans.*, **2006**, 2818-2828

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Tuning Host properties by Metalation: Anion Binding, “Allostery” and Water Solubilization

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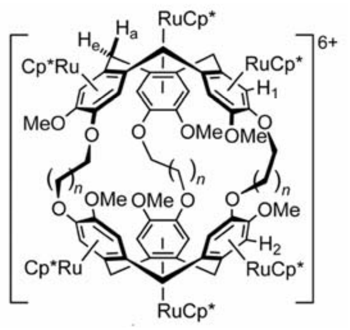
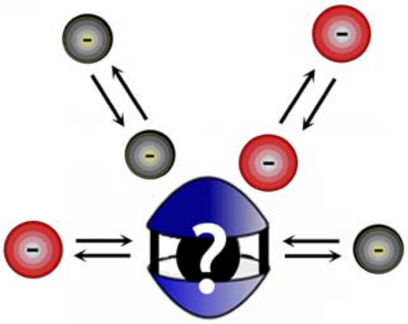
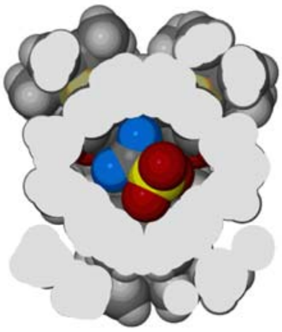
The encapsulation of small molecules by molecular “capsules” is an important field within supramolecular chemistry due to its relevance to biochemistry, waste treatment, catalysis and medicine. Much work has focused on the binding of neutral and cationic species with great success, however few hosts capable of anion encapsulation are known. Transition-metal modification of Cryptophanes A, E and O with [Cp*Ru-][CF_3SO_3] at each arene face has resulted in cationic capsules with π-acidic cavities that demonstrate a remarkable ability to selectively encapsulate anions. Importantly, binding of anions exterior to the cavity “turns off” binding at its interior in a predictable fashion. More recently, a novel synthetic route has resulted in water soluble [Cp*Ru-][Cl] metalated cryptophanes. The binding of neutral and anionic species in water by these hosts is being explored.







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Calculation of Vibronic Coupling Constant and Vibronic Coupling Density Analysis

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Vibronic coupling or electron-phonon coupling is one of the most interesting interactions in molecular physics and solid state physics since it plays an important role in Jahn-Teller (JT) effect, superconductivity, electron transfer reaction, and so on.

In this work, vibronic coupling constant V is calculated for Jahn-Teller molecules (C_5X_5, $C_6X_6^+$, and $C_6X_6^-$ (X=H, D, F, etc…)). It is shown that the symmetry breaking at Jahn-Teller crossing and violation of Hellmann-Feynman theorem occurs in the calculation based on a single Slater determinant. In order to overcome these difficulties, generalized restricted Hartree-Fock (GRHF) and state-averaged Complete Active Space Self Consistent Field (CASSCF) methods are employed for the calculation of the electronic wave functions, and the coupling constants are evaluated as matrix elements of the electronic part of vibronic operator ($\partial H / \partial Q$). Our results agree well with the experimental values [1, 2].

A concept of *vibronic coupling density* $\eta(\boldsymbol{r})$ [3], which illustrates the local property of the coupling, is proposed to explain the magnitude of the coupling from the view of the frontier electron density $\rho(\boldsymbol{r})$ and potential derivative along normal modes $v(\boldsymbol{r})$.

$$V = \left\langle \Psi \left| \frac{\partial H}{\partial Q} \right| \Psi \right\rangle = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) v(\boldsymbol{r}) = \int d\boldsymbol{r}\, \eta(\boldsymbol{r})$$

Vibronic coupling density analysis is shown to be intuitive and useful for the explanation of the order of magnitude of the coupling constant of C_5H_5 [3], $C_6H_6^+$, and $C_6H_6^-$ [4]. Moreover, this analysis is applied to the explanation of the effect of deuterium substitution and halogen substitution on the vibronic coupling.

These results could open a way to the engineering of vibronic interactions.

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Deuteration Effect in Cation Radical Salts of EDO-TTF-d_2

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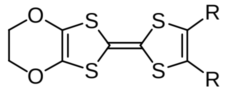

EDO-TTF: R = H
EDO-TTF-d_2: R = D

The family of $(EDO\text{-}TTF)_2X$ (X = PF_6 (**1**), AsF_6 (**2**)) shows the peculiar metal-insulator (MI) transition accompanied with the molecular deformation. In the room temperature (RT) metallic phase, flat donor molecules form almost uniform columns and the quasi-one-dimensional Fermi surface. On the other hand, in the low temperature (LT) insulating phase, the half numbers of EDO-TTF show the bent shape (*B*) and the remaining molecules exhibit the flattened shape (*F*) to afford the tetramer of [*B*, *F*, *F*, *B*] together with the lattice deformation corresponding to the nesting of the Fermi surface. In the LT phase, the charge ordering pattern is a [0, +1, +1, 0] type, corresponding to the tetramer. The counter anions exhibit the rotational disorder in the RT phase, while the rotational freedom is suppressed in the LT phase. Therefore, this system is associated with the multi-instabilities of Peierls, charge ordering, and anion ordering mechanisms [1]. Moreover, the ultra-fast and highly efficient photo-induced insulator-to-metal phase transition is demonstrated in **1** [2]. The strong coupling between the electronic state and the lattice (and/or the molecular vibrations) of EDO-TTF is claimed to play an important role in the transition.

In order to clarify the relationship between molecular vibrations and the transition, $(EDO\text{-}TTF\text{-}d_2)_2X$ (X = PF_6 (**3**), AsF_6 (**4**)) were prepared by the electrocrystallization in EtOH containing $(n\text{-}Bu_4N)X$. For **3** and **4**, the 2-3 K higher MI transition temperatures were observed in the conductivity and/or magnetic susceptibility measurements than those of **1** and **2**, respectively (Fig. 1). However, the electrocrystallization in EtOH caused the exchange between deuterium and hydrogen to reduce the deuterium content. From the mass spectrum, the deuterium content was estimated to be 90-97%. To avoid the D-H exchange, EtOD was used as a solvent to afford **4** having 98-99% of the deuterium content. The examinations of the cation radical salts of high deuterium content are underway. In the presentation, the deuteration effect on the transition temperature will be discussed.

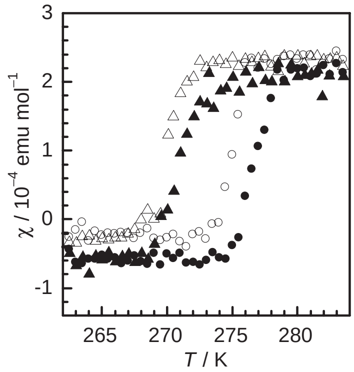

Fig. 1 Temperature dependence of the magnetic susceptibilities of **2** (△, ○) and **4** (▲, ●). Triangles and circles show cooling and heating data, respectively.

References

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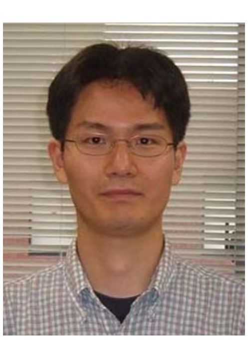

Ultrafast and Sensitive Photo-induced Phase Switching in 1/4 Filled A_2B Salt $(EDO\text{-}TTF)_2PF_6$

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Quasi one-dimensional 1/4 filled A_2B salt $(EDO\text{-}TTF)_2PF_6$ shows a phase transition between metallic (M) and insulator (I) phases at almost room temperature Tc=278 K. The origin of this transition is attributed to a charge ordering (CO) accompanied with lattice and molecular deformations. We were able to induce this phase transition by photo-excitation. The reflectivity change was probed by pump-probe technique utilizing 120 femto-second pulsed laser light. The observed spectroscopic change clearly indicates the occurrence of the photo-induced I to M transition. In addition, the transition is completed within 3 ps after excitation. Such ultrafast photo-conversion process cannot be simply explained by laser heating effect. We report that the coherent phonon generation process based on strong electron lattice coupling plays a key role for promoting the observed photo-induced I to M transition.

References

[1] A. Ota, H. Yamochi, and G. Saito, J. Mater. Chem. 12 2600 (2002).
[2] M. Chollet et al. Science, 307, 86 (2005).

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Synthesis and Properties of Mono- Substituted EDO-TTFs and Their Radical Cation Salts

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$(EDO\text{-}TTF)_2PF_6$ shows a peculiar metal-insulator transition due to the multi-instability of the metallic state. [1] This material also shows an ultra-fast and highly efficient photo induced phase transition, and the response time is around 1.5 ps. [2] Since the strong electron-molecular vibration coupling is regarded to be an origin of the peculiar features of $(EDO\text{-}TTF)_2PF_6$, a minor chemical modification of EDO-TTF is expected to provide a donor molecule, of which the cation radical salts show similar peculiarities. Here, we report the synthesis and the properties of the mono-substituted EDO-TTF, 4,5-Ethylenedioxy-4'-methyltetrathiafulvalene (MeEDO) and 4,5-Ethylenedioxy-4'-methylthiotetrathiafulvalene (MeSEDO).

MeEDO and MeSEDO were prepared in the yields of 34% and 70%, respectively. The first redox potentials of three donor molecules were in the order of MeEDO < EDO-TTF < MeSEDO, though the difference was not distinct (within 0.07 V). Also, the difference between the first and the second redox potentials was almost same for these three donor molecules.

The radical cation salts of MeEDO and MeSEDO were prepared by constant current electrocrystallization in EtOH at room temperature, but no single crystalline samples were obtained so far. The composition of these salts was estimated by elemental analysis as A_2B type in general.

The optical spectra of these salts were similar to each other despite of the different counter anions. The conductivities of radical cation salts were measured on the compressed pellets by four-probe and 2-probe method in the high temperature and low temperature regions, respectively. These salts showed high conductivities at room temperature, and some of the salts showed metallic transport behavior down to low temperature. The results of $(MeEDO)_2BF_4$ was shown in Figure 1.

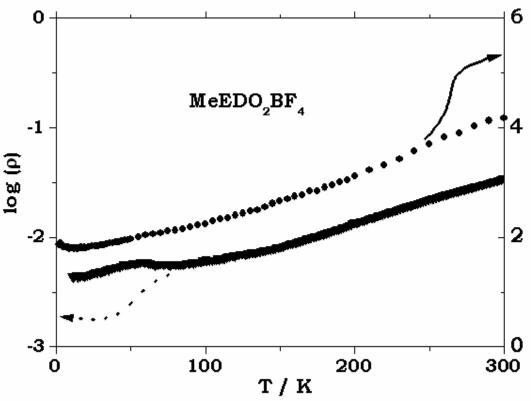

Figure 1
Temperature dependent Resistivity and Static Susceptibility of $(MeEDO)_2BF_4$

References

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Development of Biomolecule Incorporated Organic Conductor: Charge-Transfer Complexes of Cytosine with TCNQ Derivatives

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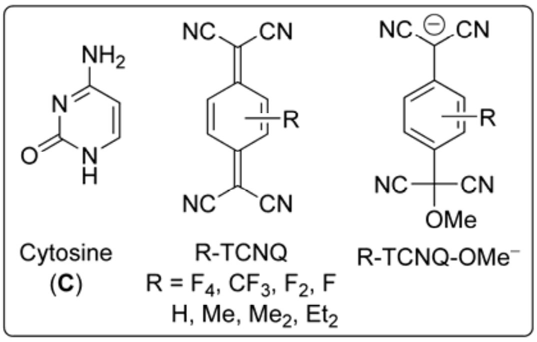

Biomolecular system has attracted much attention in the recent research for molecule-based materials. DNA is one of the candidates of biomolecular conductors, where the one-dimensional π stack of nucleobases is regarded as the hole transport path. Nucleobases are weak electron donors having the strong proton donating/accepting ability. Furthermore, the base pairing of nucleobases by the complementary hydrogen bonds (HBs) is the most important driving force in the construction of DNA duplex, and they are utilized in the field of supramolecular chemistry. In order to explore the biomolecule incorporated organic conductors, we have prepared the charge-transfer complexes of cytosine (**C**), one of the nucleobases, with a variety of TCNQ derivatives (R-TCNQs). Our investigation revealed that the reactions between **C** and R-TCNQs in alcoholic solvents afforded three kinds of products; completely ionic radical salts, highly conductive partially ionic radical salts, and insulating salts of methoxy adduct of R-TCNQ (R-TCNQ-OMe$^-$) with protonated **C**.

The pristine TCNQ salt, which was assigned to be an ionic salt, was constructed by a ribbon structure of hemiprotonated **CHC**$^+$ pairs by complementary HBs and a uniform columnar structure of TCNQ$^{\bullet-}$ (Figure 1). This salt showed the high conductivity, $\sigma_{\mathrm{rt}} = 3 \times 10^{-2}$ S cm^{-1}, as a fully ionic TCNQ$^{\bullet-}$ salt. The Me-TCNQ salt was assigned to be a partially ionic salt from the low energy charge-transfer absorption at ~3500 cm^{-1} in UV-vis-NIR spectra, and showed a high conductivity of σ_{rt} = 2 S cm^{-1} with semiconducting behaviour.

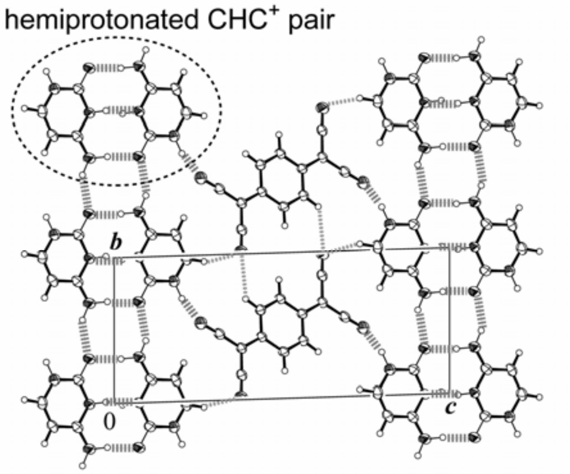

Figure 1. Crystal structure of (CHC$^+$)(TCNQ$^{\bullet-}$)

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Electronic and Magnetic Properties of Organic Charge Transfer Complexes

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Functionalised charge transfer (CT) salts have attracted more and more interests in last decades in terms of correlation between the conductivity and magnetism. The low-dimensional electronic structure of CT salts consists of π-electrons which are generated by the oxidation of the donor molecule in the columnar stacks. Recently, the CT salts, in which those π-electrons interact with localized spins of d-electrons in magnetic metal ions through the coordination, have been intensively studied. The interactions between the localized spins of d-electrons should be built up via the π-d interactions in the salts. My research is intended to reveal the physical properties of the new series of the salts.

My research consists of two parts:

The first part is featuring the magnetism of the salts in which the ligands are redox active TTF derivatives (Fig. 1) and coordinated to Fe^{2+} ion, i.e. $Fe(C_{25}H_{20}S_8N_4)_2(ClO_4)_2$ (**1**), and $Fe(C_{25}H_{20}S_8N_8)_2(BF_4)_2$ (**2**, neutral ligands), $Fe(C_{25}H_{20}S_8N_4)_2(ClO_4)_{2+x}$ (**3**, oxidized ligands). **1** and **2** show diamagnetic behaviour while **3** shows the Curie-Weiss-type susceptibility behaviour with antiferromagnetic interaction, proving that the oxidation gives rise to the localized magnetic moments on the ligands bonded to the central Fe^{2+} ion of the low spin state in **3**.

The second part is dedicated to the synthesis of TTFsq (Fig. 2). TTFsq is capable of forming the hydrogen bonds and proton-transfer in the salts. When the oxygen atoms in TTFsq are coordinated to magnetic metal ions, the π-d interactions are coexisted and correlated with the proton-transfer in the CT salts. Now TTFsq^{i}Pr is successfully synthesized and the preparation of TTFsq is proceeding.

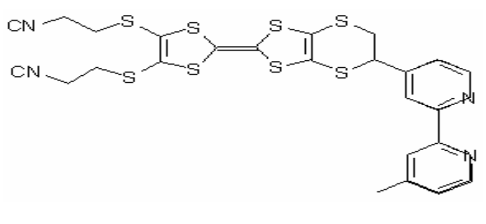

Fig. 1

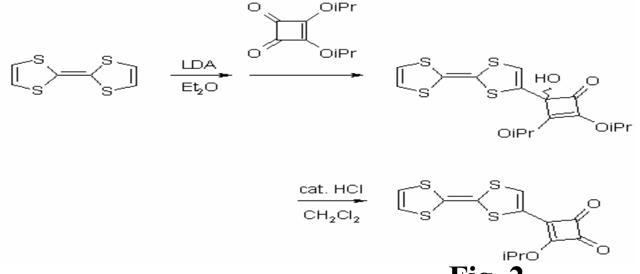

Fig. 2

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