IV-D Development of Magnetic Organic Superconductors and Related Systems

Although the first organic superconductor $(TMTSF)_2PF_6$ called Bechgaard salt possesses one-dimensional electronic band structure, its crystal structure gave a large hint to design two-dimensional metals without one-dimensional metal instabilities. In fact, with the aid of the guiding principle on the design of molecular conductors based on simple extended Hückel tight binding band picture, we could find the first κ-type organic superconductor with typical two-dimensional cylindrical Fermi surface in 1987 (κ-ET_2I_3). Since a number of κ-type organic superconductors including the system with the highest-T_c record (κ-$ET_2Cu[N(CN)_2]Cl$; T_c = 12.8 K at 0.3 kbar) have been discovered and the κ-type molecular conductors are nowadays regarded as the most typical two-dimensional metals. However the recent development of the simple typical organic superconducting systems becomes somewhat stagnant in the last decade. On the other hand, an increasing interest is going to be attracted to the magnetic organic conducting systems where the magnetic order and superconductivity are expected to coexist.

We have recently found the systems exhibiting unprecedented superconductor-to insulator transition and the first antiferromagnetic organic superconductor constructed of BETS (= bis(ethylenedithio)tetraselenafulvalene) molecules and magnetic anions containing Fe^{3+}. Furthermore, we have recently discovered a field-induced superconducting transition in another type of two-dimensional conductor, λ-$BETS_2FeCl_4$.

IV-D-1 Magnetic-Field Induced Superconductivity in a Two-Dimensional Organic Conductor

UJI, Shinya[1]; SHINAGAWA, Hideyuki[1]; TERASHIMA, Taichi[1]; YAKABE, Taro[1]; TERAI, Yoshikazu[1]; TOKUMOTO, Madoka[2]; KOBAYASHI, Akiko[3]; TANAKA, Hisashi; KOBAYASHI, Hayao
(*[1]Natl. Res. Inst. Metal; [2]Electrotechnical Lab.; [3]Univ. Tokyo*)

[*Nature* **410**, 908 (2001)]

The application of sufficiently strong magnetic field to superconductor will, in general, destroy the superconducting state. Two mechanisms are responsible for this. The first is the Zeeman effect, which breaks apart the paired electrons if they are in a spin-singlet (but not a spin-triplet) state. The second is the so-called orbital effect, whereby the vortices penetrate into the superconductors and the energy gain due to the formation of the paired electrons is lost. In this paper we have reported resistance and magnetic torque experiments on single crystals of the quasi-two-dimensional organic conductor λ-$(BETS)_2FeCl_4$, where the field-induced insulator-to metal transition has been previously discovered around 10 T. We found that for magnetic fields applied exactly parallel to the conducting layers of the crystals, superconductivity is induced for fields above 17 T at a temperature of 0.1 K. The resulting phase diagram indicates that the transition temperature increases with magnetic field.

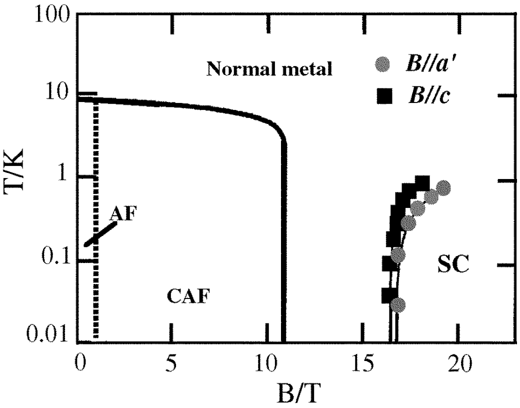

Figure 1. Temperature versus magnetic field diagram for λ-$(BETS)_2FeCl_4$.

IV-D-2 Superconductivity in an Organic Insulator at Very High Magnetic Fields

BALICAS, Luis[1]; BROOKS, James[1]; STORR, Kevin[1]; UJI, Shinya[2]; TOKUMOTO, Madoka[3]; TANAKA, Hisashi; KOBAYASHI, Hayao; KOBAYASHI, Akiko[4]; BARZYKIN, Victor[1]; GOR'KOV, Lev[1]
(*[1]Florida State Univ.; [2]Natl. Res. Inst. Metal; [3]Electrotechnical Lab.; [4]Univ. Tokyo*)

[*Phys. Rev. Lett.* **87**, 067002-1 (2001).]

We investigated by electrical transport the field-induced superconducting state (FISC) in the organic conductor λ-$BETS_2FeCl_4$. Below 4 K, antiferromagnetic-insulator, metallic and eventually superconducting (FISC) ground state are observed with increasing in-plane magnetic field. As shown in Figure 1, the superconducting state develops progressively with decreasing temperature but is suppressed for fields sufficiently away from 33 T. The temperature-magnetic field phase diagram shows the maximum temperature of the FISC phase of about 4.2 K is realized around 33 T, which is lower than T_c of λ-$BETS_2GaCl_4$ (≈ 5.5 K). The

FISC state survives between 18 and 41 T and can be interpreted in terms of the Jaccarino-Peter effect, where the external magnetic field compensates the exchange field of aligned Fe^{3+} ions. We further argue that the Fe^{3+} moments are essential to stabilize the resulting singlet, two-dimensional superconducting state.

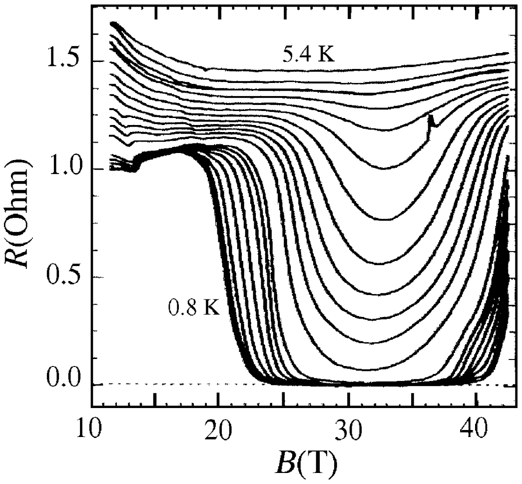

Figure 1. Resistance as a function of magnetic field B, applied along the in-plane c axis of λ-BETS$_2$FeCl$_4$ single crystal for temperature intervals of approximately 0.25 K, between 5.4 and 0.8 K.

IV-D-3 Novel Electronic Property in Organic Conductor: Superconductivity Stabilized by High Magnetic Field

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([1]Natl. Res. Inst. Metal; [2]Florida State Univ.)

[*Adv. Mater.* in press]

Organic conductors have attracted considerable interest because of the characteristic properties relating to their low dimensionality of the electronic states. Among various organic conductors, λ-(BETS)$_2$FeCl$_4$ is one of the most attractive materials in the last decade because strong competition is expected between the antiferromagnetic order of the Fe moments and the superconductivity. λ-(BETS)$_2$FeCl$_4$ is known to have a unique phase diagram. At zero magnetic field, it shows a metal-insulator transition around 8 K, while the isostructural non-magnetic salt λ-(BETS)$_2$GaCl$_4$ undergoes a superconducting transition around 6 K. The metal-insulator transition in λ-(BETS)$_2$FeCl$_4$ is associated with the antiferromagnetic (AF) order of the Fe moments with the spins $S = 5/2$. The insulating phase is destabilized by the magnetic field above about 10 T, and a paramagnetic metallic state with ferromagnetically oriented Fe^{3+} spins is recovered. Furthermore, a field-induced superconductivity (FISC) has been recently discovered at 18–41 T. FISC has been reported for a Chevrel compounds Eu$_x$Sn$_{1-x}$Mo$_6$S$_8$ with T_c = 3.8 K. As field increases, the superconductivity is destroyed at about 1 T but is restored by the field of 4 T below 0.1 K. This phenomenon is understood in terms of Jaccarino-Peter (J-P) compensation effect. Due to the antiferromagnetic coupling between the Eu spins and the conduction electrons, the exchange polarization can be compensated by an external field leading to the reappearance of superconductivity (FISC) at high magnetic field. J-P effect is considered to be essential also for FISC of λ-(BETS)$_2$FeCl$_4$.

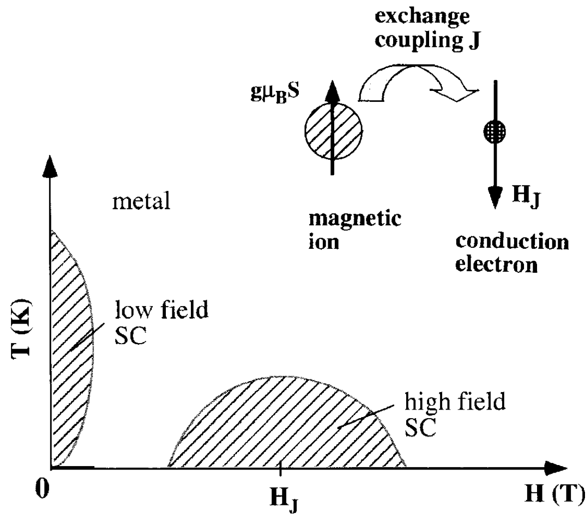

Figure 1. Schematic phase diagram of the system showing FISC and schematic picture of J-P effect.

IV-D-4 Field-Induced Superconducting Phase of λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$

KOBAYASHI, Hayao; TANAKA, Hisashi; ZHANG, Bin; KOBAYASHI, Akiko[1]; TOKUMOTO, Madoka[2]; UJI, Shinya[3]; BROOKS, James[4]
([1]Univ. Tokyo; [2]Electrotechnical Lab; [3]Natl. Res. Inst. Metal; [4]Florida State Univ.)

About a decades ago, we have tried to develop a series of BETS conductors with magnetic anions, with the aim of studying the π-d interaction in organic conductors. In fact, many interesting phenomena have been found in λ- and κ-(BETS)$_2$FeX$_4$ (X = Cl, Br). For example, λ-(BETS)$_2$FeCl$_4$ exhibits various phase transitions: (1) At ambient pressure, the system undergoes a coupled antiferromagnetic (AF) and insulating transition around 8.5 K. (2) At high pressure, this AF insulating state is suppressed and the superconducting phase is stabilized (> 3 kbar). (3) Furthermore, by applying magnetic field, the ground state is changed as, the AF insulating state → metallic state → superconducting state → metallic state with increasing magnetic field. In addition, with decreasing temperature, the alloy system, λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$FeCl$_4$ ($0.35 < x < 0.5$) exhibits the transitions as, metallic state → insulating state → superconducting state. We have recently examined the resistivities of λ-(BETS)$_2$Fe$_x$-Ga$_{1-x}$FeCl$_4$ ($x \approx 0.35$), which exhibits a subsequent metal → superconductor → insulator transition at zero magnetic field. The superconducting state can survive up to 15 T (= maximum field in this study) when magnetic field is approximately parallel to the conduction plane. Considering that the superconducting state of λ-(BETS)$_2$GaCl$_4$ is broken above 10 T, the phase diagram shown in Figure 1 is of special interest.

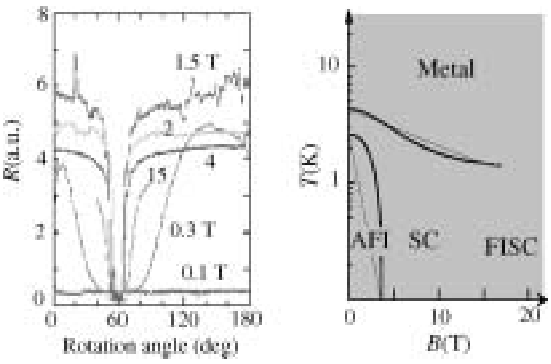

Figure 1. (a) Resistivity of λ-$(BETS)_2Fe_xGa_{1-x}FeCl_4$ ($x \approx 0.35$) for various orientation of the crystal ($T \approx$ 1–3 K) (b) Schematic *T-B* phase diagram.

IV-D-5 Antiferromagnetic Ordering of Fe^{3+} Ions in Organic Superconductor, κ-$BETS_2FeCl_xBr_{4-x}$

FUJIWARA, Emiko; FUJIWARA, Hideki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]*Univ. Tokyo)*

Recently we have found the first and second antiferromagnetic organic superconductors, κ-$BETS_2FeX_4$ (X = Br and Cl) which undergo antiferromagnetic transitions at 2.5 K (Br) and 0.6 K (Cl) and a superconducting transitions at 1.1 K (Br) and 0.1 K (Cl). In this work, the magnetic and electrical properties of κ-$BETS_2FeCl_xBr_{4-x}$ were examined by using one single crystal. The temperature dependence of the magnetic susceptibility and the field (*H*) dependence of the magnetization (*M*) at 2 K of κ-$(BETS)_2FeCl_xBr_{4-x}$ revealed that the Néel temperature (T_N) shifts to lower temperature with the increase of chlorine contents (*x*). Moreover, the easy spin axis was found to rotate from the direction parallel to *a* axis to *b* axis with increasing *x*. In other words, though the metamagnetic behavior of pure $FeBr_4$ system (x = 0) was observed for the magnetic field parallel to *a*, that of the $FeClBr_3$ system (x = 1.0) was observed for the field parallel to *b*. The magnetic field dependence of the electrical resistivities showed that both T_N where the resistivity step was observed and T_c decreased rapidly with the increase of *x*.

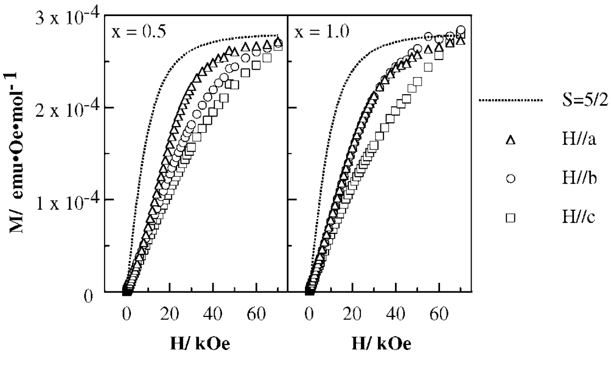

Figure 1. (a) Field (*H*) dependence of the magnetization (*M*) at 2.0 K of κ-$(BETS)_2FeCl_xBr_{4-x}$ ($x \approx$ 0.5 and 1.0). The field were applied along the three axes of crystal lattices. The Brillouin function with S = 5/2 is also shown for comparison.

IV-D-6 The *x*-Dependence of Electrical Properties and Antiferromagnetic Ordering between Fe^{3+} Ions in κ-$BETS_2Fe_{1-x}Ga_xBr_4$ System

FUJIWARA, Hideki; FUJIWARA, Emiko; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]*Univ. Tokyo)*

As reported before, both κ-$BETS_2FeBr_4$ and κ-$BETS_2GaBr_4$ salts are isostructural to each other and showed superconductivity around 1 K, but the transition of $GaBr_4^-$ salt is very broad compared to the case of $FeBr_4^-$ salt. Furthermore, $FeBr_4^-$ salt exhibited the antiferromagnetic ordering of Fe^{3+} spins at 2.5 K. Therefore we have measured the magnetic and electrical properties of the alloy system κ-$BETS_2Fe_{1-x}Ga_xBr_4$ to investigated the gallium contents-dependence of the antiferromagnetic ordering of Fe^{3+} spins and the superconducting state. The temperature dependence of the magnetic susceptibility of κ-$BETS_2Fe_{1-x}Ga_xBr_4$ (Ga = 0.1 and 0.2) revealed that the Néel temperature shifts to lower temperature with the increase of the gallium contents (2.3 K for x = 0.1 and 2.1 K for x = 0.2). On the other hand, the measurement of the electrical resistivities of κ-$BETS_2Fe_{0.9}Ga_{0.1}Br_4$ showed that the temperature of the step-like drop of resistivities, which is in good agreement with the Néel temperature determined from the magnetic measurement, also shifts to lower temperature (2.3 K) with the increase of the gallium contents. On the other hand, the mid-point of the critical temperature of superconductivity is almost the same as that of the κ-$BETS_2FeBr_4$ salt (1.1 K), but the transition became broader than the case of the κ-$BETS_2FeBr_4$ salt.

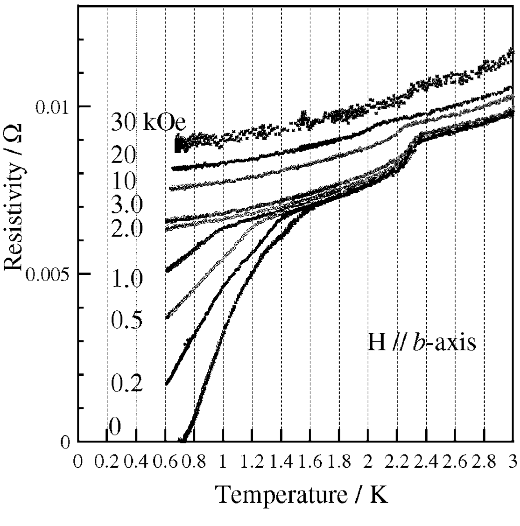

Figure 1. Magnetic field dependence of the electrical resistivities of κ-$BETS_2Fe_{0.9}Ga_{0.1}Br_4$.

IV-D-7 Organic Antiferromagnetic Metals Exhibiting Superconducting Transitions κ-$(BETS)_2FeX_4$ (X = Cl, Br): Drastic Effect of Halogen Substitution on the Successive Phase Transitions

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MIYAMOTO, Yasuhisa[1]; WADA, Nobuo[1];
FUJIWARA, Emiko; FUJIWARA, Hideki;
KOBAYASHI, Hayao
([1]Univ. Tokyo)

[*J. Solid State Chem.* **159**, 407 (2001)]

The magnetic and thermal properties of an organic conductor incorporating localized magnetic moments, κ-(BETS)$_2$FeCl$_4$ were investigated down to 60–70 mK. Similar to the Br analogue κ-(BETS)$_2$FeBr$_4$, κ-(BETS)$_2$FeCl$_4$ exhibited a successive antiferromagnetic and superconducting transitions with lowering temperature (T_N = 0.45 K, T_c = 0.1 K). That is, κ-(BETS)$_2$FeCl$_4$ is the second antiferromagnetic organic metal which exhibits a superconducting transition at ambient pressure. It became clear that the halogen exchange (Br $\rightarrow$ Cl) in the anions results in the strong reduction of both magnetic and superconducting transition temperatures. Resistivities showed a small drop at 0.45 K (= T_N), which gave a direct evidence of the existence of π-d interaction between π metal electrons and localized magnetic moments of Fe. In contrast to κ-(BETS)$_2$FeBr$_4$ exhibiting three-dimensional nature of the magnetic transition, the specific heat of κ-(BETS)$_2$FeCl$_4$ indicates the low-dimensionality of the spin system.

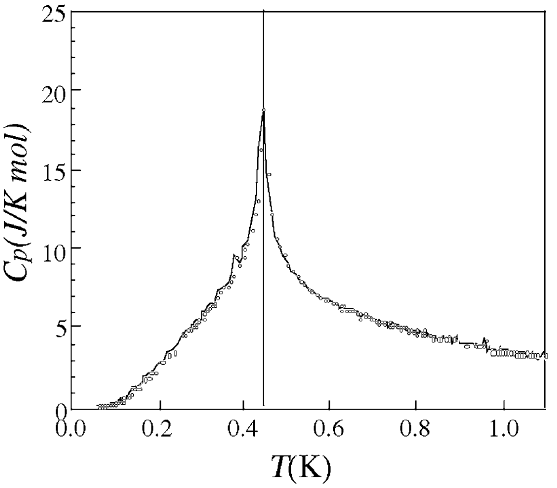

Figure 1. The specific heat of κ-(BETS)$_2$FeCl$_4$.

IV-D-8 A New Molecular Superconductor, κ-(BETS)$_2$TlCl$_4$

GRITSENKO, Victor; TANAKA, Hisashi;
KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo,)

[*J. Mater. Chem.* in press]

Since the first discovery of the κ-type organic superconductor, κ-ET$_2$I$_3$ in 1987, many organic superconductors with κ-type molecular packing were discovered. Among them, κ-ET$_2$Cu[N(CN)$_2$]Cl reported in 1990 has retained the highest Tc-record of organic superconductor (T_c = 12.8 K) for more than 10 years. About a decade ago, we have examined seven BETS conductors with tetrahalide anions MX$_4$ (M = Fe, Ga, In; X = Cl, Br) from which five organic superconductors including the first antiferromagnetic organic superconductor, κ-(BETS)$_2$FeBr$_4$ have been discovered so far. Recently we have examined the electrical resistivity of κ-(BETS)$_2$TlCl$_4$. Contrary to our previous experiments showing that the crystal was broken around 220 K, we found that the crystal could survive down to low temperatures when the cooling speed was very large. This accidental finding suggests that the resistivity measurements of this system can be made down to low temperature if the destruction of the crystal around 220 K is suppressed. Accordingly we tried to perform the resistivity measurements by using the crystal coated by epoxy resin under the expectation that "effective pressure" produced by the contraction of the epoxy resin at low temperatures will suppress the destruction of the crystal around 220 K. As was expected, we could observed the superconducting transition despite of the remaining large resistivity anomaly around 220 K.

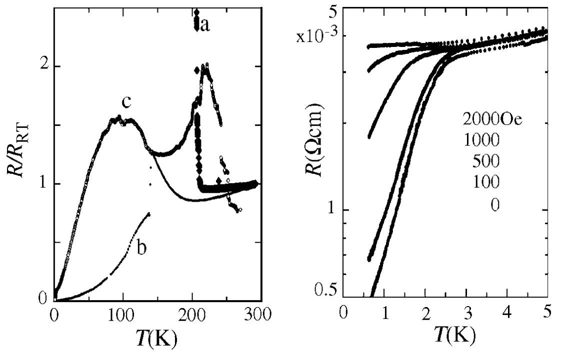

Figure 1. (a) Temperature dependence of resistivity of κ-(BETS)$_2$TlCl$_4$. a: slow cooling, b: fast cooling, c: slow cooling with epoxy resin. (b) Superconducting transition.

IV-D-9 Structure and Physical Properties of Divalent Magnetic Anion Salts Based on BETS Molecule

FUJIWARA, Emiko; GRITSENKO, Victor;
FUJIWARA, Hideki; TAMURA, Itaru;
KOBAYASHI, Hayao; TOKUMOTO, Madoka[1];
KOBAYASHI, Akiko[2]
([1]IMS and Electrotec. Lab.; [2]Univ. Tokyo)

With the aim of the development of new magnetic conductors, we have investigated BETS salts involving divalent transition metal halides such as the CoCl$_4^{2-}$, CoBr$_4^{2-}$ and MnBr$_4^{2-}$ anions with magnetic moments. X-Ray crystal structure analysis of the CoCl$_4^{2-}$ salt cleared that the salt is the κ-(BETS)$_4$CoCl$_4$(EtOH). κ-(BETS)$_4$CoCl$_4$(EtOH) showed metallic conducting behavior down to 0.7 K and its room temperature conductivity is 1–10 S·cm^{-1}, which is consistent with the result of band structure calculation giving conventional two-dimensional Fermi surfaces. Crystal structure analysis of the MnBr$_4^{2-}$ salt indicated that the salt is θ-(BETS)$_4$MnBr$_4$(EtOH)$_2$. (Figure 1) The electrical and magnetic properties of θ-(BETS)$_4$MnBr$_4$(EtOH)$_2$ showed that the system is metallic down to *ca.* 30 K with room temperature conductivities of 10–100 S·cm^{-1} and there is only a slight antiferromagnetic interaction between the manganese 3d spins because of anion-solvent-intermingled layer structure. With regard to the $CoBr_4^{2-}$ salt, the conducting behavior is almost the same as that of the $MnBr_4^{2-}$ salt.

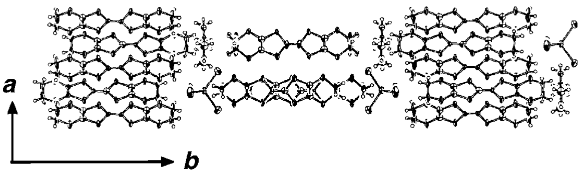

Figure 1. Crystal structure of θ-$(BETS)_4MnBr_4(EtOH)_2$ projected on to the *ac*-plane.

IV-D-10 Novel Molecular Metals Exhibiting Peculiar Magnetism Originating From Lanthanide *f* Electrons

OTSUKA, Takeo[1]; CUI, Hengbo[1]; KOBAYASHI, Akiko[1]; MISAKI, Yohji[2]; KOBAYASHI, Hayao
(*[1]Univ. Tokyo; [2]Kyoto Univ.)*

Compared with the *d*-block elements, *f*-block elements, lanthanides, will show still more unique electronic properties because of the peculiar magnetic properties of *f* orbital spins, and large magnetic moments. Since the *f* electrons are considered to be shielded by outer electrons, the spin-orbit coupling is believed to play essential role in the magnetic properties. Though the molecular metals incorporating localized *f* electrons are still very rare, the study of the '*f*-π system' will undoubtedly expand the range of functional molecular materials. We have examined the crystal structures, electronic conductivities and magnetic properties of $(BDT\text{-}TTP)_5[M(NO_3)_5]$ (BDT-TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene; M = Sm, Eu). The 4-probe resistivities measurements of $(BDT\text{-}TTP)_5[M(NO_3)_5]$ (M = Eu, Sm) showed the systems to be metallic down to 2 K, which is consistent with the two-dimensional electronic band structures. The *dc* magnetic susceptibilities were measured on SQUID (Figure 1). At first sight, weakly temperature-dependent paramagnetic susceptibility at high temperature region seems to suggest Pauli paramagnetism. The susceptibility value, however, exceeds 10^{-3} emu/mol. A contribution from Eu^{3+} ion should be taken into account. The energy levels of the lowest excited state (J = 1) and the ground state (J = 0) is very close for Eu^{3+} ion, and the excited state is easily accessed by thermal excitation. In this case, the Van Vleck paramagnetic compensation term is important. Similar but smaller Van Vleck paramagnetism was also observed in Sm system.

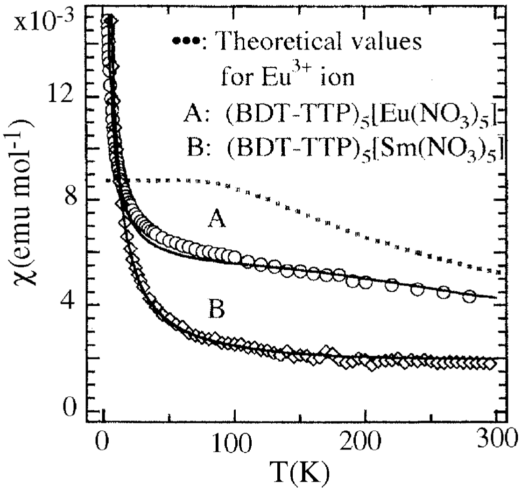

Figure 1. Paramagnetic susceptibility of $(BDT\text{-}TTP)_5$-$[M(NO_3)_5]$ (M = Eu (A), Sm (B)). The dotted curve shows the Van Vleck paramagnetism of Eu^{3+} ion.

IV-E Crystal Structure Analyses at Low Temperature and/or High Pressure

Since the molecular crystal is very soft and rich in the structural freedom, various structural phase transitions are expected by applying pressure and/or lowering temperature. Therefore the precise three-dimensional X-ray structure analyses at high pressure and/or low temperature are very important in the studies of solid state physics and chemistry of molecular crystals. The apparatus used for our present low-temperature crystal structure analyses is essentially the same to the IP (imaging plate) X-ray system equipped with liquid helium refrigerator established by us about 10 years ago. But the accuracy of the structure analysis was enhanced greatly owing to the recent slight remodeling of the apparatus. Concerning to the high-pressure X-ray structural studies, we are trying to establish the X-ray studies by combining diamond anvile cell and the IP system mentioned above. To our knowledge, accurate X-ray crystal structure determination of the soft organic crystal by diamond anvile high-pressure cell is still very rare. Very recently we have performed precise single crystal X-ray structure analysis of the crystal of organic conductor up to 2 GPa. There seems to be no difficulty to elevate the pressure up to about 5 GPa. As for the high-pressure resistivity measurements, we have recently reported the improved method of four-probe resistivity measurements for soft organic single crystals.

IV-E-1 Doubling of Lattice Constants of New Organic Superconductor κ-$(BETS)_2TlCl_4$

TAMURA, Itaru; TANAKA, Hisashi; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
(*[1]Univ. Tokyo)*

About a decade ago, we have examined the crystal structure and electronic properties of BETS conductors with tetrahalide anions such as FeX_4^- and GaX_4^- (X = Cl, Br). Among them, three superconductors with κ-type molecular arrangements have been discovered, suggesting the ground state of κ-type BETS conductor with MX_4^- anion to be superconducting. However, from the early days of the studies of κ-$BETS_2MX_4$, it was noticed that the accurate resistivity measurements of κ-type BETS salts with relatively large anions such as $FeBr_4^-$ and $GaBr_4^-$ are difficult because the crystals frequently show small resistivity jumps. Very recently we have discovered the superconductivity of the crystal of κ-$BETS_2TlCl_4$ coated with epoxy resin (fourth κ-type BETS superconductor). But the crystal without epoxy resin was always broken around 200 K, which had prevented further studies of this system. The crystal of κ-$BETS_2TlCl_4$ has orthorhombic unit cell with the space group of Pnma. In order to examine the crystal structure of this new organic superconductor, we have tried to examine X-ray diffraction patterns at low temperature by using the crystal coated by epoxy resin and found the doubling of the lattice constant *c* at low temperature (see Figure 1). The lattice constants were determined as: at room temperature, a = 11.626(2) Å, b = 36.618(8), c = 8.560(6); at 20 K, a = 11.434(1) Å, b = 36.379(5), c = 16.897(5).

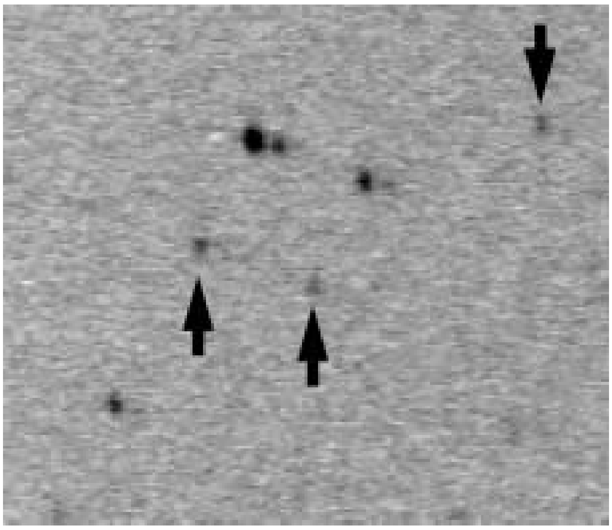

Figure 1. X-ray diffraction pattern of κ-$BETS_2TlCl_4$ at 20 K. The arrows indicate new diffraction spots developed at low temperature.

IV-E-2 High-Pressure Structure of α-(BEDT-TTF)$_2$I$_3$

TAMURA, Itaru; KOBAYASHI, Hayao

α-ET_2I_3 is one of the representative organic conductors, which undergoes a metal-insulator transition at about 135 K at ambient pressure. This metal-insulator transition is suppressed at high pressure and disappears at about 1.5 GPa. Recently, the peculiar transport property of this system observed at high pressure attracts many interests. We performed X-ray structure analyses of α-ET_2I_3 single crystal under several pressures using Diamond-anvil cell. The sample was put in a hole of gasket mounted on the Diamond anvil with 1.0 mm culet-diameter. Single crystals of α-ET_2I_3, with typical dimension of 0.28 × 0.23 × 0.15 mm^3 were used. Pressures were determined by ruby fluorescence method. X-Ray intensity data were collected by using the IP system. The oscillation photographs were taken by using a rotating anode X-ray generator with a Mo target. The lattice parameters were decreased isotropically with increasing pressure. Isotropic thermal parameters were used for all the atoms except three I atoms. The reliability factor was reduced to about 8%. Usually the bond lengths within molecules are believed to be unchanged at low pressure region. However, the I–I bond length was fairly shortened with increasing pressure (Figure 1). The data collections under higher pressures are now underway.

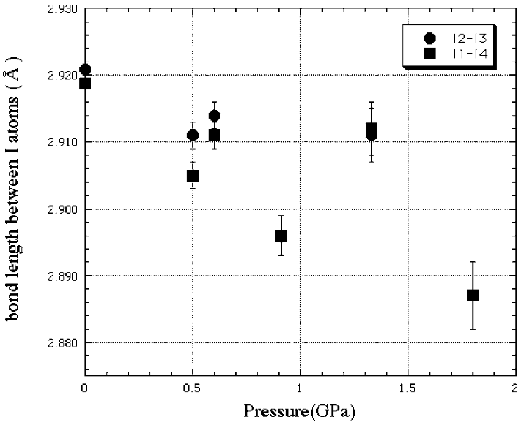

Figure 1. The pressure dependence of I–I bond length.

IV-F Development of New Molecular Conductors

The design and development of new functional molecules are most important for the progress in the field of molecular assemblies. Since the discovery of the first organic superconductors by Bechgaard and Jerome in 1980, an extremely large progress has been made in the field of molecular conductors. It is well known that all the molecular metals ever developed are the systems consisted of more than two components because the charge transfer between the molecules consisting conduction band and other molecules (or ions) has been considered to be indispensable for the carrier generation in organic systems. This means that the molecular crystal consisted of single-component molecules must be non-metallic because of the lack of the charge carriers. However, we have recently developed the first molecular metal composed of single-component molecules. This finding will indicate the possibility of the development of various unprecedented molecular conductors such as (1) superconductors composed of single-component molecules, (2) ferromagnetic metal composed of single-component magnetic molecules and (3) molecular metals soluble in organic solvents. These systems will be future targets. In addition, we are now trying to develop pure organic ferromagnetic metal based on π donor molecules containing stable radical parts.

IV-F-1 Molecular Design and Development of Single-Component Molecular Metals

KOBAYASHI, Akiko[1]; TANAKA, Hisashi; KOBAYASHI, Hayao
([1]Univ. Tokyo)

[*J. Mater. Chem.* in press]

We have examined the requirements for designing single component molecular metals, based on the results of crystal structure analyses, electrical resistivity measurements and extended Hückel tight-binding band calculations of molecular conductors composed of single-component molecules of [Ni(ptdt)$_2$] with extended TTF-ligands, ptdt. The design of π molecules with a small HOMO-LUMO gap and a TTF-like skeleton is a key step to developing single-component molecular metals. A new approach is proposed to reduce HOMO-LUMO gaps. A single-component three-dimensional molecular metal based on an analogous neutral transition metal complex molecule, [Ni(tmdt)$_2$] were prepared and characterized. Black crystals of this compound were obtained by the electrochemical method. In the crystal, which has a triclinic unit cell containing only one molecule, the planar [Ni(tmdt)$_2$] molecules are closely packed to form the lattice plane (021-). There are intermolecular short S···S contacts which indicate that the system is a three-dimensional conductor. The resistivity measurements shows that the system is metallic down to 0.6 K. The extended Hückel tight-binding band calculation gave three-dimensional semi-metallic Fermi surfaces. A metallic crystal was also prepared with an analogous molecule [Ni(dmdt)$_2$]. The formation of a single component molecular metal opens the possibilities of developing various types of unprecedented functional molecular systems such as single component molecular superconductors, ferromagnetic single-component molecular metals, molecular metals (or superconductors) soluble in organic solvent, *etc.*

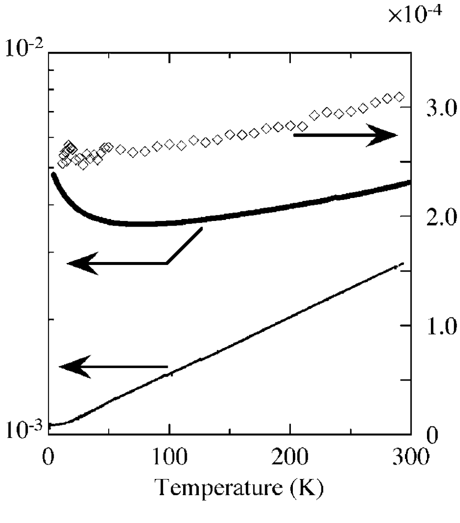

Figure 1. The susceptibility (upper) and resistivities of compacted pellet (middle) and single crystal (lower) of [Ni(tmdt)$_2$].

IV-F-2 Single Component Conductors Containing Magnetic Transition Metals

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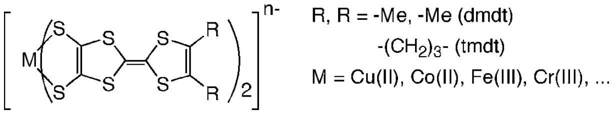
We have recently succeeded to develop the first three-dimensional molecular metal composed of single component molecules, [Ni(tmdt)$_2$], where tmdt (= trimethylenetetrathiafulvalenedithiolate) is a extended-TTF ligand. Since the single component molecular metal has been realized, one of the next targets will be the development of single component magnetic molecular metals. We have prepared metal complexes with magnetic ions (Cu^{2+}, Co^{2+}, *etc.*) coordinated by tmdt and dmdt (dmdt = dimethyltetrathiafulvalene-dithiolate). These complexes were easily oxidized by electrochemical methods. Black crystals of neutral metal complexes were obtained for [Cu(dmdt)$_2$] and the resistivity measurement was made on a compaction pellet sample. The room temperature conductivity was considerably high as for the compaction sample (3.0 Scm^{-1}) and the activation energy was very small (E_a = 60 meV). The susceptibility was consistent with the existence of localized magnetic moment of Cu^{2+}. Small antiferromagnetic interaction was observed between Cu^{2+} ions (C = 0.327(3) emu K mol^{-1}, Θ = –4.18(6) K). X-Ray crystal structure analysis showed that [Cu(dmdt)$_2$] is a non-planar molecule though the dmdt ligand moiety is ideally planar. Four sulfur atoms of two bidentate ligands coordinate the central copper atom with a distorted tetrahedral geometry.



Scheme 1.

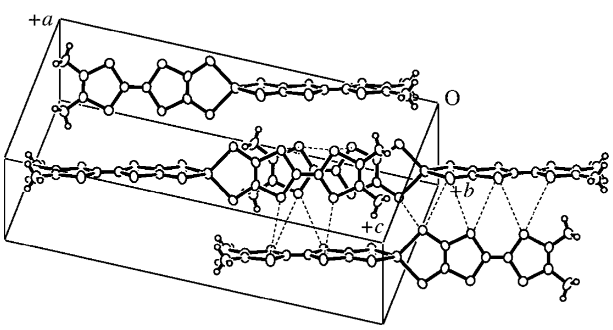


Figure 1. Crystal structure of [Cu(dmdt)$_2$].

IV-F-3 Synthesis, Structures and Properties of New Organic Donors Connecting to a TEMPO Radical Through a Pyrrolidine Ring

FUJIWARA, Hideki; FUJIWARA, Emiko; KOBAYASHI, Hayao

The molecular conductors and superconductors containing magnetic transition metal anions have been studied for the investigation of the interplay between the conductivity and magnetism. On the other hand, several attempts have been also performed using donors containing a stable TEMPO or NN radical to investigate the interaction between conduction electrons and localized spins of the organic stable radical parts for the development of novel multifunctional materials and ferromagnetic metals. Herein we report the synthesis, structures and physical properties of new TEMPO-containing electron donors in which a TEMPO radical part connects to the EDT-TTF (**1**) or EDO-TTF (**2**) skeletons through a pyrrolidine ring. The ESR spectra of them indicated three absorption lines characteristic of the TEMPO radical. The donors are paramagnetic and showed a slight antiferromagnetic interaction at low temperature region ($\theta = -2.4$ and -3.2 K, respectively). The CV measurement showed two pairs of reversible redox waves originated from the TTF part and one oxidation wave from the TEMPO radical part and indicated the possibility of the coexistence of both the cation-radical and localized spins.

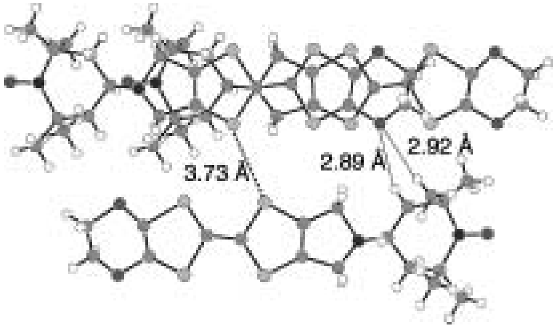


Figure 1. Crystal structure of **2**.

IV-F-4 Synthesis, Structures and Properties of New TTF and TTP Donors Containing a PROXYL Radical

FUJIWARA, Hideki; FUJIWARA, Emiko; KOBAYASHI, Hayao

To investigate the interaction between conduction electrons of the TTF-type donors and localized spins of the organic stable radical parts we have synthesized and studied the molecular conductors containing a stable TEMPO radical so far. Herein we report the synthesis, structures and physical properties of novel TTF (**1a**, **b**) and TTP (**2**) donors containing a PROXYL radical. X-Ray structure analysis of **1** showed that the PROXYL part has a racemic structure and connects to the TTF part in the chair-formed conformation. The ESR spectra of them indicated three absorption lines characteristic of the PROXYL radical. The donors **1a**, **b** are paramagnetic and showed a slight antiferromagnetic interaction at low temperature region ($\theta = -2.1$ and -8.7 K, respectively) and **1b** showed a rapid decrease of magnetic susceptibilities around 5 K, which seems to be originated from an antiferromagnetic transition. The CV measurement of **1a**, **b** showed two pairs of reversible redox waves originated from the TTF part and one oxidation wave from the PROXYL radical part and indicated the possibility of the coexistence of both the cation-radical and localized spins.

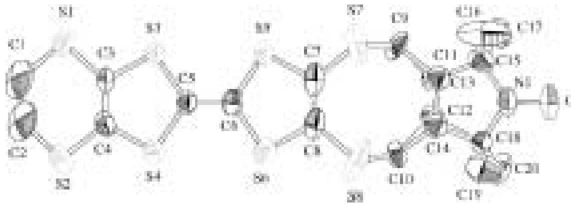
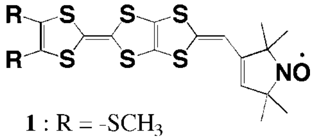


Figure 1. Crystal structure of **1a**.

IV-F-5 Syntheses, Structures and Physical Properties of New π-extended TTF Derivatives Containing a Organic Radical

FUJIWARA, Emiko; FUJIWARA, Hideki; KOBAYASHI, Hayao

We have succeeded in the syntheses of several donors **1**–**3** containing TTF moiety and 2,2,5,5-tetramethylpyrrolin-1-yloxyl (radical part) within single-molecules. Crystal structure analysis on a red crystal of the donor **3** revealed that the TTF moiety is almost planar. Electrochemical properties of the donor **1**–**3** were investigated by cyclic voltammetry. All the donors showed four pairs of reversible redox waves (E = 0.58, 0.86, 0.95, 1.67 V for **1**, E = 0.60, 0.85, 0.96, 1.63 V for **2**, E = 0.59, 0.88, 0.96, 1.69 V *vs.* Ag/AgCl in PhCN for **3**). On the other hand the aldehyde of 2,2,5,5-tetramethylpyrrolin-1-yloxyl showed one reversible redox wave (0.98 V) under the identical conditions, suggesting that the third redox process at 0.95–0.96 V occurs at radical part. The ESR spectra of benzene solutions of the donors **1**–**3** were measured to confirm the existence of the NO radical part. All of them showed three absorption lines ($g = 2.0059$ and $a_\mathrm{N} = 14.3$–14.4 G) characteristic of the NO radical. The static magnetic susceptibilities of the donor **2**–**3** were measured by SQUID magnetometer. Both of them showed Curie-Weiss temperature dependence with slight antiferromagnetic interaction and magnetization corresponding to one $S = 1/2$ spin per molecule ($C = 0.398\ \mathrm{K \cdot emu \cdot mol^{-1}}$, $\theta = -2.3$ K for 2 and $C = 0.355\ \mathrm{K \cdot emu \cdot mol^{-1}}$, $\theta = -0.73$ K for **3**). Preparation of cation radical salts of the donor **3**, where TTF moiety and radical part are expected to bear conducting and magnetic properties respectively, was carried out, and they showed semiconducting behavior.



1 : R = $-\mathrm{SCH_3}$
2 : 2R = $-\mathrm{SCH_2S}-$
3 : 2R = $-\mathrm{SCH_2CH_2S}-$

Figure 1. Structure of **1**–**3**.