IV-G Magnetism and Superconductivity of BETS Conductors

Since the discovery of one-dimensional organic metals in early 1970s, a large progress has been made in the field of molecular conductors. The first discovery of organic superconductor $(TMTSF)_2PF_6$ was reported in 1980. We have found two new organic superconductors in 1986-87, one of which was the first κ-type organic superconductor, κ-$(BEDT\text{-}TTF)_2I_3$. The tremendous boom of copper oxide superconductor was started around the same time. Although many organic superconductors (especially κ-type organic superconductors based on BEDT-TTF) have been discovered since then, almost all people do not think that T_c of the hitherto-reported type of organic superconductor will become able to compete with the T_c of oxide superconductor. Therefore, it may be natural that the development of multifunctional conductors such as magneto-conducting systems attracts an increasing attention.

We have examined a series of BETS (= bis(ethylenedithio)tetraselenafulvalene) conductors with tetrahalide anions, MX_4 (M = Ga, Fe; X = Cl, Br). Our main interest is in the development of new types of conducting systems by incorporating Fe^{3+} magnetic ions in organic conductors having stable two-dimensional metal states. Two years ago, we have discovered an unprecedented superconductor-to-insulator transition in λ-type BETS conductors, λ-$BETS_2Fe_{1-x}Ga_xCl_4$ ($0.35 < x < 0.5$), where the interaction between localized magnetic moments of Fe^{3+} ions and π conduction electrons play an essential role. We have recently discovered the first antiferromagnetic organic metal exhibiting a superconducting transition.

IV-G-1 Chemical Control of Electrical Properties and Phase Diagram of a Series of λ-Type BETS Superconductors, λ-$BETS_2GaBr_xCl_{4-x}$

TANAKA, Hisashi[1]; KOBAYASHI, Akiko[1]; SATO, Akane; AKUTSU, Hiroki; KOBAYASHI, Hayao
([1]Univ. Tokyo)

[*J. Am. Chem. Soc.* **121**, 760 (1999)]

λ-$BETS_2GaBr_xCl_{4-x}$ ($0 < x < 2$) is a molecular superconductor with strongly correlated conduction electrons. At ambient pressure, the superconducting transition could be observed for $x < 0.75$. The pressure and x dependencies of T_c were examined. The *M-H* curve at 2 K indicated the almost perfect Meissner state of the superconducting phase of λ-$(BETS)_2GaCl_4$ (*M* = magnetization; *H* = magnetic field). The magnetic susceptibility of λ-$BETS_2GaBr_xCl_{4-x}$ increases with decreasing temperature down to about 60 K, below which the susceptibility becomes x-dependent and tends to be suppressed with increasing x. The isotropic decrease of the static susceptibility at lower temperature observed in the insulating system with $x > 1.0$ indicates the insulating ground state seems not to be antiferromagnetic but probably non-magnetic. The crystal structure determinations of a series of λ-$BETS_2GaBr_xCl_{4-x}$ and the calculations of the intermolecular overlap integrals of the highest occupied molecular orbital of BETS were made to elucidate a key factor of the superconducting transition mechanism. The x dependence of intermolecular overlap integrals seems to suggest that the magnitude of the "spin gap" of the non-magnetic insulating state tends to be diminished with decreasing x.

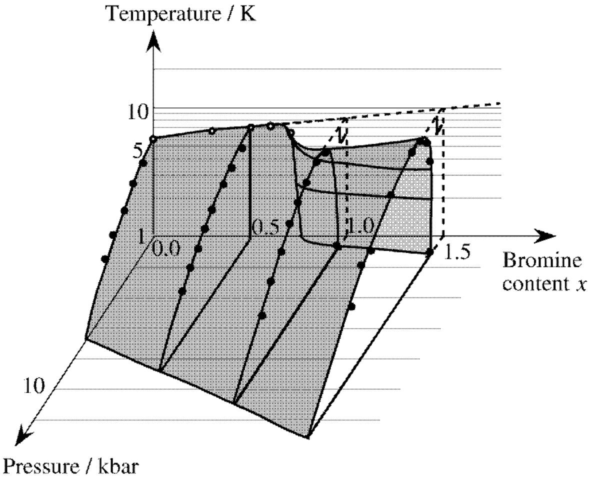

Figure 1. *T-P-x* phase diagram of λ-$BETS_2GaBr_xCl_{4-x}$. The region surrounded by shaded plane corresponds to the superconducting region.

IV-G-2 Evidence for the First Order Transition between High-temperature Superconducting and Low-temperature Insulating Phases in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.45$)

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

We have recently discovered a novel superconductor-to-insulator transition in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($0.35 < x < 0.5$). A sharp drop of the susceptibility at superconducting transition (T_c) and its recovery at lower temperature ($T_{SC\text{-}I}$) indicated that the crystal once transforms into superconducting state and then returns to the non-superconducting state with decreasing temperature. The large diamagnetic susceptibility at $T_{SC\text{-}I} < T < T_c$ observed by SQUID magnetometer showed conclusively the SC-I transition to be a bulk transition. In order to contribute to the better understanding of this unprecedented superconductor-to-insulator transition, we have carefully measured the temperature dependence of the resistivity on the freshly prepared crystal of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x = 0.45$). As shown in Figure 1, the crystal showed the SC and SC-I transitions with decreasing temperature. In contrast to the sharp superconducting transition at 4.6 K, the SC-I transition showed a distinct hysteresis, showing the first-order nature of the SC-I transition.

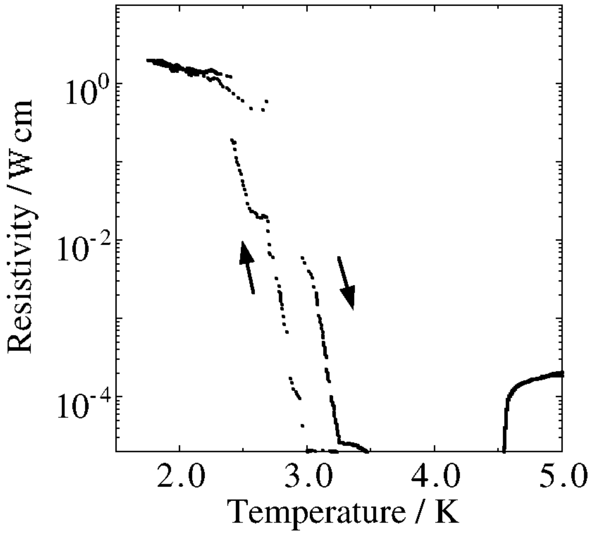

Figure 1. Resistivity behavior of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($x \approx$ 0.45).

IV-G-3 Coexistence of Antiferromagnetically Ordered Fe^{3+} Spins and Metal π-Electrons in λ-BETS$_2$FeCl$_4$

SATO, Akane; OJIMA, Emiko; KOBAYASHI, Hayao; HOSOKOSHI, Yuko; INOUE, Katsuya; KOBAYASHI, Akiko[1]; CASSOUX, Patrick[2]
([1]Univ. Tokyo; [2]CNRS)

[*Adv. Mater.* in press]

Recently we have studied the magnetic properties of λ-BETS$_2$FeCl$_4$ at high pressure. Since the 30 mg of the crystals was required for the high-pressure magnetic susceptibility measurements, the electrocrystallization experiments were repeated 25 times. The susceptibility was measured on SQUID magnetometer by using oriented thin needle crystals of λ-BETS$_2$FeCl$_4$ sealed in Teflon capsule and the Ti-Cu alloy high-pressure cell. The magnetic field was applied along the needle axes of the crystals (//*c*). At 2 kbar, sharp drop of magnetization suggesting strong π-d coupling was disappeared and only abroad maximum was observed at low magnetic field. The broad maximum indicating the separation between π and d electron systems at high pressure became conspicuous with decreasing magnetic field. Only Fe^{3+} spins seems to be antiferromagnetically ordered at low temperature. Similar behavior was also observed at 3, 4 and 5 kbar. The *M-H* curve measured at 1 bar, 3 kbar and 5 kbar showed the spin flop behavior, consistent with the antiferromagnetic ordering of Fe^{3+} spins with easy axis along *c*. These facts indicate λ-BETS$_2$FeCl$_4$ to be the first organic conductor with the antiferromagnetic metal phase at high pressure.

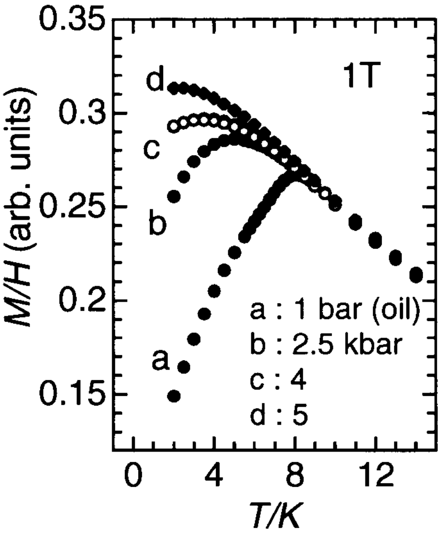

Figure 1. Temperature dependence of the susceptibility of λ-BETS$_2$FeCl$_4$ at high pressure.

IV-G-4 Pressure-Induced Superconducting Transition of λ-(BETS)$_2$FeCl$_4$ with π-d Coupled Antiferromagnetic Insulating Ground State at Ambient Pressure

TANAKA, Hisashi; ADACHI, Takafumi[1]; OJIMA, Emiko; FUJIWARA, Hideki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[2]; CASSOUX, Patrick[3]
([1]IMS and Electrotech. Lab.; [2]Univ. Tokyo; [3]CNRS)

[*J. Am. Chem. Soc.* in press]

The resistivities of λ-(BETS)$_2$FeCl$_4$ were measured at high pressure down to 0.5 K. The characteristic π-d coupled antiferromagnetic insulating ground state was destabilized under pressure and the superconducting transition was observed above 3 kbar. Since the Fe^{3+} spins has been reported to be antiferromagnetically ordered at the temperature region above the superconducting phase, the present results suggest that λ-(BETS)$_2$FeCl$_4$ undergoes a transition from antiferromagnetic metal phase to superconducting phase at high pressure. T_c was decreased with increasing pressure: the value of dT_c/dP (–0.5 deg/kbar) is almost equal to that of λ-(BETS)$_2$GaCl$_4$. The field-restored highly conducting state (FRHCS) was observed at 2.5 kbar. The critical magnetic field of FRHCS (55 kOe) was almost a half of that at ambient pressure (110 kOe). When the magnetic field was applied perpendicular to the ac plane (conduction plane) at 3.5 kbar and 0.55 K, the superconducting state was broken at 5–8 kOe. While, for the field parallel to the *ac* plane, the resistivity began to appear at 0.5 kOe and increased up to 13 kOe.

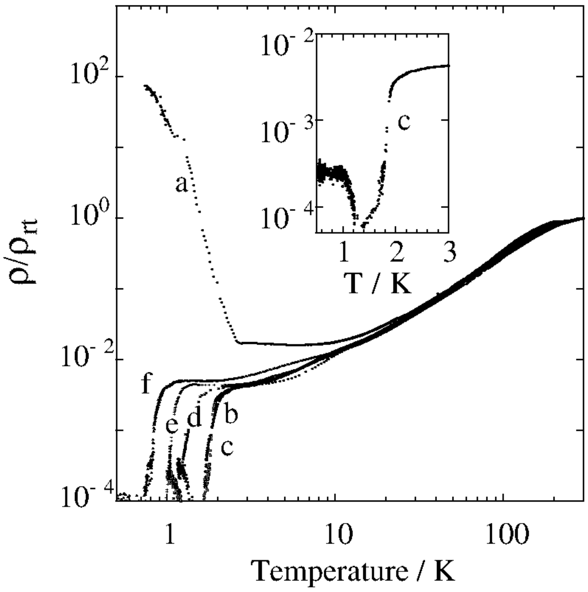

Figure 1. The resistivity of λ-$(BETS)_2FeCl_4$ at 2.5 (a), 3.0 (b), 3.2 (c), 4.0 (d), 4.5 (e) and 5.0 (f) kbar. The inset shows the anomalous resistivity behavior observed at 3.2 kbar.

IV-G-5 Electric and Magnetic Properties of BETS Conductor with Modified λ-type Structure, λ'-$BETS_2GaBr_4$

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

[*Chem. Lett.* 133 (1999)]

We have studied a series of BETS conductors with mixed-halogen gallate anions, $GaBr_xCl_{4-x}^-$. The anion sites of the λ-type salt cannot accommodate large anions. Then the structure is modified into "λ'-structure" for $x > 2.0$. The physical properties of λ'-$(BETS)_2GaBr_4$ are quite different from those of λ-$(BETS)_2GaBr_xCl_{4-x}$. The resistivity was almost temperature independent down to 50 K below which it increased gradually. Above *ca.* 3 kbar, the metallic state was stabilized, but the superconducting behavior could not be found down to 2 K. Extended-Hückel tight-binding band calculation and temperature dependencies of resistivity and magnetic susceptibility of λ'-$(BETS)_2$-$GaBr_4$ suggest the semimetal-to-insulator transition around 50 K. Thus despite of the apparent structural similarity of the λ- and λ'-salts, the electronic state of these two systems are completely different.

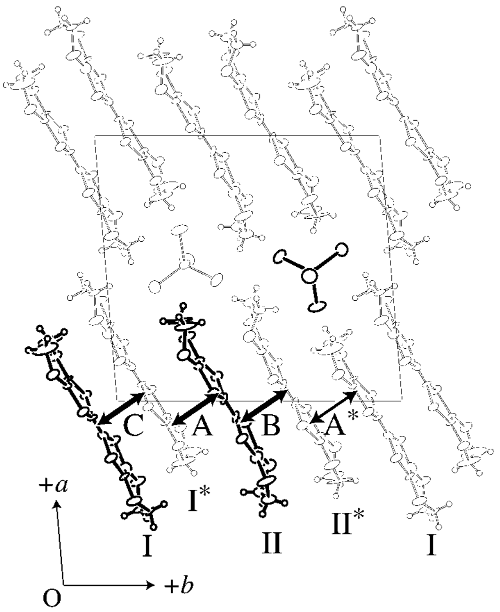

Figure 1. Crystal structure of λ'-$BETS_2GaBr_4$ viewed along the *c* axis.

IV-G-6 Antiferromagnetic Organic Metal Exhibiting Superconducting Transition, κ-$(BETS)_2FeBr_4$

OJIMA, Emiko; FUJIWARA, Hideki; KATO, Kiyonori; KOBAYASHI, Hayao; TANAKA, Hisashi[1]; **KOBAYASHI, Akiko**[1]; **TOKUMOTO, Madoka**[2]; **CASSOUX, Patrick**[3]
([1]Univ. Tokyo; [2]Electrotech. Lab.; [3]CNRS)

[*J. Am. Chem. Soc.* **121**, 5581 (1999)]

The electric and magnetic properties of κ-$(BETS)_2$-$FeBr_4$ show this system to be the first ambient-pressure antiferromagnetic organic metal (T_N = 2.5 K). The characteristic field dependence of the magnetization at 2 K indicates a helical spin structure. When the magnetic field is applied to the conduction plane (// crystal plane), the magnetization increases very rapidly and tends to be saturated above 20 kOe. While the magnetization increases almost linearly up to about 70 kOe for the field perpendicular to the crystal plane. A small resistivity drop observed at T_N gives a clear evidence for the existence of the interaction between π metal electrons and localized magnetic moments. Furthermore, this system undergoes a superconducting transition at 1.0 K.

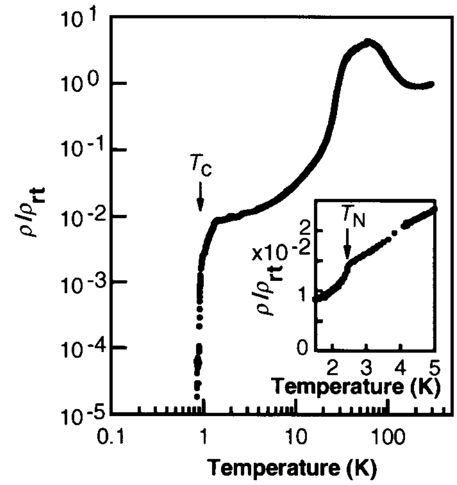

Figure 1. Resistivity of κ-(BETS)$_2$FeBr$_4$ at 0.5-300 K measured along the *ac* plane.

IV-G-7 A New κ-Type Organic Superconductor Based on BETS Molecules, κ-(BETS)$_2$GaBr$_4$

TANAKA, Hisashi; OJIMA, Emiko; FUJIWARA, Hideki; NAKAZAWA, Yasuhiro; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have recently reported that κ-(BETS)$_2$FeBr$_4$ undergoes successive phase transitions with lowering temperature from paramagnetic metal state to antiferromagnetic metal state at 2.5 K (T_N) and from antiferromagnetic metal state to superconducting state at 1.0 K (T_c). Furthermore, it is highly possible that κ-(BETS)$_2$FeBr$_4$ is the first antiferromagnetic organic superconductor, which was one of the final targets of the studies on the development of new organic conductors. Since the resistivity behavior of κ-(BETS)$_2$GaBr$_4$ has been reported to resemble to that of κ-(BETS)$_2$FeBr$_4$, a superconducting transition will be expected also in κ-(BETS)$_2$GaBr$_4$. In fact, we have found the superconducting transition of κ-(BETS)$_2$GaBr$_4$ around 0.5-1.0 K. This finding indicates T_c of κ-(BETS)$_2$MBr$_4$ (M = Fe, Ga) to be almost independent of the existence of magnetic anions. A way to develop novel organic superconductors with controlled antiferromagnetic interactions is suggested.

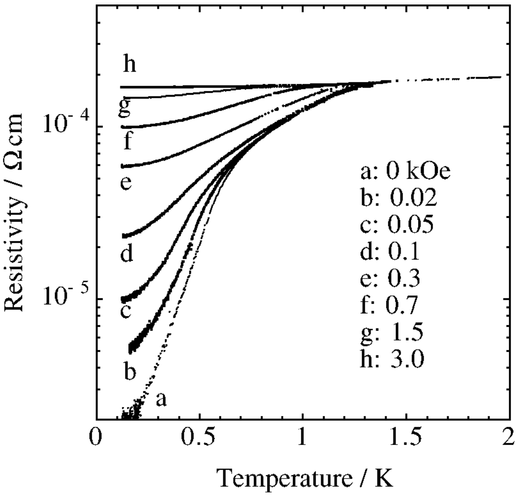

Figure 1. The magnetic field-dependence of the resistivities of κ-(BETS)$_2$GaBr$_4$ at 0–3.0 kOe.

IV-H Structural and Electrical Properties of Molecular Crystals at Low Temperature and/or High Pressure

Since the molecular crystal is very soft and rich in the structural freedom, various structural phase transitions will be expected at high pressure and/or low temperature. Moreover, the electronic properties of molecular crystal are very sensitive to the structure change. Therefore the precise three-dimensional X-ray structure analyses at high pressure and/or low temperature are important in the studies on solid state properties of molecular crystals. More than several years ago we have developed a simple X-ray imaging plate system equipped with low-temperature refrigerator, which made the low-temperature X-ray study very easy. At present, we are trying the high-pressure (or high-pressure and low-temperature) X-ray experiments by using specially designed diamond anvil cell and X-ray imaging plate system.

Usually, the high-pressure resistivity measurements of molecular conductors have been made by using clamp type pressure cell, which enables us to measure the resistivities up to about 20 kbar. For the studies on the solid state properties of molecular solid at high pressure, it is highly desired to find a way to perform the resistivity measurements by using diamond anvil cell. We have recently succeeded to measure the resistivity of thin needle crystals of organic materials up to 100 kbar.

IV-H-1 Low Temperature Structure Analysis of Unannealed TDAE*C$_{60}$ Single Crystal

NARYMBETOV, Bakhyt[1]**; KOBAYASHI, Hayao; TOKUMOTO, Madoka**[2]**; OMERZU, Ales**[3]**; MIHAILOVIC, Gragan**[3]
([1]IMS and Uzbek Acad. Sci.; [2]Electrotech. Lab.; [3]Jozef Stefan Inst., Slovenia)

[*Chem. Commun.* 1511 (1999)]

Since the discovery of the ferromagnetism in TDAE*C$_{60}$ compound (TDAE = tetrakis(di-methylamino)ethylene) with the T_c = 16 K it has been intensively studied by various experimental methods. However, till now a detailed crystal structure based on single crystal diffraction data has not been determined because in this materials the C$_{60}$ molecules have orientational disorder at room temperatures. We have carried out an X-ray diffraction study of an unannealed TDAE*C_{60} single crystal at low temperatures down to 7 K which have allowed access to detailed structural characteristics of the compound (freshly grown, unannealed crystal of TDAE*C_{60} doesn't show the ferromagnetic properties but they become ferromagnet after annealing the crystal at 20–100 °C). The structure was solved and refined based on the space group *C2/c* for the set of data obtained at 7 and 11 K. There are four chemically equivalent $C_{60}\cdot C_2(NC_2H_6)_4$ units per unit cell. The packing of the unit cell shows that C_{60} anions are located at inversion centers and form a chain along the *c*-axis with the shortest distance between molecular centers equal to 9.915 Å at that temperatures. The obtained configurations of TDAE are in reasonable agreement with predictions, which testifies to a charge state of TDAE of +1.

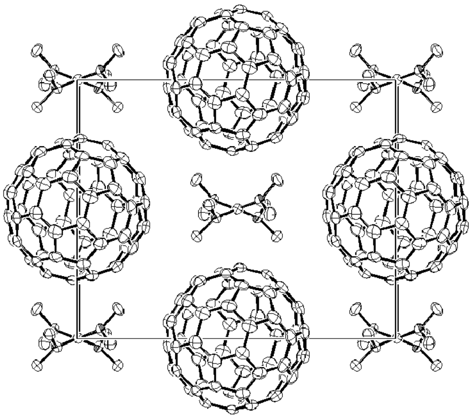

Figure 1. The projections of the C_{60}*TDAE crystal structure along: the *c*-axis.

IV-H-2 X-Ray Diffraction Study of a TDAE*C_{60} Single Crystal

NARYMBETOV, Bakhyt[1]**; KOBAYASHI, Hayao; TOKUMOTO, Madoka**[2]**; OMERZU, Ales**[3]**; MIHAILOVIC, Gragan**[3]
([1]IMS and Uzbek Acad. Sci.; [2]Electrotech. Lab; [3]Jozef Stefan Inst., Slovenia)

Despite extensive efforts of researchers, there still remain questions about the origin and the nature of low temperature ground state of a TDAE*C_{60} compound. It has been suggested that there is a rotational randomness of C_{60} molecules in TDAE*C_{60} crystals and that the magnetism could strongly depend on the merohedral degree of freedom. The freshly grown single crystals are found to be ordered antiferromagnetically and annealing in temperature range 20–100 °C results in an enhanced ferromagnetic ordering of the samples. We have performed X-ray diffraction studies of TDAE*C_{60} single crystal in temperature range 270–7 K before and after annealing the crystal at 70 °C as well as it's structure characterization at temperatures 160, 30, 11 and 7 K for unannealed sample and at low temperatures (below 16 K) for annealed sample. These studies show that for both unannealed and annealed TDAE*C_{60} single crystal at low temperatures there are structure transformations below 50 K. Remarkable changes of X-ray diffraction patterns occur below 50K and a characteristic feature of it is an appearance of diffuse lines. Observed appearance of diffuse lines on diffraction patterns below 50 K confirms the presence of ordering process, which proceeds several hours. Low temperature state of unannealed crystal is characterized by disappearing of the diffuse lines after keeping the crystal at temperatures below 50 K for about 3–4 hours. Distinctive feature in the case of annealed TDAE*C_{60} crystal is that below 50 K with the time the diffuse lines are transformed in an additional diffraction spots. X-ray oscillation patterns show that the positions of additional spots coincide with those for a primitive unit cell, which testify to a tendency of the crystal lattice to transformation from C-centered type to primitive one.

IV-H-3 Structure Transformation of a C_{60}*Na_x-$(THF)_y$ below 70 K

NARYMBETOV, Bakhyt[1]**; OJIMA, Emiko; OGATA, Hironori; KOBAYASHI, Hayao; KOBAYASHI, Akiko**[2]**; MORIYAMA, Hiroshi**[3]
([1]IMS and Uzbek Acad. Sci.; [2]Univ. Toky; [3]Toho Univ.)

$Na_x(THF)_yC_{60}$ is the first metallic single crystal C_{60} compound grown by an electrocrystallization process. The studies of conductivity and magnetic properties of the crystals have revealed presence of metal-metal transition at 175 K and another phase transition at around 50 K. It has been found that the crystals have a hexagonal unit cell and the presence of phase transition around 170 K has been confirmed by X-ray diffraction experiments ealier. We have carried out low temperature X-Ray diffraction studies of $Na_x(THF)_yC_{60}$ by using the IP system equipped with liquid helium cooling device. The obtained diffraction patterns testify that there is a structure transformation of the crystal below 70 K which is shown as increase of the unit cell volume three times. Observed reflections on the diffraction patterns at low temperatures are indexed in hexagonal unit cell and the lattice parameters at 15 K are: a = 26.207(12), c = 9.868(3) Å, V = 5869 (8) Å^3. Analysis of the collected intensity array shows that the space group is *P-3c1* (or *P-3*) with the six molecules of C_{60} per unit cell, one independent position for C_{60} molecule and two positions for $Na_x(THF)_y$ with partial population of the equivalent positions. It seems that even at low temperatures fullerene molecules have a strong orientational disorder as well as a strong disorder of $Na_x(THF)_y$ on the symmetrically equivalent positions.

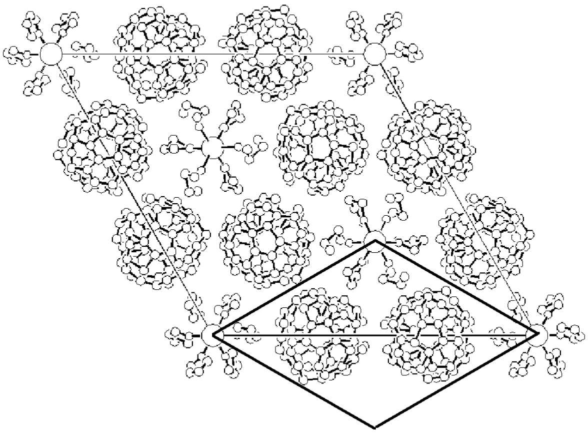

Figure 1. Schematic presentation of $C_{60}Na_x(THF)_y$ unit cell below 50 K. Unit cell at room temperature is shown by bold lines.

IV-H-4 High Pressure Structure of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$

ADACHI, Takafumi[1]; NARYMBETOV, Bakhyt[2]; KOBAYASHI, Hayao; KOBAYASHI, Akiko[3]
([1]IMS and Electrotech. Lab.; [2]IMS and Uzbek Acad. Sci.; [3]Univ. Tokyo)

With the aim of setting up the high pressure (or high-pressure and low-temperature) single crystal X-ray apparatus by using diamond anvile cell, we are examining the crystal structure of a high-pressure superconductor, $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ (T_c = 4 K at 2.4 kbar). Several years ago, we have proposed a HOMO-LUMO inversion mechanism to explain an anomalous *P-T* phase diagram of $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ where the insulating phase appears at higher pressure region above the superconducting phase. We have analyzed the structure up to 10 kbar by using specially designed diamond anvil cell without Be-supporting disks. The diffraction spots were detected by X-ray imaging plate. In order to obtain the information on the high-pressure structure at low-temperature, we are trying the high-pressure X-ray experiments by using low-temperature imaging plate system.

IV-H-5 High-Pressure Four-Probe Resistivity Measurements of the Soft Organic Single Crystals up to 100 kbar

ADACHI, Takafumi[1]; KOBAYASHI, Hayao; MIYAZAKI, Takafumi[2]; TOKUMOTO, Madoka[3]
([1]IMS and Electrotech. Lab.; [2]Ehime Univ.; [3]Eletrotech. Lab.)

Recently, the electric properties of solids at extremely high pressure has attracted much attention. The superconductivity of oxygen discovered around 1 Mbar by using diamond anvil cell may be one of the best examples. On the other hand, the pressure of the usual clamp-type high pressure cell used for the single crystal experiments on the organic compounds cannot exceed *ca.* 25 kbar. In order to obtain the sufficiently accurate resistivity data above 100 kbar, an improvement of diamond anvile technique seems to be inevitable. Since the report by Mao and Bell who measured the resistivity of string-shaped metal sample by using MgO gasket and pressure medium of soft powder (*e.g.* NaCl), the four-prove high-pressure resistivity measurements were made by diamond anvil cell. In order to apply high-pressure resistivity technique to soft organic crystals, the requirements for good Ohmic contacts and quasi-hydrostatic pressure will be essential. We have recently established an improved method applicable for the single crystal resistivity measurements up to 100 kbar.

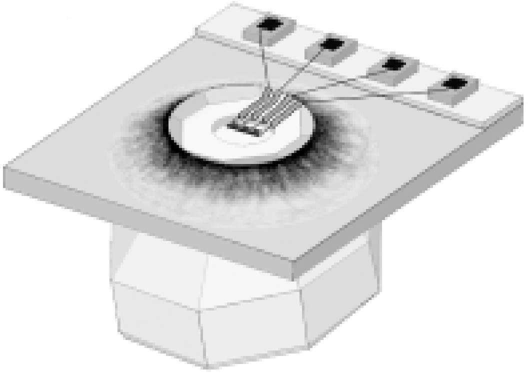

Figure 1. An illustration of the setup of diamond anvil four-probe resistivity cell .

IV-H-6 Resistivity Behavior of Organic Conductor, β'-$(BEDT\text{-}TTF)_2ICl_2$ up to 100 kbar

ADACHI, Takafumi[1]; KOBAYASHI, Hayao; MIYAZAKI, Takafumi[2]; TOKUMOTO, Madoka[3]
([1]IMS and Electrotech. Lab.; [2]Ehime Univ.; [3]Eletrotech. Lab.)

β-$(BEDT\text{-}TTF)_2I_3$ is one of the well-known organic superconductors discovered in 1984. An analogous conductor with smaller anions and modified β-type structure, β'-$(BEDT\text{-}TTF)_2ICl_2$ has an antiferromagnetic insulating ground state at ambient pressure. We have tried to check the possibility of the superconducting transition at high pressure by adopting the diamond anvil four-probe resistivity technique. The resistivities were successfully measured up to 100 kbar. To our knowledge, this is the first four-probe resistivity measurements on single organic crystal around 100 kbar. The activation energy was decreased with increasing pressure and metallic state appeared around 80 kbar. The room-temperature resistivity was 10^{-2} Ω cm around 80 kbar, which was about three orders of magnitude smaller than that at ambient pressure (20 Ω cm). However, the superconducting phase could not be found. Unexpectedly, around 100 kbar, the resistivity was gradually increased with the time, indicating a pressure-induced solid state reaction.

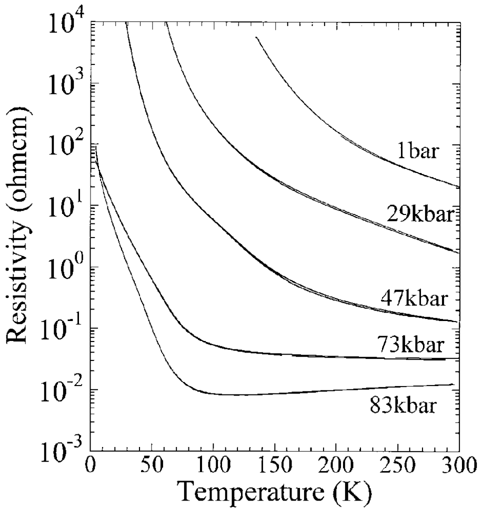

Figure 1. Resistivities of β'-(BEDT-TTF)$_2$ICl$_2$ up to 80 kbar.

IV-I Development of New Molecular Conductors

The development of new materials is the most important driving force for the field of solid state chemistry. The recent progress in the concept of the molecular design enriched greatly the physics and chemistry of crystalline molecular solids. The appearance of various types of molecular metals, superconductors and molecular ferromagnets have attracted an increasing interest of chemists and physicists. We must grow out of the conventional design of molecular conductors for the future development. In these points of view we have performed the development of several types of new molecular components for organic molecular conductors. In the study of ditellurium bridged polyacene donors and propyleneditelluro substituted TTF, we have determined the whole of the crystal structures and physical properties. We are now examining new guiding principles for designing the organic conductors. Furthermore we have developed the novel organic donor containing a stable organic radical part to investigate the interaction between itinerant electrons of the charge-transfer complexes and localized spins of the organic stable radical parts for the development of novel organic conducting-magnetic hybrid materials.

IV-I-1 New Stable Metallic Salt Based on a Donor Molecule Containing *peri*-Ditellurium Bridges, TMTTeN(SCN)$_{0.88}$

OJIMA, Emiko; NARYMBETOV, Bakhyt; FUJIWARA, Hideki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]; TAKIMIYA, Kazuo[2]; OTSUBO, Tetsuo[2]; OGURA, Fumio[3]
([1]Univ. Tokyo; [2]Hiroshima Univ.; [3]Kinki Univ.)

[*Chem. Lett.* 845 (1999)]

Recently we have discovered the TMTTeN salts with Ag(CN)$_2^-$ and Au(CN)$_2^-$ anions showing metallic behavior down to 50 K. They have tetragonal structures and quasi three-dimensional Fermi surfaces. Recently, we have found a new stable metallic salt, TMTTeN(SCN)$_{0.88}$. The crystal structure is not isostructural to the structures of the Ag(CN)$_2^-$ and Au(CN)$_2^-$ salts. That is, penetration of the SCN$^-$ anion into the TMTTeN lattice leads to a modification of the packing of the TMTTeN molecules along the *c*-axis of the crystals. As shown in Figure 1, there are many intermolecular Te···Te contacts less than the sum of the van der Waals radii (4.2 Å) and three-dimensional network through the tellurium atoms is developed. The salt shows very high room-temperature conductivities (400–600 S cm^{-1}) and stable metallic behavior down to low temperature (4.2 K). The paramagnetic susceptibility of TMTTeN(SCN)$_{0.88}$ is almost constant throughout the temperature range, indicating Pauli paramagnetism of the system [1.6–1.9 × 10^{-4} emu mol^{-1}]. Thus, the salt is considered to keep stable metallic nature down to liquid helium temperature.

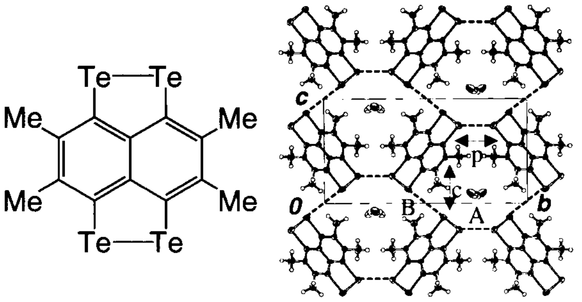

Figure 1. Structure of TMTTeN and crystal structure of TMTTeN(SCN)$_{0.88}$.

IV-I-2 Synthesis, Structures and Properties of New Organic Conductors Based on Tellurocycle-Fused TTF Donor Molecules

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

[*Adv. Mater.* in press]

In the search for excellent electron donors composing organic conductors, the concern for the tellurium-containing tetrathiafulvalene (TTF) derivatives has been growing for the last several years because a new metallic system with wide bandwidth and high dimensionality is expected to appear due to the large electron cloud of tellurium atoms. In addition, the conducting salts based on tellurium-containing donor molecules are interesting because the tellurium network is dominant for the construction of whole the crystal structure. Therefore we focused on the tellurocycle-fused TTF donor molecules. In this communication we reported the synthesis, crystal structure and electrochemical property of a new tellurocycle-fused TTF donor, 4,5-dimethyl-4',5'-propyleneditelluro-TTF **1**. We clarified the DA type crystal structure of the TCNQ complex of **1**. Furthermore, we prepared the several cation radical salts by use of the donor **1** and cleared that the unsymmetrical donor **1** are subject to the transformation to the dimerized donor **2** during the electrochemical oxidation. Although the obtained conducting salts are all semiconductors, those tellurium-containing donors have very interesting and unique molecular and crystal structures.

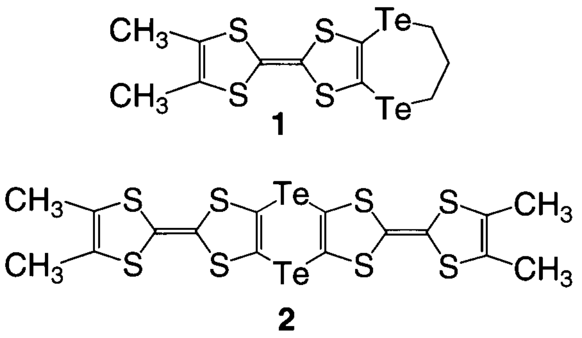

Figure 1. Structures of **1** and **2**.

IV-I-3 New π-Extended Organic Donor Containing a Sable TEMPO Radical as a Candidate for Conducting-Magnetic Multifunctional Materials

FUJIWARA, Hideki; KOBAYASHI, Hayao

[*Chem. Commun.* in press]

Recent studies on the molecular conductors and superconductors containing magnetic transition metal anions, such as the $(ET)_2[(H_2O)Fe(C_2O_4)_3]\cdot C_6H_5CN$ salt, a series of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ alloy salts and κ-$(BETS)_2FeBr_4$ salt, have stimulated the interest for the investigation of the interplay between the conductivity and magnetism in the research for new organic conductors. From the view point of realization of metallic conductivity, we supposed a molecular design as a fusion of a stable TEMPO radical part to the DTET-TTF [methylidene-1,3-dithiolo[4,5-*d*]-4,5-ethylenedithio-TTF] skeleton, which is a promising building block for realizing stable metallic behavior down to low temperature, such as the cases of MeDTET and CPDTET salts. We have examined the structure and physical properties of the $Au(CN)_2^-$ salt of TEMPOET. The $Au(CN)_2^-$ salt was electrochemically prepared. X-Ray crystallographic analysis revealed that the D:A ratio of this salt is 2:3 and the TEMPOET donors form sheet-like structures. There is short O···O contacts (3.24(2) Å) between donor sheets. The room temperature electrical conductivities is low value of 10^{-3} S cm^{-1} due to the highly oxidized state and undesirable stacking of donors. The small room temperature magnetic susceptibility (9.6×10^{-4} emu mol^{-1} for 2:3 salt) suggests the existence of intramolecular spin singlet formation and/or intermolecular strong antiferromagnetic spin configuration.

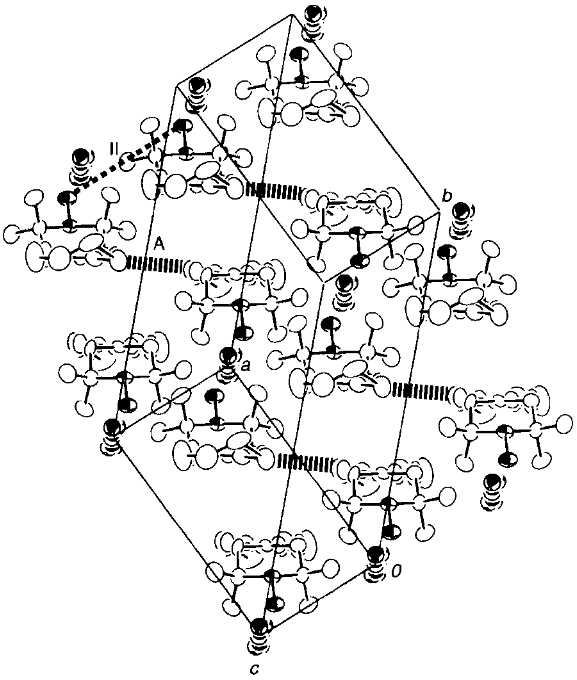

Figure 1. Crystal structure of $(TEMPOET)_2[Au(CN)_2]_3$.

IV-I-4 Synthesis and Properties of New Organic Donor Containing Two Sable TEMPO Radical Parts

FUJIWARA, Hideki; KOBAYASHI, Hayao

Organic molecular magnetism has become very active field of research for the material chemistry and physics since the discovery of the first pure organic ferromagnet in *p*-nitrophenyl nitronyl nitroxide (β-NPNN) in 1991 and successive development of several ferromagnets based on aminoxyl radicals such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and 4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide (NN) radicals. On the other hand, recent studies on the molecular conductors and superconductors containing magnetic transition metal anions have stimulated the interest for the investigation of the interplay between the conductivity and magnetism in the research for new organic conductors. Recently we have synthesized a donor molecule containing a stable TEMPO radical part and reported its electrochemical and magnetic properties. Furthermore we have prepared several cation radical salts and investigated their conducting and magnetic properties. In this context, further development of such stable radical-containing donor molecules is of interest. In this work, we synthesized a new donor molecule containing two TEMPO radical parts **1** and investigated its ESR spectra and magnetic susceptibility.

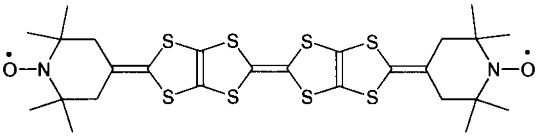

Figure 1. Structure of **1**.

IV-I-5 Origin of the High Electrical Conductivity of Neutral [Ni(ptdt)$_2$] —A Route to Neutral Molecular Metal

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A novel neutral nickel complex molecule with the extended TTF dithiolato ligand, propylenedithiotetrathiafulvalenedithiolate [ptdt^{2-} = (S$_8$C$_9$H$_6$)$^{2-}$], was synthesized. In the [Ni(ptdt)$_2$] crystal, [Ni(ptdt)$_2$] molecules form one-dimensional columns along the *a* axis, having short intermolecular transverse S···S contacts. The crystal exhibited an extremely high electrical conductivity (7 S cm^{-1}) at room temperature as a neutral molecular crystal. High-pressure resistivity measurements was made up to 72 kbar. But contrary to usual low-dimensional organic conductors, the resistivity could not be suppressed by applying high pressure. The tight-binding band structure calculation indicated that the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) form "the crossing bands," whose Fermi surfaces tend to be vanished by HOMO-LUMO interactions. Only very small electron and hole pockets appear in the Fermi surface owing to the transverse interactions between neighboring columns. Based on these analyses, the requirements for the design of molecular metals composed of single molecules have been clarified.

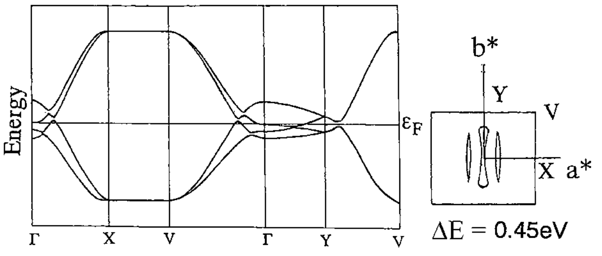

Figure 1. Tight-binding band of neutral [Ni(ptdt)$_2$] crystal. The Energy difference between HOMO and LUMO is tentatively assumed to be 0.45 eV.

IV-I-6 Structural, Electrical and Magnetic Properties of Low-dimensional Conductors Based on Unsymmetrical π Donor EDT-TTF and Analogous Selenium-substituted Molecules

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[*J. Mater. Chem.* **9**, 2365 (1999)]

Organic conductors based on unsymmetrical π donor molecules EDT-TTF (ethylenedithiotetrathiafulvalene) or its selenium-substituted analogs (EDST, EDTS) and tetrahedral anions GaCl$_4^-$ were prepared. The crystal structure determinations and the extended Hückel tight-binding band calculations indicated these systems to be quasi-one dimensional conductors similar to TMTTF or TMTSF systems (TM systems). Electrical resistivity and magnetic susceptibility measurements and low-temperature X-ray diffraction experiments suggested the spin-Peierls ground state of (EDT-TTF)$_2$GaCl$_4$. (EDST)$_2$GaCl$_4$ and (EDTS)$_2$GaCl$_4$ exhibited metallic behavior down to *ca.* 40 K. The electric and magnetic properties of (EDST)$_2$GaCl$_4$ suggested a semimetallic state at low temperature. In spite of the similarity in the crystal and electronic band structures between TM and EDT systems, these two series of quasi-one dimensional conductors do not share the same "generalized phase diagram." The electron-lattice interaction seems to be important in EDT conductors. The electric and magnetic properties of the isostructural systems with magnetic FeCl$_4^-$ anions were also examined. The magnetic interaction between the high-spin Fe^{3+} ions was found to be very weak.