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A new molecular superconductor, κ-$(BETS)_2TlCl_4$ [BETS = bis(ethylenedithio)tetraselenafulvalene]

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An organic conductor with two-dimensional κ-type molecular arrangement, κ-$(BETS)_2TlCl_4$, has been revealed to be a new organic superconductor with $T_c = 2.5$ K (onset) by careful resistivity measurements using a single crystal coated by epoxy resin.

Since the discovery of the first organic superconductor, Bechgaard salt $(TMTSF)_2PF_6$ more than two decades ago,[1] a number of organic superconductors have been discovered, especially in the systems based on BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] and various mono-anions (I_3^-, ReO_4^-, $Cu[N(CN)_2]Br^-$, *etc.*).[2] Nevertheless, the highest T_c record for an organic superconductor remains unchanged since 1990 when the superconductivity of $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ was discovered under "soft pressure" ($T_c = 12.8$ K at 0.3 kbar).[2,3] On the other hand, there seems to be increased interest recently concentrated on the development of new types of conductors such as magnetic molecular conductors,[4–6] exotic molecular metals composed of single-component molecules,[7] and also the development of new π donors affording new organic conductors.[8]

BETS [bis(ethylenedithio)tetraselenafulvalene] is a BEDT-TTF analogue where four sulfur atoms in the central TTF skeleton are replaced with selenium atoms. In the early 1990s, by utilizing the strong tendency of BETS to produce a stable metallic state, we tried to prepare new types of organic conductors which enabled us to study the interplay between conductivity and magnetism in organic systems at low temperature.[9] We have recently found an unprecedented superconductor-to-insulator transition,[10] the antiferromagnetic superconducting state[11–13] and magnetic field-induced metallic[14] and superconducting[15] states in BETS conductors incorporating Fe^{3+} ions. Thus BETS systems seem to catch the rapidly growing interest in the field of molecular conductors.

From the early days of the studies on BETS conductors with tetrahalide anions, $(BETS)_2MX_4$ (M = Ga, Fe, In; X = Cl, Br), 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 mainly because the crystals frequently show small resistivity jumps (see the figure of temperature dependencies of the resistivities of κ-$(BETS)_2MX_4$ presented in ref. 9). Nevertheless, we have recently found three κ-type BETS superconductors: κ-$(BETS)_2FeBr_4$,[12] κ-$(BETS)_2FeCl_4$[13,16] and κ-$(BETS)_2GaBr_4$.[17] We have previously examined the crystal structures and electronic properties of BETS conductors with relatively large anions, κ-$(BETS)_2M'X_4$ (M′ = In, Tl; X = Cl, Br) and found resistivity anomalies presumably related to some structure modifications at the temperature range of 100–250 K.[18] It may be possible that some structural freedom is frozen in these conductors at low temperatures, which will tend to prevent their superconducting transitions.[18] Recently we have found that the anomalous resistivity behavior of κ-$(BETS)_2TlCl_4$ can be controlled to some extent by changing cooling rate and/or coating the crystal by epoxy resin and have discovered the superconducting transition at around 2 K.

Black plate crystals of κ-$(BETS)_2TlCl_4$ were prepared electrochemically. X-Ray examination revealed the crystal to be isostructural to those of other κ-type BETS conductors with MX_4^- anions.[9,19] That is, the crystal belongs to the orthorhombic system with space group *Pnma*. One of two Cl atoms of the $TlCl_4^-$ anion located on the mirror plane has a large temperature factor. Similarly a large temperature factor of one of the Cl atoms on the mirror plane was also found in the crystal structure of κ-$(BETS)_2InCl_4$ where the position of the Cl atom tends to deviate from the mirror plane at low temperature.[18]

The resistivity of κ-$(BETS)_2TlCl_4$ was measured by the standard four-probe method. Gold wires with 15 μm diameter bonded to the crystal by gold paste were used as contacts. The room-temperature conductivity measured along the crystal plane (//(010)) was about 20 S cm^{-1}. When the crystal was cooled with a normal cooling speed (~1 K min^{-1}), the crystal was broken at 220 K (see Fig. 1). It was found that the temperature dependencies of the resistivities of κ-$(BETS)_2MX_4$ (M = Fe, Ga, In; X = Cl, Br) show anomalies (jumps or sharp

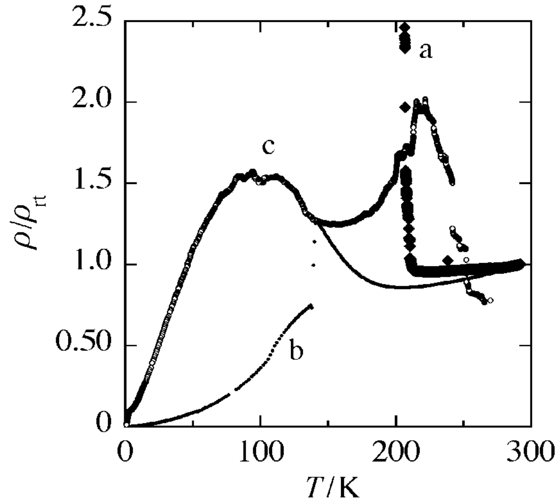

Fig. 1 Temperature dependence of the normalized resistivity of κ-$(BETS)_2TlCl_4$. (a – slow cooling without epoxy resin, b – fast cooling without epoxy resin, c – slow cooling with epoxy resin).

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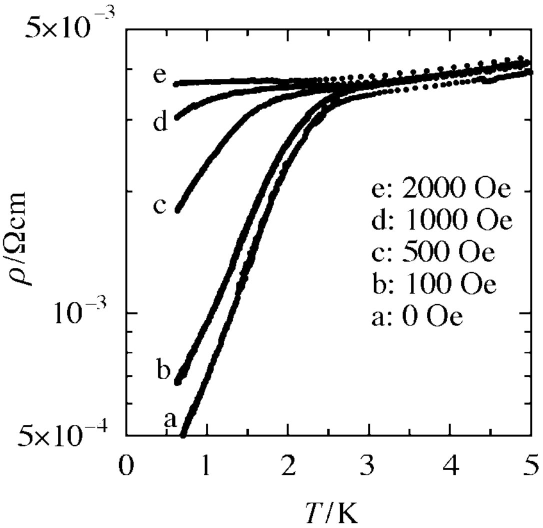

Fig. 2 The magnetic field-dependence of the resistivities of κ-$(BETS)_2TlCl_4$.

bending) except for the systems with relatively small anions ($GaCl_4^-$, $FeCl_4^-$).[9,18] However we found that the resistivity anomaly of κ-$(BETS)_2TlCl_4$ due to the destruction of the crystal around 220 K could be suppressed in a fast cooling process, where the crystal was cooled very rapidly down to *ca.* 170 K ($\sim$2–3 K min^{-1}) (see curve b in Fig. 1). Below 170 K, the crystal was cooled slowly, where the crystal showed a large resistivity drop around 140 K. Since the resistivity showed a metallic behavior between 140 and 4 K, the crystal was heated again up to 170 K and kept overnight to see a possible "annealing effect", then the temperature was lowered slowly. The resistivity jump took place around 130–150 K in every temperature cycle. The resistivity drop indicating the superconducting transition was observed at around 1.5 K.

In the case of isostructural antiferromagnetic organic superconductor κ-$(BETS)_2FeBr_4$, which usually exhibits small resistivity jumps around 120 K, the lattice constant *b* shows an anomalous temperature dependence at the same temperature region ($\sim$130 K).[12] Although any clear evidence for the structural change has not been obtained yet by low-temperature structure determination of κ-$(BETS)_2FeBr_4$, it will be natural to imagine that the large resistivity anomalies of κ-$(BETS)_2TlCl_4$ will be related to some structural phase transition. Since the electrical properties of organic conductors are usually very sensitive to so-called "soft pressure", the resistivity measurements were made by using a crystal coated with epoxy resin, whose contraction at low temperature is expected to produce the "soft pressure". The temperature was lowered with normal speed down to about 150 K and then very slowly ($\sim$0.2 K min^{-1}). As shown in Fig. 1, the resistivity anomaly around 220 K due to the destruction of the crystal was reduced to some extent, which permitted the low-temperature resistivity measurements. Below 220 K, the resistivity changed rather smoothly and showed a round maximum similar to those of typical κ-type organic superconductors around 90 K.[2] As shown in Fig. 2, the resistivity decrease showing the superconducting transition was observed below 2.5 K (T_c(onset) = 2.5 K). The superconducting transition was suppressed by applying a magnetic field of about 2000 Oe parallel to the crystal plane.

In conclusion, we have discovered a new organic superconductor, κ-$(BETS)_2TlCl_4$ with $T_c = 2.5$ K (onset) by using the crystal covered with epoxy resin. Without epoxy resin, the resistivity measurements could not be made down to low temperatures due to the destruction of the crystal if the cooling speed at around 220 K was not extremely fast.

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16 The superconducting transition of the first antiferromagnetic organic superconductor, κ-$(BETS)_2FeBr_4$ ($T_N = 2.4$ K, $T_c = 1.1$ K) was observed in both resistivity and susceptibility measurements but that of the second antiferromagnetic organic superconductor, κ-$(BETS)_2TlCl_4$ was detected by susceptibility measurements performed down to 60 mK ($T_N = 0.45$ K, $T_c = 0.1$ K) (Ref. 13).

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19 The crystal data of κ-$(BETS)_2TlCl_4$ are: orthorhombic, space group, *Pnma*; lattice constants, $a = 11.611(6)$, $b = 36.59(2)$, $c = 8.557(3)$ Å, $U = 3635(2)$ Å^3. Owing to the destruction of the crystal at 220 K, the low-temperature structure has not been examined.