# ドープ型有機超伝導体の実験研究
# Studies of a doped-type organic superconductor

谷口弘三
Hiromi Tanigcuhi

**物質科学部門物質基礎領域　助教授**

The organic superconductors, κ-(BEDT-TTF)$_2X$ ($X$=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br etc.) and high-$T_c$ cuprates share similarities such as proximity of superconductivity (S) to an antiferromagnetic (AF) insulator(I), possibility of d-wave symmetry of cooper pairs, and pseudogap behavior in the vicinity of a Mott transition, as well as the two-dimensianality of electron system. However, this organics can be regarded as superconductors realized by the control of the bandwidth at fixed band filling[1], in contrast to filling-controlled cuprates. In this case, with increasing pressure, the electrons localized at dimers of BEDT-TTF experience the first-order insulator-metal transition[2] and show Fermi liquid behavior[3] just as they start to delocalize.

The (BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ is an ambient-pressure superconductor with $T_c$ of 4.3K[5]. This salt is also known to crystallized into the κ-type structure[5]. However, there is structural characteristic not seen in other κ-type salts. This salt has incommensurate structure between lattice periodicity of mercury chains and that of halogens and donor molecules[5]. Due to this incommensurability, the electron filling is possibly shifted from the usual half-filled state of 2:1 salts, and therefore kind of hole-doped stats may be realized. Indeed this salt shows metallic temperature variation and superconductivity at 4.3K[4] in spite of highly enhanced U/W value (U/W=1.79)[5]. In order to obtain information about nature of the normal and the superconducting states in this doped-type superconductor, we performed the detailed characterization of the transport properties of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ as function of temperature and pressure.

Single crystal of κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$ (hereafter abbreviated to as the Hg$_{2.89}$Br$_8$ ) were prepared by the electrochemical oxidation of BEDT-TTF in 1,1,2-trichloroethane in the presence of corresponding electrolyte[6,7]. The electrical resistivity measurements were performed with the standard four-probe method with DC current parallel or perpendicular to the conducting layers under ambient and high pressures. We used a piston-cylinder-type pressure cell with pressure medium (Daphene 7373).

The electrical resistance of the Hg$_{2.89}$Br$_8$ salt is plotted in Fig.1 as a function of temperature for various pressures. As observed in the figure, the resistance showed monotonous decrease with increasing pressure. Superconductivity is detectable over the whole pressure-range examined here. The organic superconductor that shows superconductivity at ambient pressure generally shows disappearance of superconductivity below 10kbar, reflecting softness of organics. In this sense, the present organic superconductor is unusually insensitive against pressure.

Moreover, transition temperature, $T_c$, showed curious pressure dependence. $T_c$ defied as an onset is plotted as a function of pressure in an upper panel in Fig.2. With increasing pressure, $T_c$ increases toward the maximum value around 7 kbar, and then maintains to decrease until pressure reach approximately 18kbar. However, further increase of pressure makes $T_c$ elevated abruptly. This phase diagram is not similar to that of any other organic superconductors.

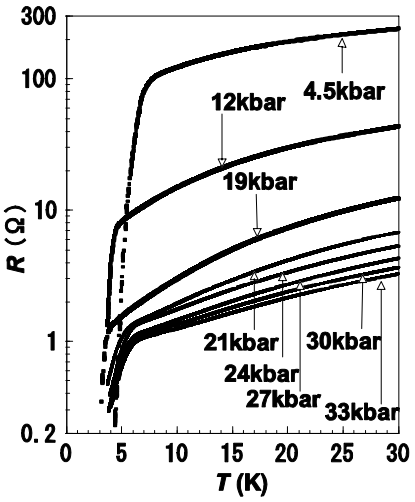


Fig. 1. Temperature dependence of out plane of resistance of the Hg$_{2.89}$Br$_8$ salt for various pressures.

To get information about this curious phase diagram, we investigated the normal-state properties. We found that in-plane resistivity was well fitted by $R=R_0+AT^n$ in the low-temperature region just before superconducting transition. Obtained $n$ is plotted as a function of pressure in a lower panel in Fig.2. As observed in the figure, resistance shows $T$-linear behavior at low pressures. For example, the data of 4.5kbar was well fitted by $R=R_0+aT^n$ with $n$=1.0 and 1.1, respectively. The fitted temperature-ranges were 7.4-20K for 4.8kbar and 7.9-25K for 5.0kbar. The $T$-linear behavior is reminiscent of anomalous metallic state of under-doped cuprate or rare earth compounds that situate near the quantum critical point[8].

The power shows the distinct variation with increasing pressure until pressure reaches approximately 20kbar. After that, the $n$ is almost stabilized around 2. This power of 2 is characteristic of so-called Fermi liquid state and is usually observed in the ordinal (non-doped) organic superconductors. A change of slope at approximately 20kbar is detectable in the figure. This almost corresponds to the pressure at which $T_c$ has the minimum. Thus a transition or a crossover is observed also in the normal state properties.

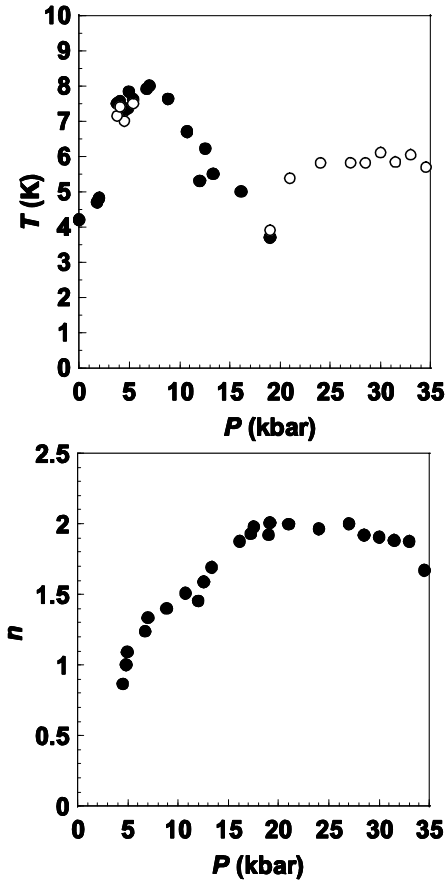


Fig. 2. Upper panel: *P*-*T* phase diagram of the $Hg_{2.89}Br_8$ salt. Lower panel: Pressure dependence of the power, n, where n is a fitting parameter in $R=R_0+AT^n$.

We believe that the $Hg_{2.89}Br_8$ salt is realized by the (natural) doping. In the high-$T_c$ cuprates, anomalous transport properties including T-linear behavior of resistivity is observed in the under-doped region. In other words, anomalous behavior appears near the insulating phase. It is a reasonable hypothesis that the $Hg_{2.89}Br_8$ salt at low pressures situates near the insulating phase, although the insulating salt has not been found near the present material. Since the electron correlation is suppressed by pressure through broadening of the bandwidth, appearance of the Fermi liquid state is naturally expected, as in the case of over-doping in the cuprate. The most important finding in the present study is the discovery of the apparent boundary in this process.

In summary, we uncovered that the $Hg_{2.89}Br_8$ salt has anomalous two-peak structure in the Tc diagram. And we found that the variation of the power, n, in $R=R_0+AT^n$, correlated with Tc. We consider that a critical pressure separating non-Fermi liquid and Fermi liquid states exists in the process of suppressing the correlation effect.

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